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4.19

Two Adjacent Heteroatoms with at least One Other Element

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4.19.1 INTRODUCTION

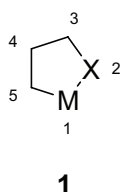
Ring systems with two adjacent heteroatoms and at least one other element were reviewed in the first and second editions of *Comprehensive Heterocyclic Chemistry* (CHEC-I <84CHECI(1)665> and CHEC-II <96CHECII(3)783>). This chapter covers reports up to the end of 2005. The literature was searched by groups within the periodic table.

4.19.1.1 Scope

Contrary to the second edition of *Comprehensive Heterocyclic Chemistry* (CHEC-II) where only rings which have relatively strong σ -bonds between adjacent atoms were reviewed, syntheses of heterocyclic complexes will also be described in this chapter. The chemistry of such “chelates” or “coordination compounds” is very interesting as the carbon-metal bond is labile and subject to various reactions such as insertion, protonation or substitution. However, even though the synthesis of these intramolecular complexes will be described in section 4.19.9, their physical properties will not be reported in this chapter. As the cyclic complex is in equilibrium with its open-chain form, the structural properties of such compounds may not be indicative of the heterocycle ring at all.

4.19.1.2 Nomenclature

IUPAC nomenclature is generally followed using the numbering shown in **1**. The cyclic structure, when X is a non-metallic heteroatom and M is a metal, is called a metallaheterocycle or a cyclometallic compound. Most metallaheterocyclopentanes have a stabilizing aromatic ring fused to the five-membered ring but a few cases of unfused stable metallaheterocyclopentanes are known.



4.19.2 THEORETICAL METHODS

There are no reports of *ab initio* or semi-empirical methods being used on five-membered ring heterocycles of this class.

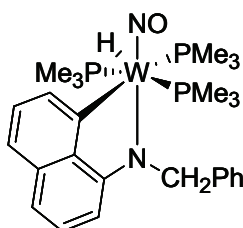
4.19.3 EXPERIMENTAL STRUCTURAL METHODS

4.19.3.1 X-ray Diffraction Studies

X-ray diffraction data have focussed on determining the conformation of the five-membered ring or substituents, or the geometry around the metal atom. Over the past ten years, X-ray crystallography has been used routinely and most of the new heterocycles

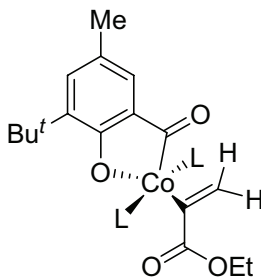
synthesised have been examined by this method. Mention of these results is made in the appropriate sections dealing with the synthesis of the heterocycle.

The crystals of **2** were submitted to single-crystal X-ray diffraction and the structure revealed a distorted pentagonal bipyramidal geometry around the tungsten center bearing one nitrosyl group, one hydride ligand, three PMe₃ ligands, and the bidendate η²-benzyl-naphthylamide ligand <2005JCS(D)580>.



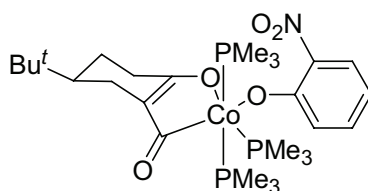
2

The structure of the pentacoordinate vinylcobalt(III) **3** (L = trimethylphosphine) has been determined by an X-ray diffraction analysis <2005ZAAC1929>. The cobalt atom is located above the base of a square pyramid and attains penta-coordination with two equatorial phosphorus atoms of *trans*-trimethylphosphine ligands, a carbon atom of the vinyl group, and an oxygen atom of the phenoxy group. The carbon atom of the acyl group is located at the apex of the square pyramid.



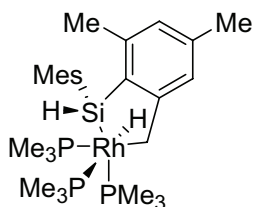
3

The molecular structure structure of **4** showed a hexacoordinate cobalt and three *P*-donor atoms lying in a plane, and two phenolate-*O* donors and an acyl group arranged in a plane perpendicular to the first <2003ICA179>.



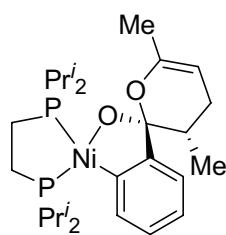
4

The structure of **5** was also determined by X-ray diffraction. The Rh-Si distance was 2.365(7) Å, hydrogen atoms on rhodium and silicon were located and refined to provide Rh-H and Si-H distances of 1.541(3) and 1.456(3) Å. The small Si-Rh-C angle of 80.16(7)° was indicative of some strain in the five-membered ring <1998OM2912>.



5

Conclusive evidence for the structure of **6** was obtained from an X-ray analysis, which confirmed the presence of a spirocyclic unit, with the expected *trans* disposition of C-2 and C-12 <2003CC1742>.

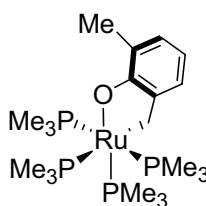


6

4.19.3.2 NMR Studies

Structural characterisation by NMR methods is routine and, in general, mention of the results has been deferred to the sections dealing with the synthesis of particular heterocycles. This section includes results where sufficient work has been performed to suggest patterns and where more unusual techniques have been discussed.

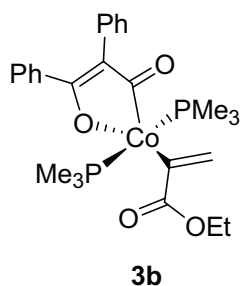
The $^3\text{P}\{^1\text{H}\}$ NMR spectrum of complex **7** showed an AM_2X pattern at -13.8, -0.96 and 10.7 ppm, indicating two *trans* and two *cis* PMe_3 ligands in an octahedral geometry. The ^1H NMR spectrum showed three magnetically inequivalent PMe_3 ligands at δ 0.90, 1.00 and 1.17 ppm <1998OM501>.



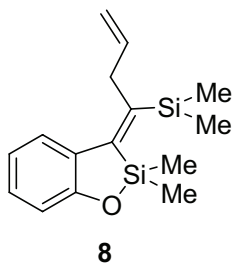
7

The ^1H NMR spectrum of **3b** showed a pseudo triplet at 1.0 ppm with strong coupling ($|^2J_{\text{P,H}} + ^4J_{\text{P,H}}| = 8.1$ Hz) to the *trans* PMe_3 ligands. The signals of the two geminal protons in the alkenyl group were found in the range expected of alkenyl-CH groups, with coupling

constants $^2J = 3$ Hz. In the ^{31}P NMR spectrum at -30 °C, singlet for the *trans* PMe_3 groups were observed. The diamagnetic properties of **3b** were compatible with a square pyramidal configuration <2005ZAAC1929>.



In 1998, the structure of compound **8** was determined by various physical methods, including ^1H - ^1H and ^1H - ^{13}C correlation spectroscopy (COSY), HMBC, nuclear Overhauser and exchange spectroscopy (NOESY) <1998TL6891>.



4.19.3.3 Ultraviolet and Infrared Spectroscopy

Most of the studies have been carried out on non-stable metallacycles with one or more weak bonds in the intended five-membered ring. However, compound **2**, previously described in section 4.19.3.1, has been analysed by IR spectroscopy <2005JCS(D)580>. The spectrum revealed a band at 1535 cm^{-1} , which provided the evidence for the presence of an

NO group in this complex. Complex **3** has also been analysed by IR and its spectrum showed bands at 1659 and 1641 cm^{-1} characteristic of the presence of C=O <2005ZAAC1929>.

4.19.4 THERMODYNAMIC ASPECTS

Because of the wide range of atoms that can occupy sites in the heterocycle ring, it is not possible to make many generalisations about physical and thermodynamical properties. However, it is possible to conclude that many metal-carbon bonds are weak or subject to easy reactions such as protonation, insertion, or redox reactions. Many metal bonds to nitrogen, oxygen, sulfur, silicon, and phosphorus are also labile. Particular attention should be paid to the valence states of heteroatoms: those, whose normal valence state is satisfied without closure of the ring, or those whose valence is exceeded on ring closure, are generally in equilibrium with open-chain or polymeric structures (physical properties of such complexes will not be covered in this section).

4.19.4.1 Physical Properties

A common feature of many metallaheterocyclopentanes is their sensitivity to hydrolysis, insertion of carbon monoxide, or oxidation on exposure to air. Many are subject to dimerisation reactions that are thermally induced or thermally reversed.

4.19.4.2 Conformational Studies

There have been no conformational studies on metallaheterocyclopentanes over the period of this review.

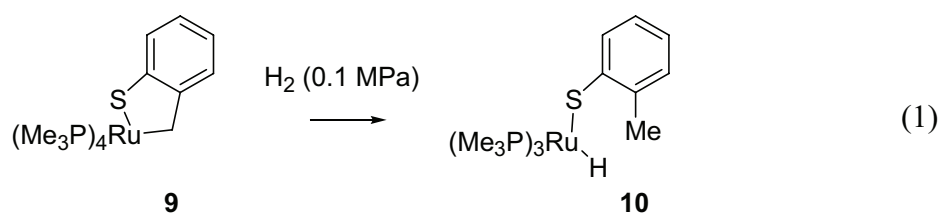
4.19.5 REACTIVITY OF FULLY CONJUGATED RINGS

Metallaheterocycles with the metal atom capable of supporting a carbon-metal double bond, and with oxygen, nitrogen, sulfur, or selenium as the second heteroatom are the only structures capable of full conjugation. These compounds show furan-like aromaticity with the heteroatom *p*-electrons participating. No examples of this type of ring system were uncovered, undoubtedly due to the stability of the metalla-carbon double bonds required for their formation.

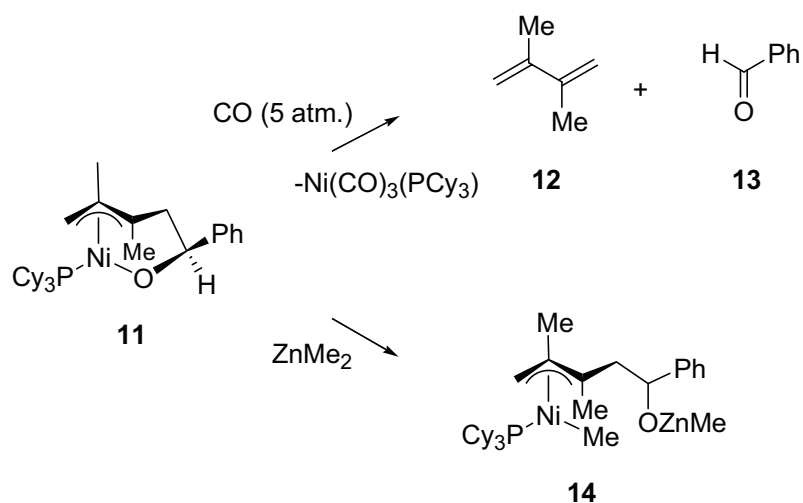
4.19.6 REACTIVITY OF NON-CONJUGATED RINGS

This section considers both reduced or partially reduced metallaheterocycles, i.e. means with one or no double bonds.

Exposure of the thiaruthenacycle **9** to hydrogen gas (0.1 MPa) in C₆D₆ led to hydrogenolysis (Equation (1)) <2005OM4799>.

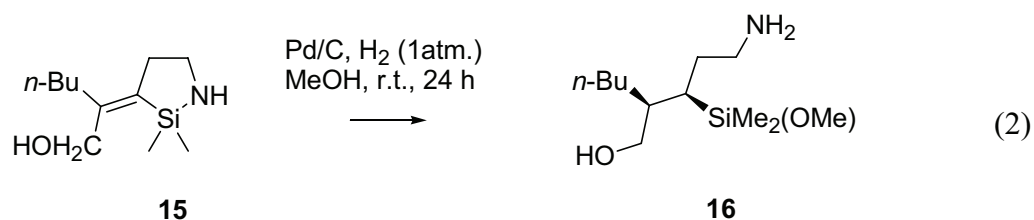


Treatment of the nickel complex **11** with carbon monoxide (5 atm.) led to the formation of butadiene **12** and aldehyde **13** with the formation of $\text{Ni}(\text{CO})_3(\text{PCy}_3)$ <2006JA7077>. The scission of the nickel-oxygen bond of the alkoxy complex **11** was also achieved with ZnMe_2 to afford **14** in very good yield (Scheme 1).

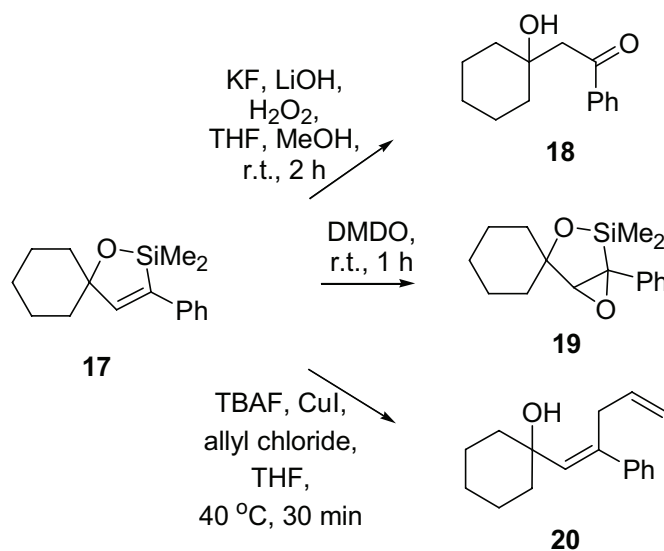


Scheme 1

Ring opening of azasilacycle **15** has also been observed (Equation (2)) <1999OM5103>.

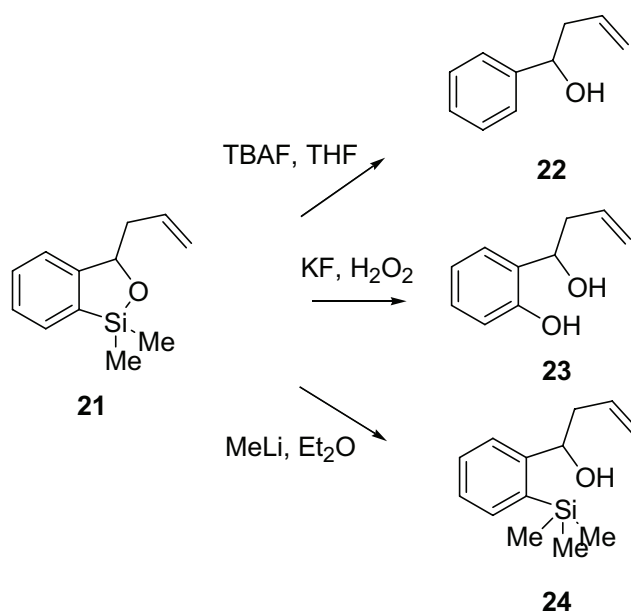


Oxacyclopentene **17** underwent a variety of transformations, like Tamao oxidation, yielding the β -hydroxy ketone **18** efficiently, an epoxidation reaction, and transformation into 1,4-diene **20** (Scheme 2) <2005OL4995>.



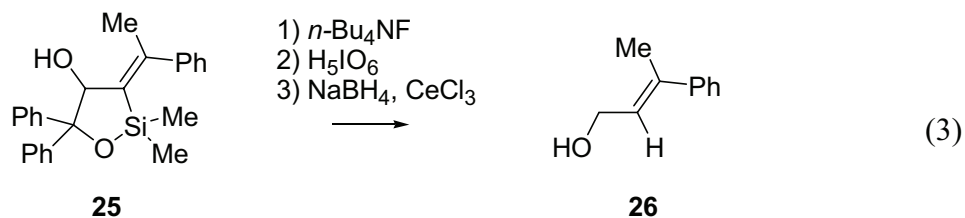
Scheme 2

Reactivity of benzo[1,2]oxasilole **21** was also studied <2004CC122>. Homoallylic alcohol **22**, was obtained by treatment with TBAF. Tamao reaction provided the desilylated *ortho*-phenolic benzyl alcohol **23**. Finally, treatment with methyllithium resulted in nucleophilic methylation on silicon and opening of the Si-O bond (Scheme 3).



Scheme 2

Instead of using Tamao conditions, Woerpel *et al.* have oxidised the C-Si bond with *t*-BuOOH, cesium hydroxide and cesium fluoride <1997T16597, 2002JA6524>. Oxidation of oxasilacyclopentanes with alkyl hydroperoxides to provide 1,3-diols was also described <2002JA12648>. Silicon-tethered ynals were converted into allylic alcohols *via* a cleavage process that involved stereospecific protodesilylation of the vinyl functionality (Equation (3)) <2001TL3259>.

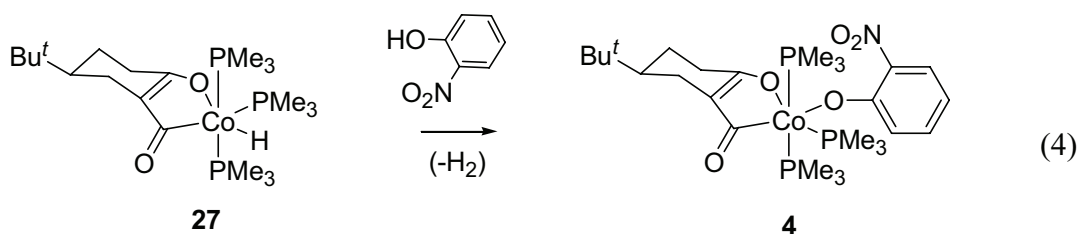


4.19.7 REACTIVITY OF SUBSTITUENTS ATTACHED TO RING CARBON ATOMS

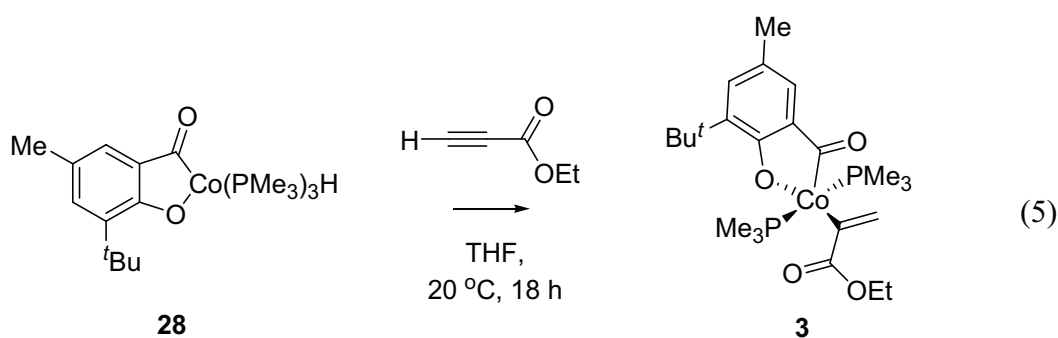
Substituent chemistry is that expected from analogous reactions of those substituents on saturated cyclic hydrocarbons or on aromatic heterocycles.

4.19.8 REACTIVITY OF SUBSTITUENTS ATTACHED TO RING HETEROATOMS

Acylphenolato(hydrido)cobalt(III) complexes were found to react smoothly with 2-nitrophenol, according to Equation (4) <2003ICA179>.



Formal insertion of propynoic acid ethyl ester into Co-H functions afforded pentacoordinate vinylcobalt(III) **3** (Equation (5)) <2005ZAAC1929>.



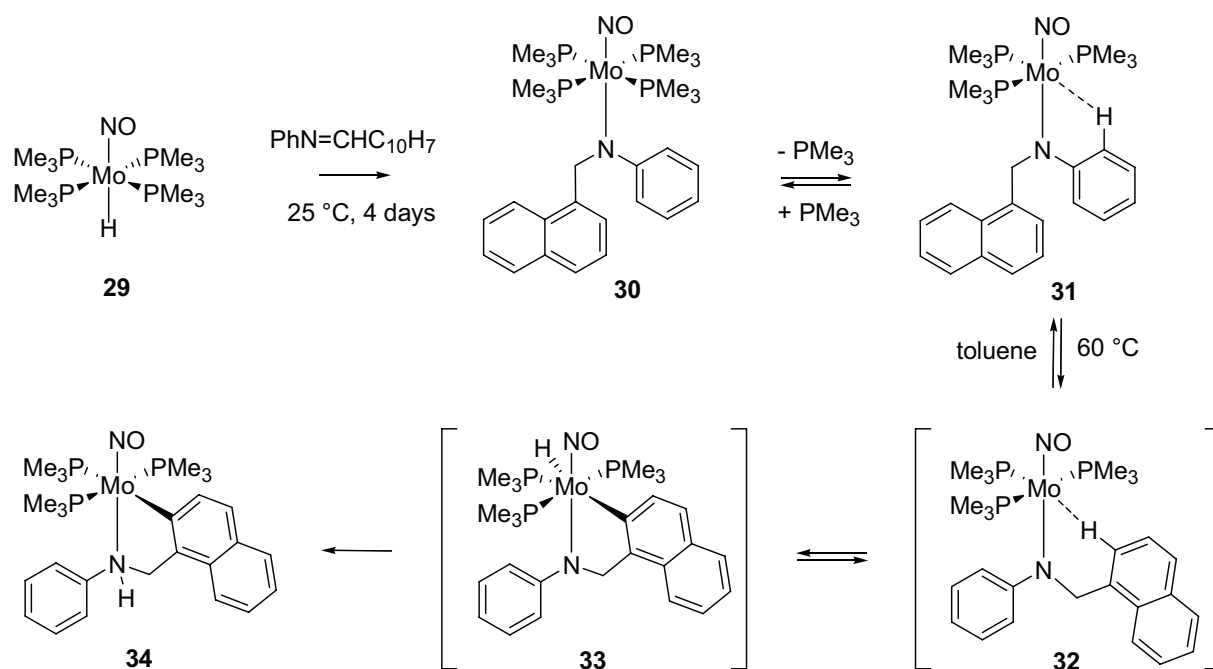
4.19.9 RING SYNTHESSES - FULLY SATURATED OR PARTIALLY SATURATED DERIVATIVES

In general, ring-forming reactions which result in hypervalent heteroatoms give complexes, where one of the ring bonds is weaker than the other ring bonds, i.e., the intended ring bond, between the metal atom and the heteroatom, generates a formal charge on one or more atomic centers. As such, these complexes are in equilibrium with their open-chain and polymeric structures. Contrary to the second edition of *Comprehensive Heterocyclic Chemistry* (CHEC-II) where only rings which have relatively strong σ -bonds between adjacent atoms were reviewed, the syntheses of heterocyclic complexes are also described in this section.

4.19.9.1 Group 6: Chromium, Molybdenum, and Tungsten

Only one example of a chelated tetracarbonyl chromium-containing complex has been reported during the period under review <1997T17297>. Molybdenum, and tungsten-containing complexes have also been studied.

Imine insertion into the Mo-H bond of the tetrakis(trimethylphosphine)-molybdenum nitrosyl hydrido complex **29** was performed by Berke and coworkers <2006JCS(D)73>. Treatment of **29** with an equimolar amount of *N*-naphthylideneaniline in toluene- d_8 , at room temperature during 4 days afforded the amido complex **30** as the only product (Scheme 3). When the reaction was carried out at 60 °C, with one equivalent of *N*-naphthylideneaniline, the amino complex **34** was obtained within 2 weeks.

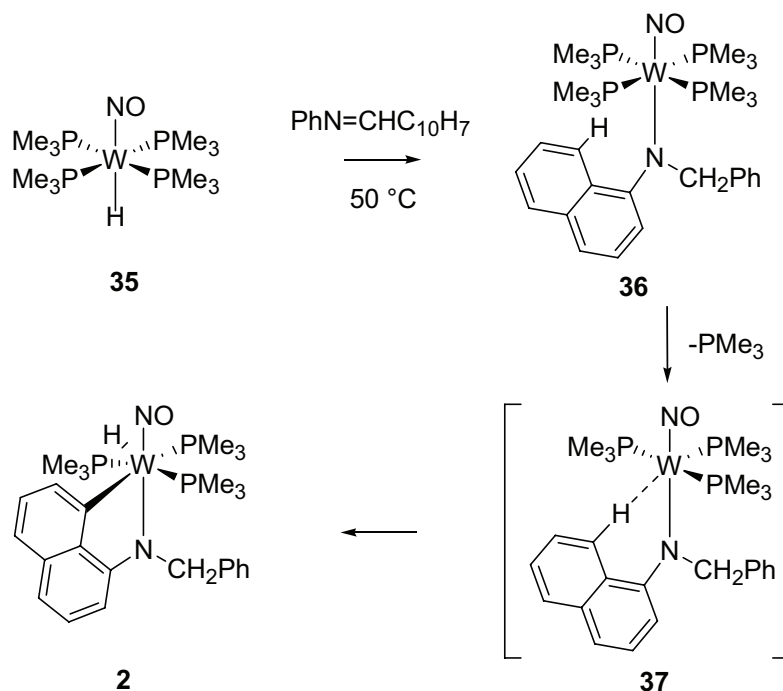


Scheme 3

Scheme 3 presents a plausible pathway for the formation of **34**. The first step is the imine insertion into the Mo-H bond to form the amido complex **30**, which subsequently loses one PMe₃ ligand and establishes an equilibrium with the agostic complex **31**. When the system is heated to 60 °C, other equilibria are assumed to come into play leading to the agostic species **32**. Oxidative addition of the agostic C-H bond produces **33** and proton transfer to the amide ligand eventually gives **34**.

Similar studies have been investigated by the same research group, by replacing the molybdenum by a tungsten atom <2005JCS(D)580>. Indeed, an insertion reaction of the imine C₁₀H₇N=CHPh into the W-H bond of the hydridonitrosyltetrakis(trimethylphosphine)-tungsten(0) **35**, followed by an oxidative addition of the C-H bond to the tungsten center gave

the complex $[W(NO)(H)(PMe_3)_3(C_{10}H_6NCH_2Ph)]$ **2**, which structure was studied by X-ray diffraction (Scheme 4).



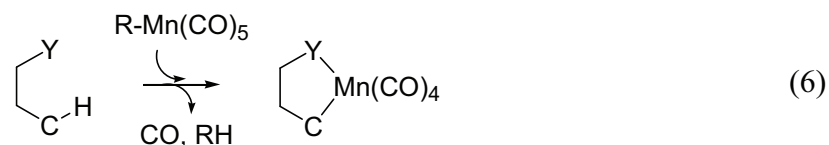
Scheme 4

The insertion of imine into the M-H bond transition metal hydride is believed to be an important step in the catalytic hydrogenation of such substrates. The reaction was observed when a toluene- d_8 solution of **35** was heated at 50 °C during 20 days with *N*-benzylidene-1-naphthylamine affording **2** in 78% yield.

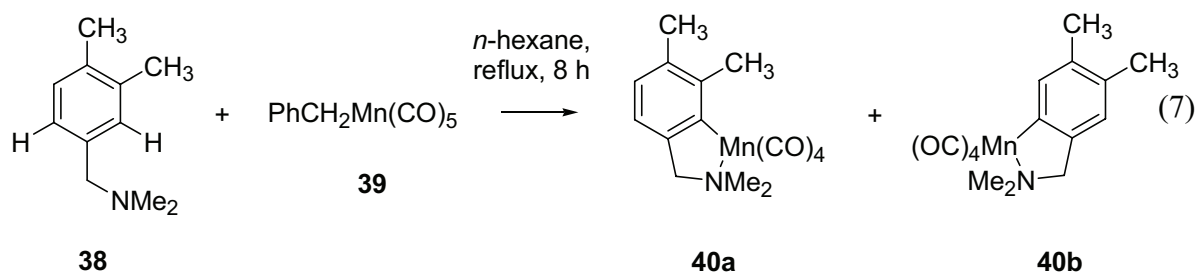
4.19.9.2 Group 7: Manganese, Technetium, and Rhenium

Many types of aromatic substrates are known to undergo a cyclometallation reaction when exposed to alkylpentacarbonylmanganese complexes under thermal conditions. It is well established that the treatment of ligand appended arenes with

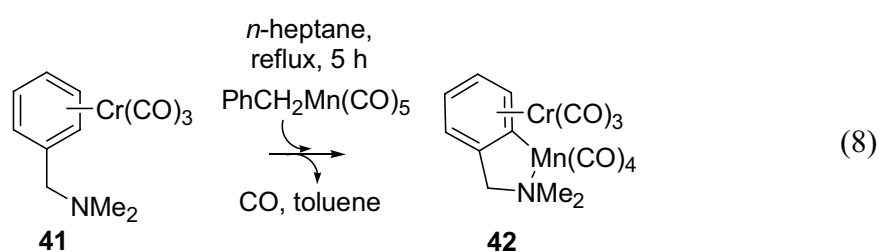
alkylmanganesepentacarbonyl complexes can lead to the formation of [C,Y] heterochelates of $\text{Mn}(\text{CO})_4$ (Y being a two electron donor ligand) (Equation (6)).



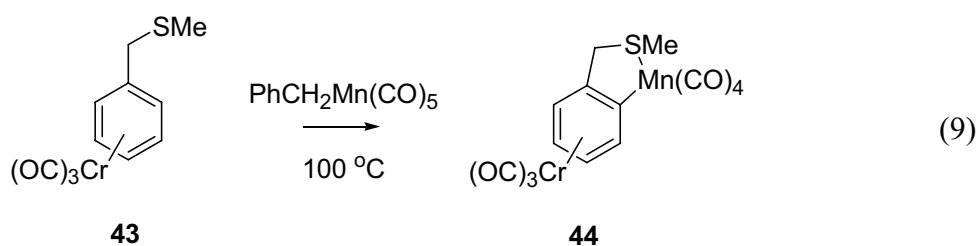
For instance, aromatic compounds such as *N,N*-dimethylbenzylamine, alkyl benzyl thioethers, 2-phenylpyridine, acetophenone, benzaldehyde and diazobenzene can be readily transformed into the corresponding cyclomanganated products when treated with alkyl-pentacarbonylmanganese complexes <1995COMCII(6)21>. The reaction of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ with the tertiary amine 3,4- $\text{Me}_2\text{C}_6\text{H}_3\text{CH}_2\text{NMe}_2$ **38** in refluxing *n*-hexane, afforded the corresponding neutral *C,N*-cyclometalated Mn(I) compounds of stoichiometry $\text{Mn}(\text{C-N})(\text{CO})_4$ **40a** and **40b** (Equation (7)). The net yield was 88% and the relative **40a:40b** ratio was 1:2 <1995IC643>. In this reaction, with two potential cyclometallation sites, the observed orientational preference was to avoid a steric interaction between the methyl group *ortho* to the Mn-C bond and a CO unit.



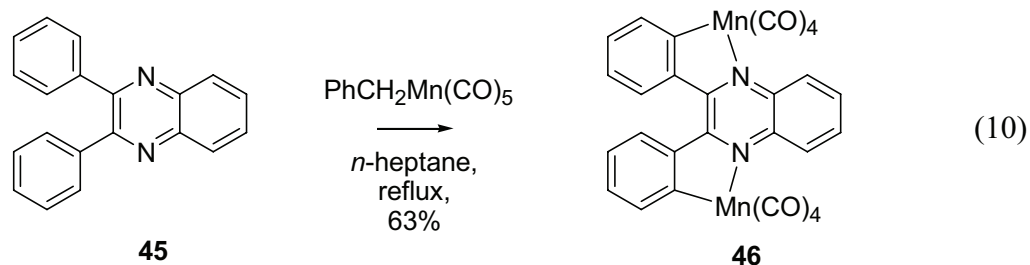
Cyclomanganation reactions of (η^6 -acylaryl)tricarbonylchromium complexes have been investigated and the novel heterobimetallic complexes synthesized characterised by X-ray crystallography <1996JOM109>. Complementary studies have been carried by Djukic *et al.* <1997OM657, 1998JOM65>, who studied the metallation with (η^6 -arene)tricarbonylchromium substrates taking as a model the *ortho*-manganation reaction promoted by benzylpentacarbonylmanganese (Equation (8)).



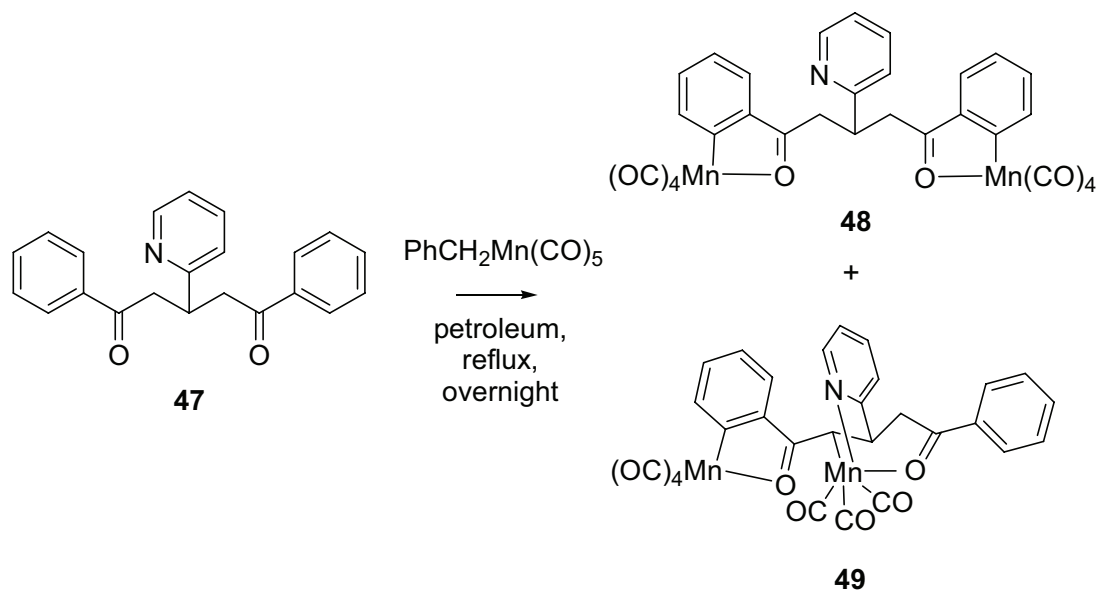
A thioether such as **43** also afforded a cyclomanganated product **44** (Equation (9)).



Some examples of bis-cyclomanganation have also been reported <2002OM3519, 2002TL5241, 2005JOM4822>. For example, the reaction of 2,3-diphenylquinoxaline **46** with $\text{PhCH}_2\text{Mn}(\text{CO})_5$ afforded the dinuclear complex **47** <2002CC638> (Equation (10)).

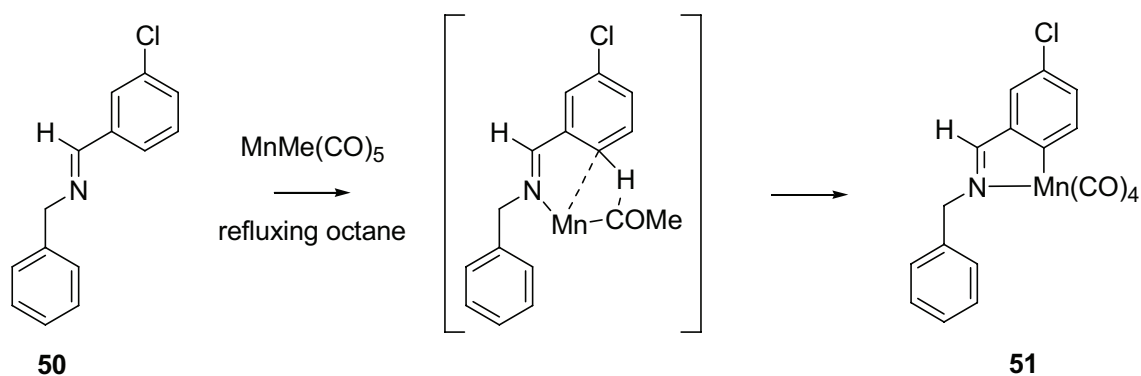


Reaction of the 1,5-diphenyl-3-(2-pyridyl)pentane-1,5-dione **47** with 2.5 equivalents of benzylpentacarbonylmanganese in petroleum under reflux gave a small amount of the symmetrical di-aryl-manganated product **48** but mostly the complex **49**, which is manganated at only one aryl carbon (by Mn(CO)_4) but also (by Mn(CO)_3 with *N* and *O* coordination) at the methylene carbon adjacent to the Mn(CO)_4 -coordinated ketone carbonyl (Scheme 5). The latter is a rare example of direct cyclomanganation at a saturated carbon and the only known case adjacent to carbonyl <2005JOM3348>.



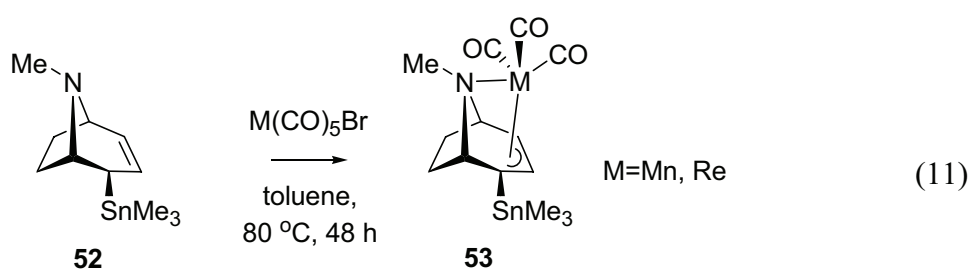
Scheme 5

The synthesis of cyclomanganated metallocycles has also been carried out by reaction between Benzyl-benzylidene imines and the metallating agent $\text{MnMe}(\text{CO})_5$ <2004JOM4889>. Complex **51** has been characterised by FABMS and NMR analysis. The proton spectrum provided conclusive evidence on the metallation position: the methinic proton signal in **51** appeared at a δ value close to that of the methinic proton of the free imines, in agreement with an *E*-configuration for this ligand (Scheme 6).

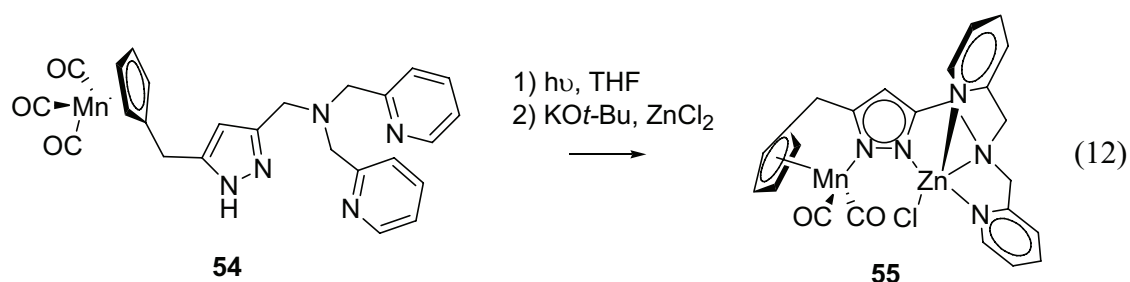


Scheme 6

The preparation of tropidinyll transition metal complex **53** was achieved by reaction of 4-trimethylstannyltropidine **52** with $M(\text{CO})_5\text{Br}$, $M=\text{Mn}$, Re <2003ZAAC(629)2408>. In complex **53**, the tropidinyll ligand is coordinated through the three-carbon allylic system which serves as a $2\sigma/4\pi$ -electron donor. It has been characterised by single-crystal X-ray diffraction analysis (Equation (11)).

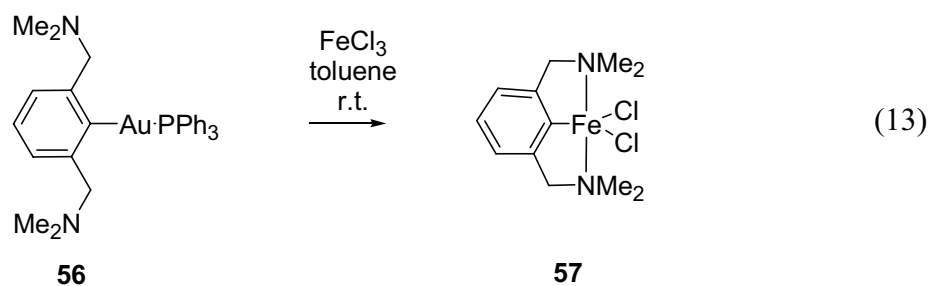


Finally, pyrazole, binding to manganese(I) has been achieved by photoinduced substitution of CO, and the adjacent N_4 -coordination pocket is suited to accommodate a second metal ion (Equation (12)). The heterodinuclear MnZn complex **55** was characterised crystallographically and its redox chemistry investigated by spectroelectrochemical methods <2002JOM113, 2005IC3863>.

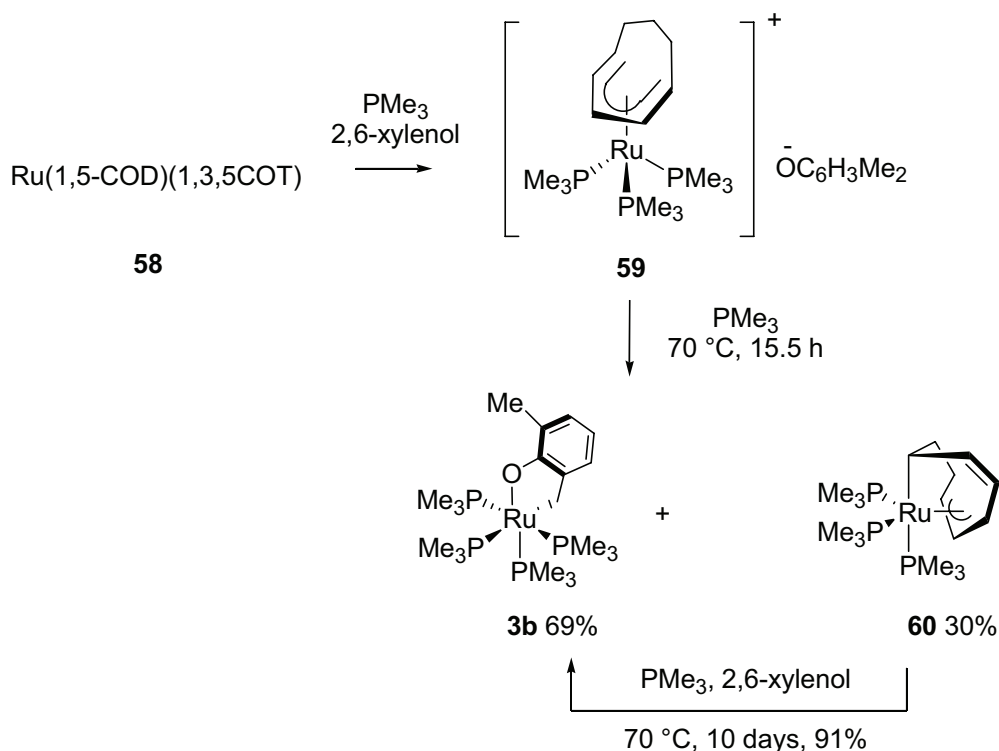


4.19.9.3 Group 8: Iron, Ruthenium and Osmium

The synthesis of only one iron-containing heterocycle was described between 1995 and 2006. The formation of paramagnetic **57** from a stable arylgold(I) phosphine, $[\text{Au}(\eta^1\text{-C-NCN})(\text{PPh}_3)]$ **56** and anhydrous FeCl_3 in toluene at room temperature was confirmed by X-ray diffraction techniques <2002OM4556>. The reaction was carried out on millimolar scale and **57** was obtained in good yield. Moreover, the reaction was performed at room temperature, which underlines the nonreductive character of **56** giving an easy access to the formation of C-Fe^{III} bonds (Equation (13)).



Komiya and coworkers have studied the successive O-H and sp^3 C-H bond activation of *ortho*-substituted phenols by a ruthenium(0) complex <1998OM501>.

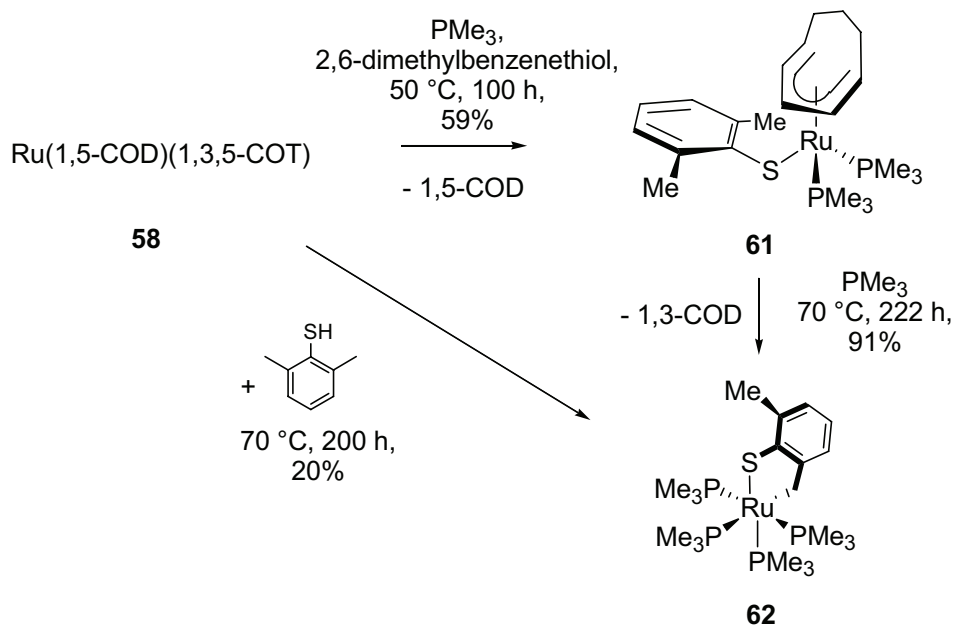


Scheme 7

The reaction of Ru(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) **58** with PMe₃ and 2,6-xyleneol in hexane caused immediate precipitation of [Ru(η⁵-C₈H₃-2,6)]⁻[HOC₆H₃Me₂-2,6] **59** as a white powder (Scheme 7) <2000JOM18>. Treatment of **59** with PMe₃ at 70 °C for 15.5 hours resulted in sp³ C-H bond cleavage of the *ortho* methyl group in the aryloxo anion giving an oxaruthenacycle complex $\text{cis-Ru}[\text{OC}_6\text{H}_3(2\text{-CH}_2)(6\text{-Me})]\text{PMe}_3\text{PMe}_3\text{PMe}_3\text{PMe}_3$ **3b** in 69% yield with concomitant formation of 1,3-cyclooctadiene and 2,6-xyleneol. A small amount of **60** was also formed in the reaction. The η⁵-C₈H₁₁ moiety was considered to act as the hydrogen acceptor for the C-H bond activation liberating 1,3-cyclooctadiene. Complex **3b** has been characterised by NMR, IR and elemental analysis.

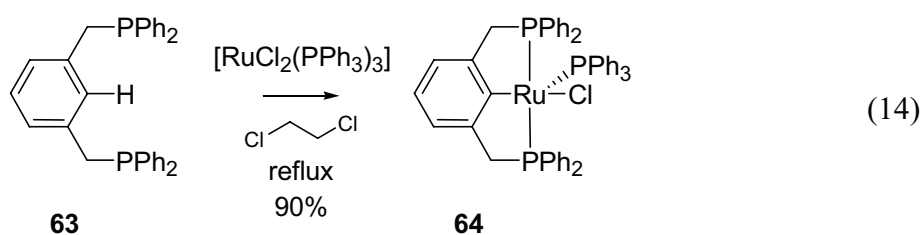
With the O-H and sp³ C-H bond activation of *ortho*-substituted phenols methodology in hand, Komiya and coworkers carried their research forward by synthesising a divalent

thiaruthenacycle complex, the *cis*-Ru[SC₆H₃(2-CH₂)(6-Me)-κ²S,C](PMe₃)₄ **62** (Scheme 8) <2005OM4799>.

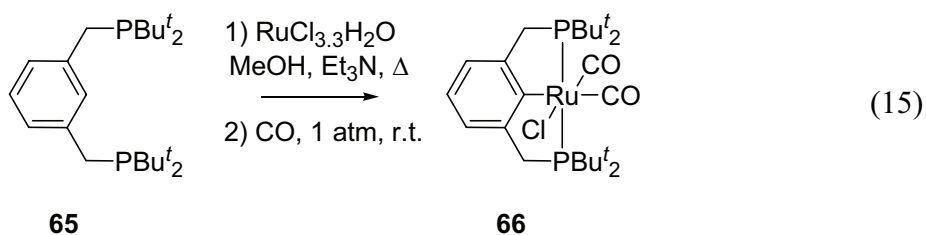


Scheme 8

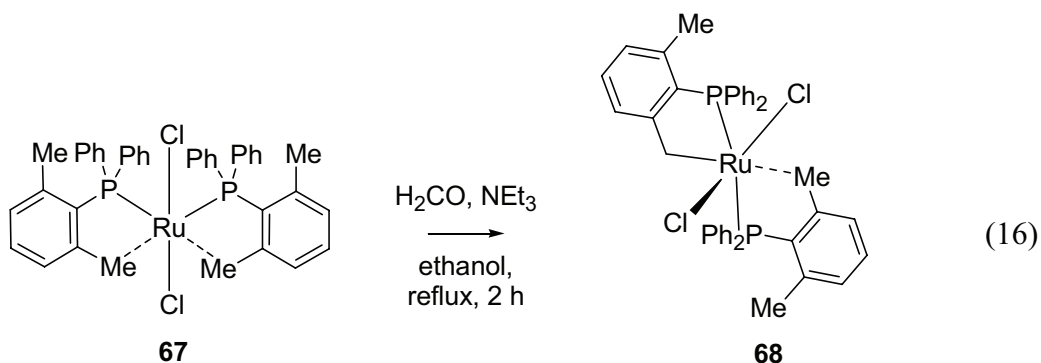
The synthesis, characterisation and reactivity of various ruthenium(II) complexes has been studied extensively by Koten and coworkers (Equation (14)) <1996OM5687, 1997JA11317, 2000OM5287, 2001EJI125, 2004OM5833>.



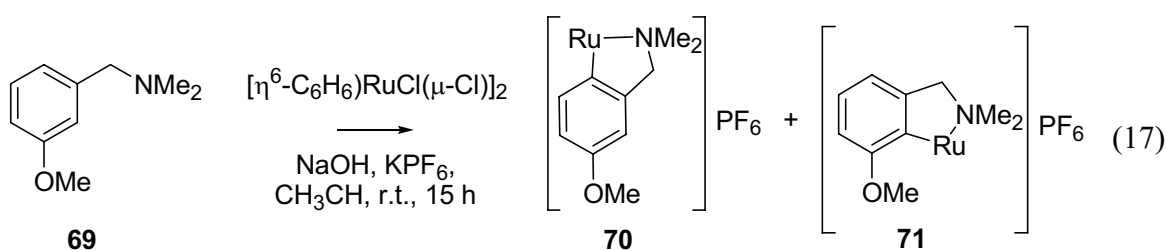
Treatment of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ with an equimolar amount of the bisphosphine ligand [2,6-($\text{CH}_2\text{P}^t\text{Bu}_2$) $_2$ - C_6H_4] **65** in methanol at 80 °C in a pressure vessel followed by reaction with carbon monoxide (1 atm) at room temperature resulted in the formation of the saturated complex **66** (Equation (15)) <2004ICA1854>.



In 2004, Baratta *et al.* achieved the synthesis of the five-coordinate complex $\text{RuCl}[2\text{-CH}_2\text{-6-MeC}_6\text{H}_3\text{PPh}_2][(\text{CO})(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{-PPh}_2]$ **68**, according to Equation (16) <2004OM6264>. The reaction of the 14-electron complex $\text{RuCl}_2[(\text{CO})(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{-PPh}_2]_2$ **67** with formaldehyde in presence of triethylamine proceeded in high yield *via* cyclometalation of an *ortho* methyl group and aldehyde decarbonylation.

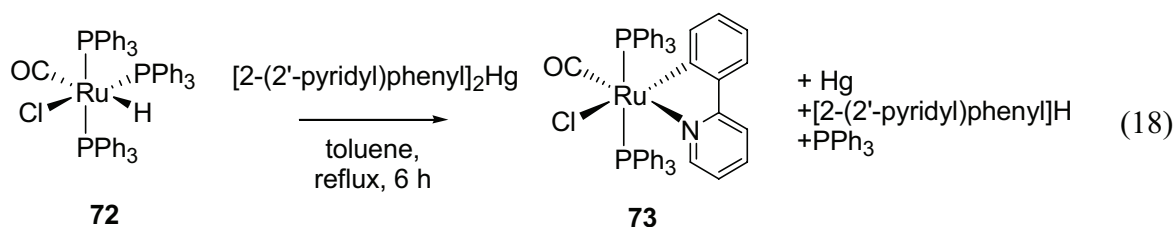


The cycloruthenation of substituted *N,N*-dimethylbenzylamines by $[\eta^6\text{-C}_6\text{H}_6]\text{RuCl}(\mu\text{-Cl})_2$ in acetonitrile in the presence of NaOH and KPF_6 , which led to the formation of corresponding cycloruthenated complexes in good to moderate yields has also been studied <1999OM2390>. For example, the work of Le Lagadec *et al.* is illustrated in Equation (17) <2004JOM4820>.

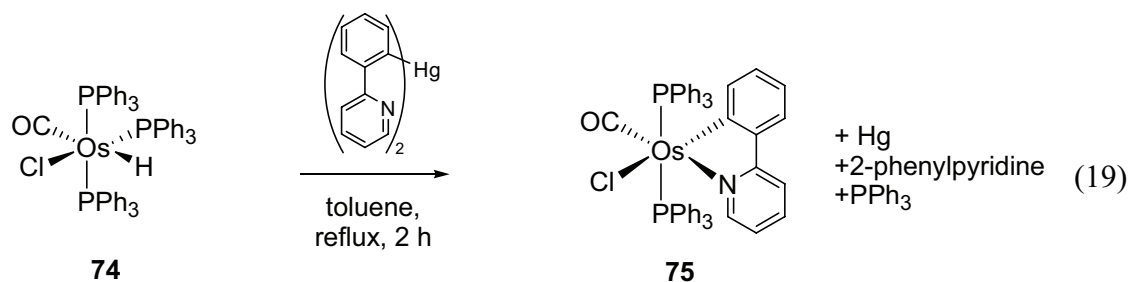


As shown in Equation (17), the cycloruthenation of the 3-substituted *N,N*-dimethylbenzylamine **69** afforded two positional isomers as a result of the Ru(II) attack at the C-2 or C-6 aromatic carbons.

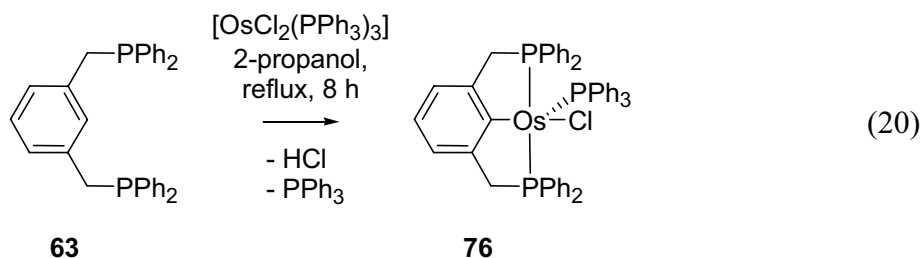
Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with $[\text{2}-(2'\text{-pyridyl})\text{phenyl}]_2\text{Hg}$ proceeded smoothly to form $[\text{Ru}(\eta^2\text{-}[\text{2}-(2'\text{-pyridyl})\text{phenyl}])\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ <1999OM2813>. In this complex, the $[\text{2}-(2'\text{-pyridyl})\text{phenyl}]$ ligand is bound as a stable five-membered chelate ring (Equation (18)).



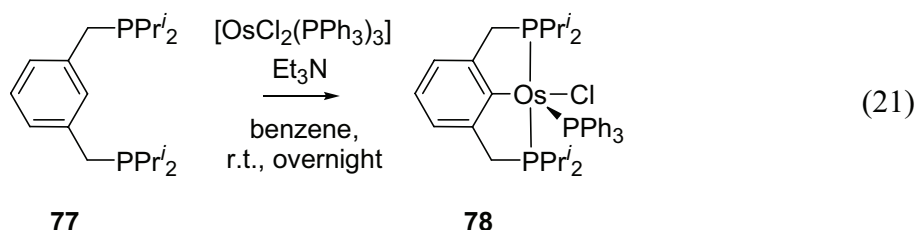
Similar transmetallation reactions using mercury reagents of the form Ar_2Hg have been performed by Clark *et al.* to deliver osmium complexes $\text{Os}[\eta^2\text{-C,N-(2-phenylpyridyl)Cl(CO)(PPh}_3)_2]$ **75** (Equation (19)) <1999OM2813, 2000JOM262>.



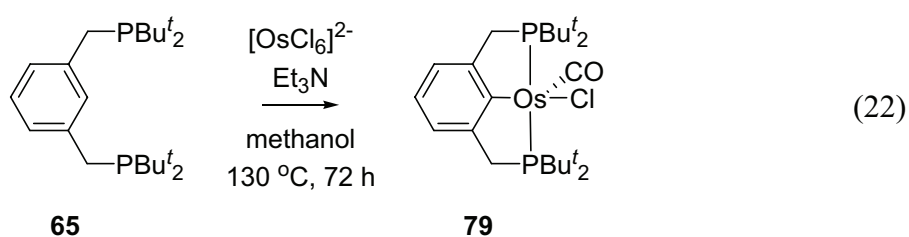
Preparation and spectroscopic characterisation of $\text{OsCl(PPh}_3)_3(\text{PCP})$ **76** ($\text{PCP} = 2,6\text{-Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3$) has been performed by Jia and coworkers <2000OM3803>. Treatment of $\text{OsCl}_2(\text{PPh}_3)_3$ with 1,3-($\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ **63** in 2-propanol indeed led to the formation of the coordinatively unsaturated complex **76** (Equation (20)). The spectroscopic data of the green compound **76** were consistent with a square-pyramidal complex with PPh_3 occupying the apical position.



An analogous complex **78** has been synthesised by Gauvin *et al.* <2001OM1719>, by reaction between the diphosphine **77**, $\text{OsCl}_2(\text{PPh}_3)_3$ and Et_3N (Equation (21)).

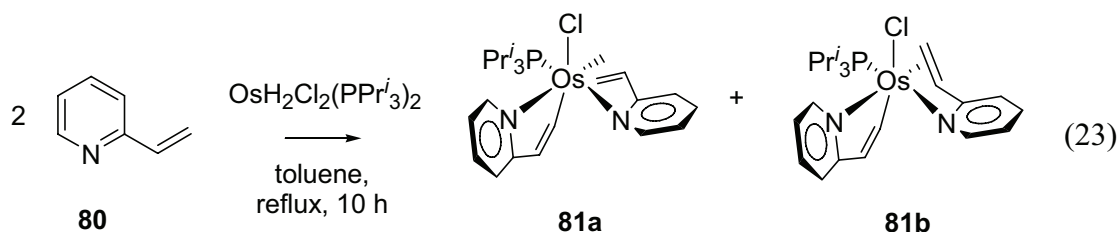


Similar conditions have been used by Gusev *et al.* to synthesise complex **54** <2001OM1001>. From OsCl_6^{2-} , they obtained the 16-electron chloride square-pyramidal compound **54**, using triethylamine and methanol as solvent ((Equation (22)).



More recently, C-H bond activation and subsequent C-C bond formation promoted by osmium have been investigated by Esteruelas *et al.* <2006JA4596>. Treatment of $\text{OsH}_2\text{Cl}_2(\text{P}i\text{-Pr}_3)_2$ with 2 equivalents of 2-vinylpyridine in toluene under reflux gave rise to the

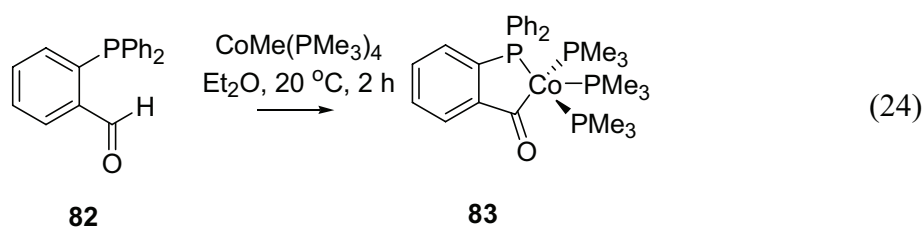
release of H₂ and [*i*-Pr₃PH]Cl and the formation of the red complex **81**, which was isolated in 70% yield as a 6:4 mixture of the isomers **a** and **b** shown in Equation (23).



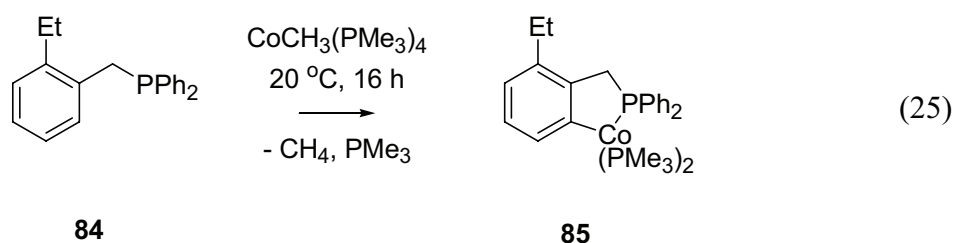
Complex **81** contains two substrate molecules. One of them is metalated, as a consequence of C(sp²)-H bond activation of the CH₂ group of the vinyl substituent, whereas the other one is coordinated to the osmium atom by the nitrogen atom and the C=C double bond of the olefin.

4.19.9.4 Group 9: Cobalt, Rhodium, and Iridium

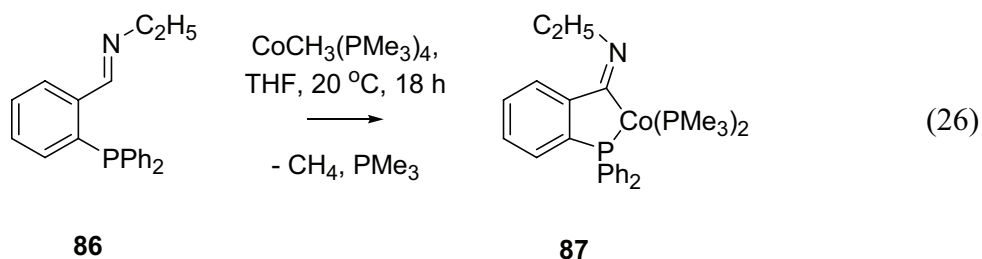
Only a few syntheses of cobalt-containing metalacycles have been carried out over the period under review. In 1998, Klein and coworkers reported the synthesis of the 18-electron cobalt(I) complex **83**, smoothly formed by an aldehyde reaction with a suitable methylcobalt(I) according to Equation (24) <1998OM4196>.



From 1996 to 2005, this research group published extensively on the synthesis of such cobaltacycles <2000EJI2295, 2002EJI3305, 2003EJI853, 2005OM2612>. They notably described the reaction between the benzyldiphenylphosphane **84** with $[\text{CoMe}(\text{PMe}_3)_4]$ at -70 °C in THF affording the selectively *ortho*-metalated complex **85** (Equation (25)).



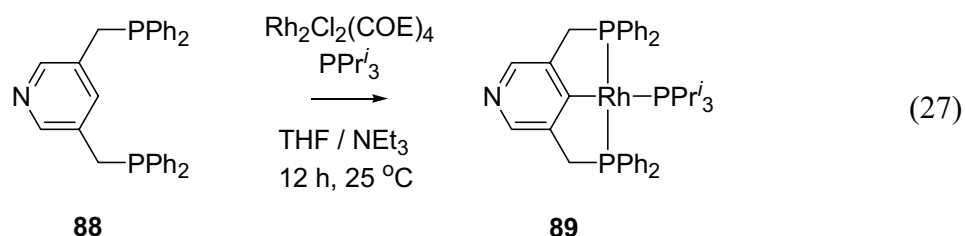
Analogously, the formation of the *C*-metalated complex **87** occurred at -70 °C according to Equation (26).



Rhodium-containing complexes have been extensively studied over the period review. Particularly, chelating ligand systems based on 1,3-disubstituted benzenes have been used to

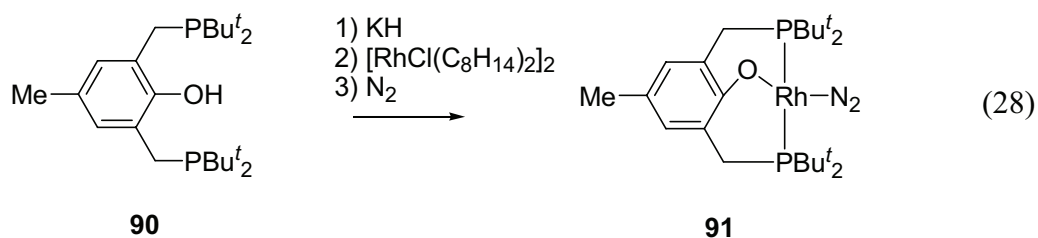
obtain the *ortho*-metalated complexes <1998CC917, 1998JA13415, 1999JA4528, 1999JA6652, 2000JA7723, 2003JA6532, 2003JA11041, 2005CEJ2319, 2006OM2292>.

The reaction of the chelating bis(phosphine)-3,5-bis((diphenylphosphino)-methyl)pyridine **88** with $\text{Rh}_2\text{Cl}_2(\text{COE})_4$ (COE = cyclooctene) and $\text{P}i\text{-Pr}_3$ in THF / Et_3N (3 : 1) led to the formation of the mononuclear Rh(I) complex **89** (Equation (27)) <1996IC1792>.

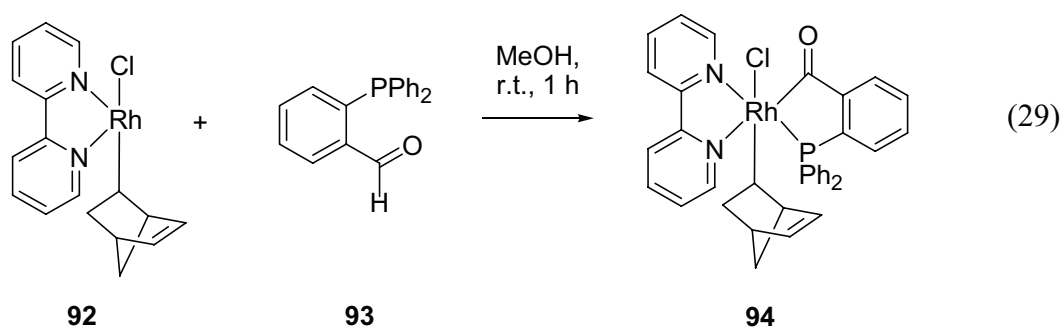


As expected, **89** exhibited two signals in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum (intensity ratio 2 : 1) in accord with the X-ray structure determination (*vide infra*).

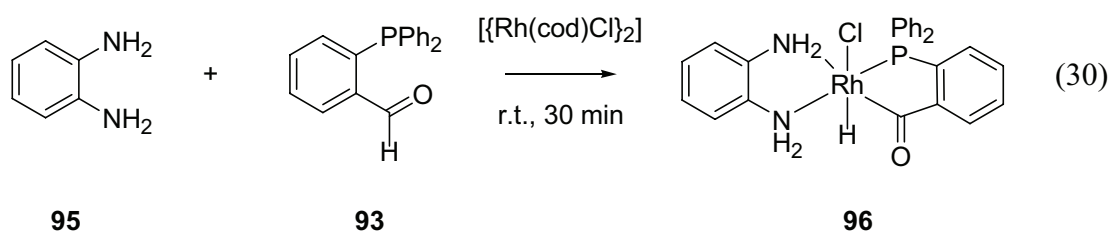
A similar reaction has been carried out between the aromatic phosphine alcohol **90** and $[\text{RhCl}(\text{C}_8\text{H}_{14})_3]_2$ in THF under a nitrogen atmosphere at room temperature affording the complex **91**, as proved spectroscopically by ^1H , $^1\text{H}\{-^{31}\text{P}\}$ and $^{31}\text{P}\{\text{H}\}$ NMR, IR and FD-MS measurements (Equation (28)) <1998JA6531>.



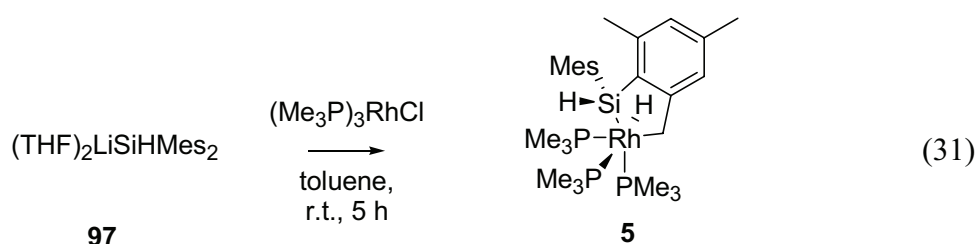
When $[\text{Rh}(\text{Cl})(\text{Nbd})(\text{bipy})]$ (Nbd = norbornadiene) **92**, prepared *in situ* was treated with $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{CHO})$ **93** in methanol, oxidative addition of aldehyde to rhodium followed by insertion of norbornadiene into the Rh-H bond occurred (Equation (29)) <2005EJI1671>. NMR spectroscopy, including 2D experiments allowed complete characterisation of complex **94**.



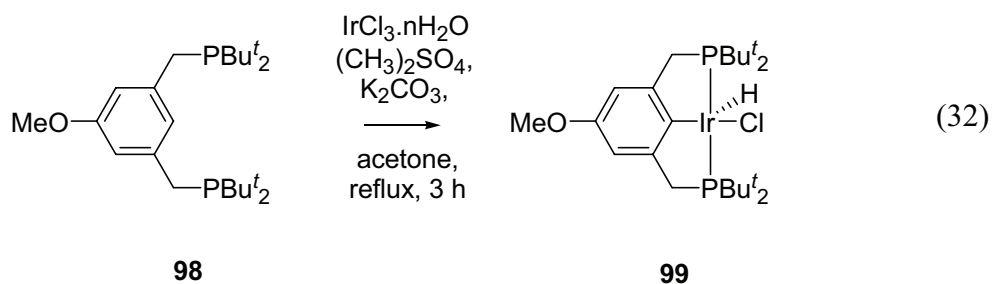
In addition, the reaction of $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ (cod = 1,5-cyclooctadiene) with $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{CHO})$ **93** in the presence of 1,2-phenylenediamine(daphen) **95** led to the formation of the chelate-assisted oxidative addition product $[\text{Rh}(\text{Cl})(\text{H})[\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})](\text{daphen})]$ **96** with displacement of 1,5-cyclooctadiene as shown in Equation (30) <2004ICA2818>.



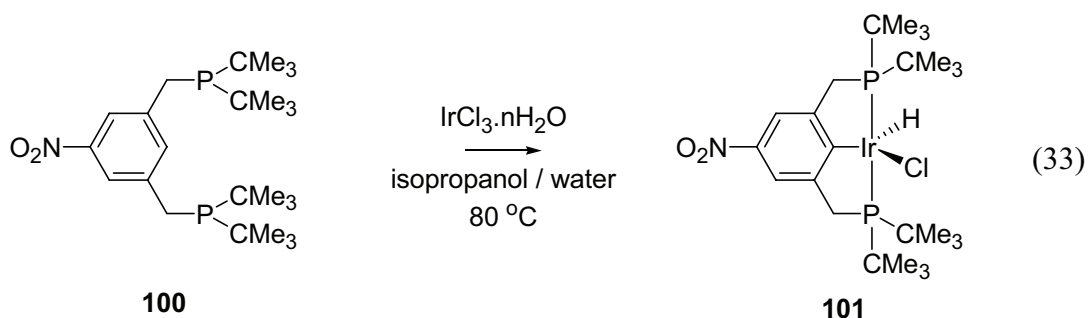
In 1998, Mitchell *et al.* described the synthesis of a new rhodium silyl complex <1998OM2912>. Reaction of $(\text{Me}_3\text{P})_3\text{RhCl}$ with $(\text{THF})_2\text{LiSiHMe}_2$ (Mes = 2,4,6-trimethylphenyl) in toluene resulted in formation of a light yellow solution, from which colorless crystals of **5** were isolated after work-up. The presence of both Rh-H ($\delta = -9.90$) and Si-H ($\delta = 5.76$) resonances in the ^1H NMR spectrum of **5**, and five separate methyl signals suggested the structure shown in Equation (31).



Iridium-containing complexes have also been studied over the period review <2000ICC511, 2002OM5775>. Treatment of the methoxy functionalised ligand **98** with $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ in 2-propanol / water gave the chlorohydrido complex **99** (Equation (32)).

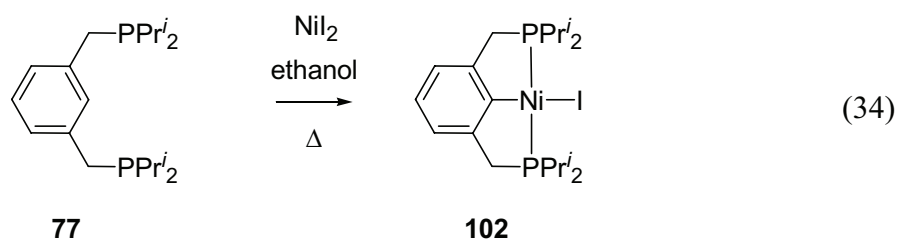


In a similar way, Grimm *et al.* isolated the iridium hydrochloride complex **101**, obtained by heating an isopropanol / water solution of the ligand **100** in the presence of iridium(III)chloride to 80 °C (Equation (33)). The red complex **101** dissolved well in polar organic solvents and was air-sensitive in solution, whereas in the solid state, no decomposition was observed while handling in air.

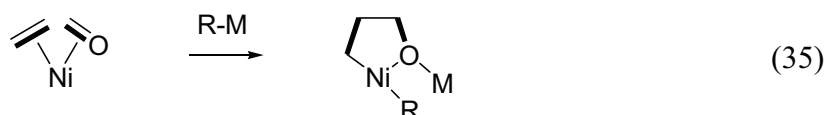


4.19.9.5 Group 10: Nickel, Palladium, and Platinum

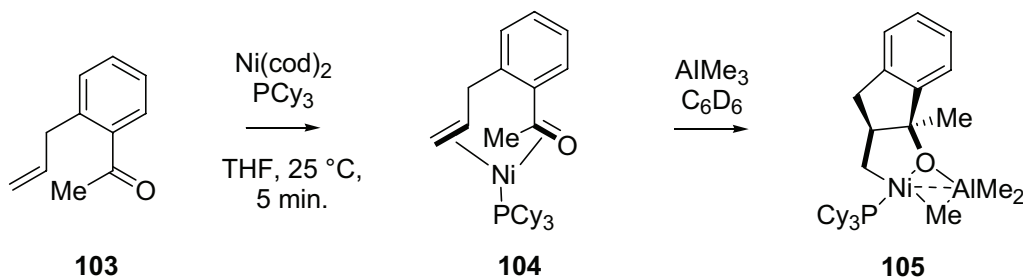
From 1996 to 2005, the synthesis of pincer nickel complexes has been widely described <1999OM277, 2000JA12112, 2002OM4556, 2004JCS(D)2957, 2004OM5653>. For example, reaction of **77** with a stoichiometric amount of NiI₂ in ethanol at 130 °C in a sealed pressure vessel led to the formation of the aryl-nickel complex **102** as shown in Equation (34) <2004ICA4015>. Similar reactions were achieved by Castonguay *et al.* using different nickel halides (Cl and Br) <2006OM602>.



Kurosawa and coworkers have been studying the oxidative cyclisation of an $\eta^2:\eta^2$ -2-allylbenzophenone nickel complexes leading to the formation of nickelhydrofurans (Equation (35)) <2004JA11802, 2006JA7077>.

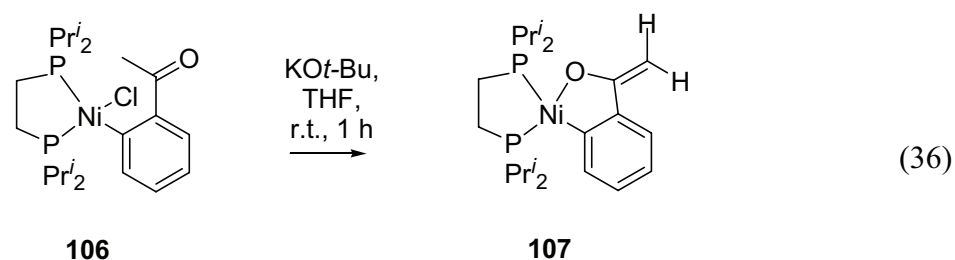


The reaction of 2-allylacetophenone **103** with $\text{Ni}(\text{cod})_2$ and PCy_3 gave an $\eta^2:\eta^2$ -1,5-enone nickel complex **104** quantitatively (Scheme 9). The following reaction of **104** with AlMe_3 in C_6D_6 proceeded very rapidly to give a deep-orange solution of cyclized compound **105**. Its structure was confirmed by X-ray diffraction analysis, showing a unique nickelacycle with a bridging methyl group <2005JA12810>.

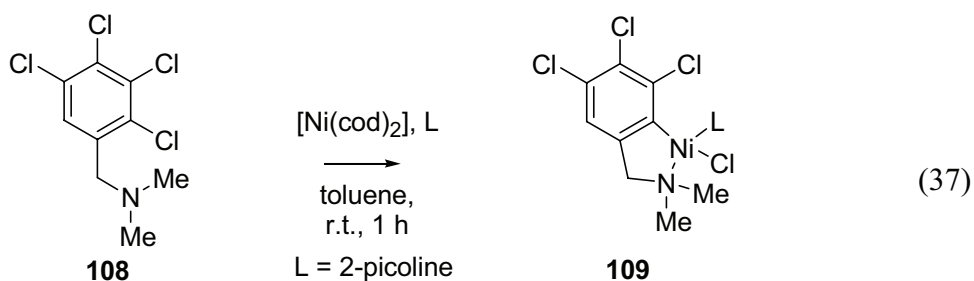


Scheme 9

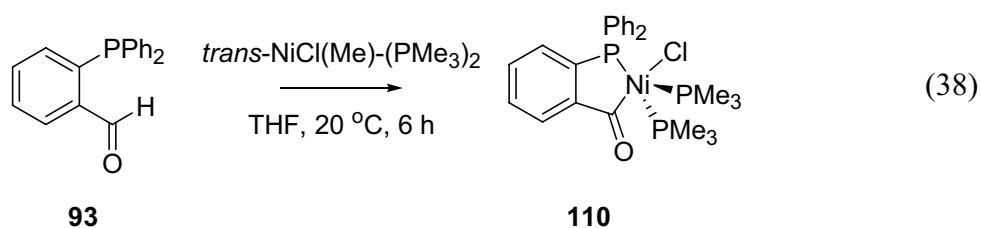
In addition, the synthesis of enolate complexes of nickel has been carried out by Campora and coworkers <2003CC1742, 2003JA1482>. Treatment of a THF solution of Ni(C₆H₄-*o*-C(O)CH₃(Cl)(dippe) **106** with one equivalent of KO*t*-Bu allowed the preparation of the nickel enolate **107** in good isolated yield (60%). *O*-Coordination of the enolate fragment could be proposed on the basis of the NMR spectra. Thus, the terminal methylene group gave rise to two signals in the ¹H spectrum, at δ = 4.62 and 4.79 ppm that correlated (¹H-¹³C HETCOR experiment) with a ¹³C resonance at 75.9 ppm which exhibited no coupling to phosphorus (Equation (36)).



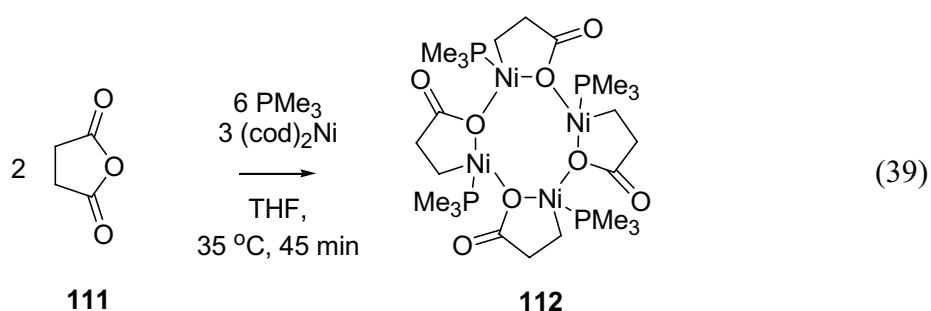
Five-membered nickelacycles have also been investigated by Ceder *et al.* (Equation (37)) <1995OM5544>.



In 1998, Klein *et al.* showed that methylnickel complex activates the C(O)-H function of 2-diphenylphosphinobenzaldehyde **93** to form a five-membered ring Ni(Ph₂PC=O) which occupy OC-axial and P-equatorial positions in the trigonal bipyramidal configuration of nickel compound **110** (Equation (38)) <1998OM4196>.



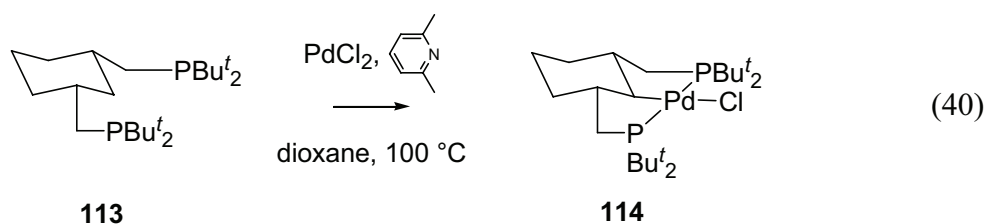
Finally, the reaction of succinic anhydride **111** with a 1:2 mixture of (cod)₂Ni and a monodentate phosphine generated a reactive monomeric nickelalactone, which underwent rapid aggregation to form cyclic oligomer **112** (Equation (39)) <2005OM272>.



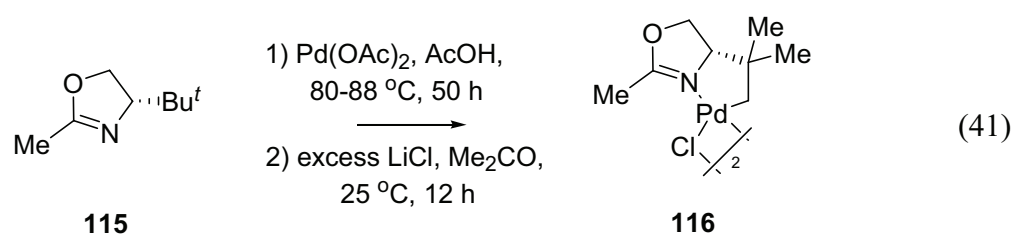
Palladacycles have also been investigated. They are a fascinating family of organometallic complexes with many applications in many areas including total synthesis, materials science and biological and supramolecular chemistry. Moreover, they are often air

stable, are readily synthesised and possess a range of types of metalated carbon and different types of donor groups bound to palladium (P-, N-, S- and O- containing groups).

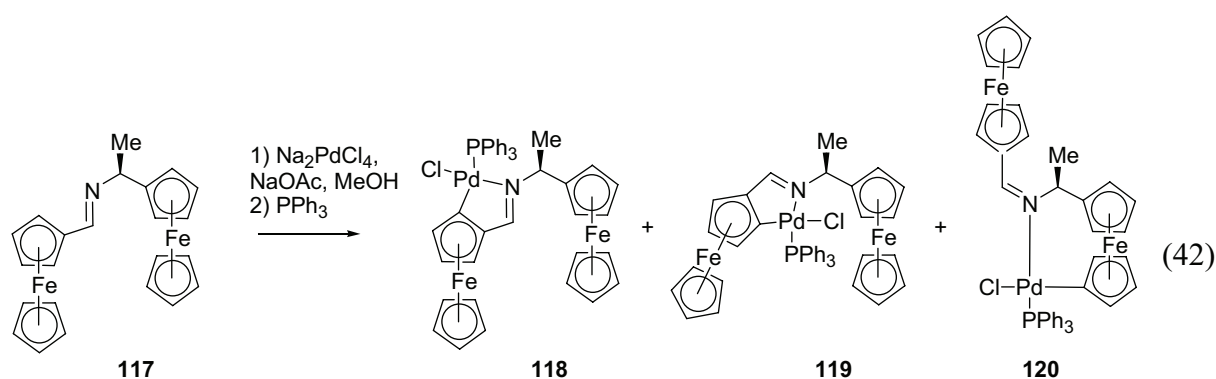
Several pincer complex syntheses have been described over the review period <1995JOM223, 2002OM3221>. The more recent one is the reaction of the *cis*-bis(di-*t*-butylphosphinomethyl)cyclohexane (*cis*-PCyP) **113** with palladium chloride affording C₈ and C₁ symmetrical complex **114**, where the PCyP ligands are coordinated in a meridional fashion through the two phosphorus atoms and the cyclometalated C-1 carbon of the cyclohexane ring (Equation (40)) <2006ICA2806>.



In addition, dimer palladacycles have been extensively studied over the last ten years. Phosphapalladacycles <2000TA3967, 2003CC3002, 2005JA2388, 2005JOM3193> and nitropalladacycles syntheses have been widely described <1995ICA91, 1995JOM215, 1995OM1393, 1995TA2731, 1998TA1917, 1999OM2683, 2000JOM138, 2000OL1823, 2002ICC552, 2002JOM46, 2003JCS(D)3350, 2003OM5243, 2003TA2331, 2004JOC8101, 2004JOM1806, 2005JOC648, 2005OM77, 2005OM5665>. One of many examples is the successful cyclopalladation of compound **115** achieved only using Pd(OAc)₂ as the palladation agent in acetic acid solution, followed by treatment with LiCl (Equation (41)) <2004JOM2382, 2005OM4159>.

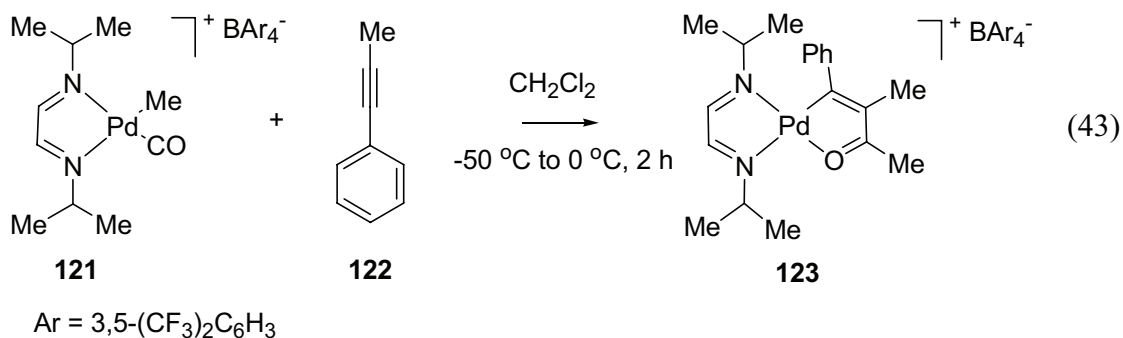


Ferrocene-based palladacycles have also been investigated <1999P2583, 2003OM2396, 2004OM224>. Among several studies, Troitskaya *et al.* achieved the cyclopalladation of the Schiff base **117** with a chiral centre (Equation (42)), leading to a mixture of three products, two of which were planar chiral diastereoisomers formed from homoannular substitution into the aldehyde fragment. The third product was a result of an unusual heteroannular palladation of the nitrogen in starting aldimine <2005JOM3976>.



Cyclopalladated sulfur-containing <1995JOC1005> and oxygen-containing complexes <2003OM3967, 2005CEJ3268> have also been synthesised. The insertion of phenylacetylene

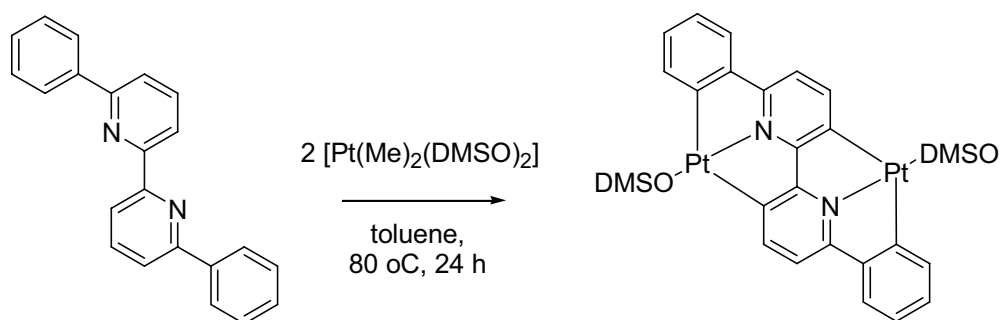
122 into the palladium-carbon bond of complex **121** yielded the palladacycle **123** (Equation (43)).



Similar reactions have been achieved with platinum. Phosphaplatinacycles <2003AG(E)105>, and nitroplatinacycles <2005OM2944> syntheses have been described using PtCl₂(cod) (cod = cyclooctadiene) or PtMeCl(cod).

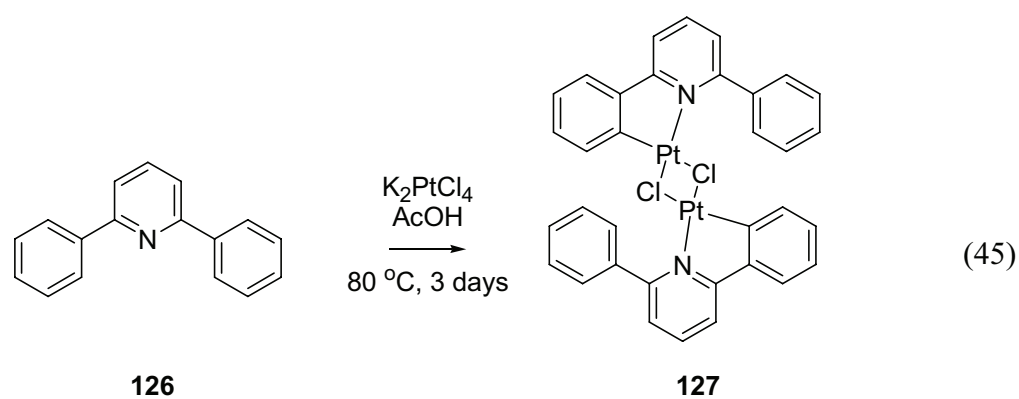
Intramolecular activation of C(aryl)-X bonds (X = Br, Cl, F and H) at platinum(II) has been achieved for amine-imine ligands such as RCH=NCH₂CH₂NMe₂, in which R was an aryl group <1996P1981>.

A series of complexes with bipyridine ligands has also been described <2003EJI2749, 2004EJI4484, 2006OM2074>. The reaction between 6,6'-diphenyl-2,2'-bipyridine **124** and [Pt(Me)₂(DMSO)₂] was carried out with a platinum / ligand ratio of 2 : 1 in toluene at 80 °C (Equation (44)). The reaction was slow and led to the isolation of a yellow product that was insoluble in the reaction medium, was stable in air and had high thermal stability <2006OM2253>.



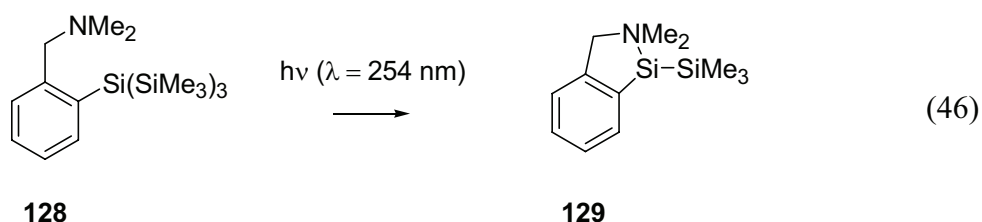
As previously observed for the palladium complexes, pincer ligand systems coordinated to Pt(II) centers have been described in the literature between 1995 and 2005 <2004, IC725, 2004OM5432>.

Platinum-containing dimer compounds have also been synthesised <2003JOM112, 2005IC2443>. Metalation of 2,6-diphenylpyridine **126** by potassium tetrachloroplatinate in acetic acid gave a monocyclometalated chloride-bridged dimer **127** (Equation (45)) <2000OM1355>.

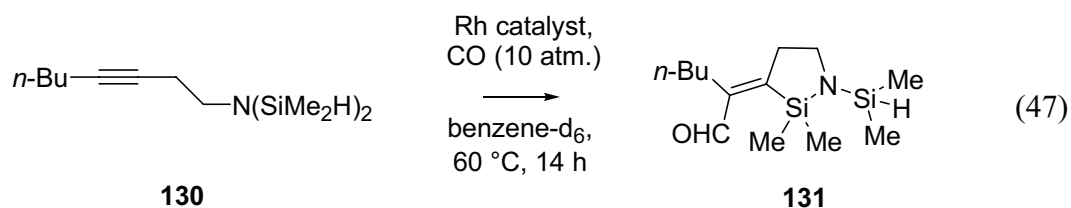


4.19.9.6 Group 14: Silicon-containing Heterocycles

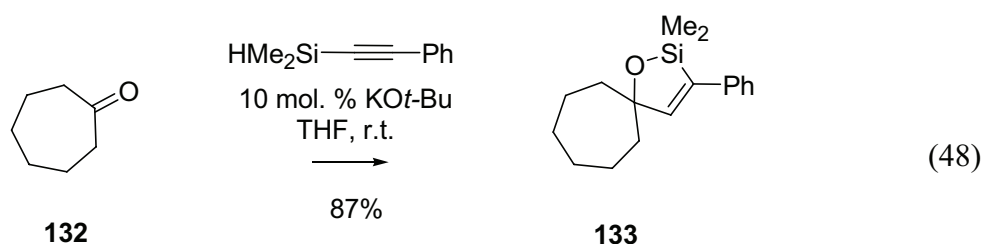
Silicium-containing heterocycles have been widely studied over the period review. Belzer *et al.* have studied nitrogen-containing silacycles <1996JOC3315> and within their research work, they described the photolysis of a trisilane **128** in a hydrocarbon matrix at -196 °C and observed an intense absorption at $\lambda_{\text{max}} = 478$ nm, which was attributed to the intramolecularly coordinated silylene **129** (Equation (46)) <1998CEJ852>.



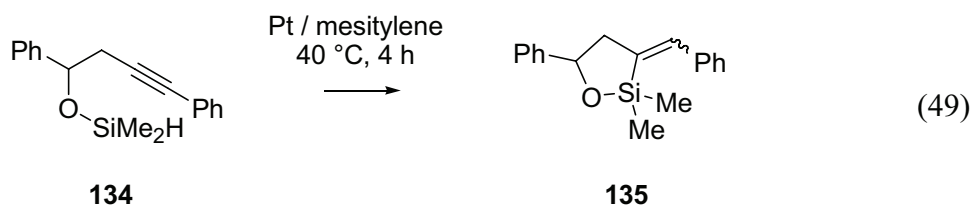
Nitrogen-containing silacycles have also been synthesised by thermolysis of bis(pentacoordinate) silicon compounds in the presence of butyllithium <2003JOM215>, by reaction of various (dichloromethyl)oligosilanes $\text{R}(\text{Me}_3\text{Si})_2\text{-SiCHCl}_2$ with alkyllithium derivatives <2004EJI1538>, and have also been obtained by intramolecular silylformylation of 1-bis(dimethylsilylamino)-3-octyne **130** in the presence of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, in toluene at 60 °C (Equation (47)) <1999OM5103>.



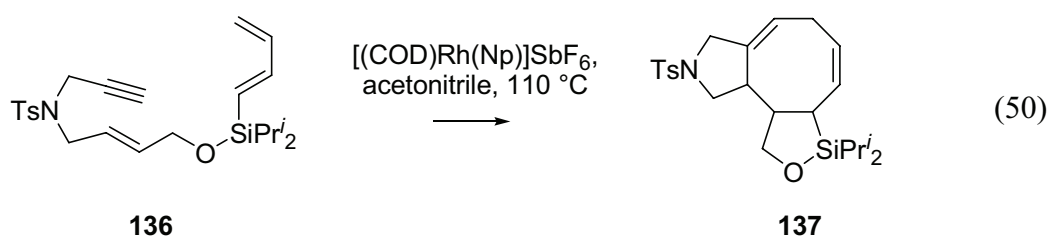
Oxasilacyclopentenes have been synthesised either by silacyclopropenation of alkynes utilizing Ag_3PO_4 as catalyst <2004JA9522>, either by reaction of ketones and alkynylsilanes in the presence of a catalytic amount of a nucleophilic initiator (Equation (48)) <2005OL4995>.



Oxasilacyclopentanes have been extensively studied over the period review and many different methodologies have been developed for their syntheses. Intramolecular radical cyclisations <2001JOC1966>, intramolecular silylformylation of silyloxyalkynes promoted by catalysts such as Rh <2001OL1303>, Ni <2001TL3259>, hydrosilylation of homopropargyl hydrodimethylsilyl ethers promoted by solvated Pt-atoms (Equation 49)) <1998JOM57>, and also photoinduced intramolecular cyclisation of alkynyl-substituted pentamethyldisilanes <1998TL6891> have been reported.



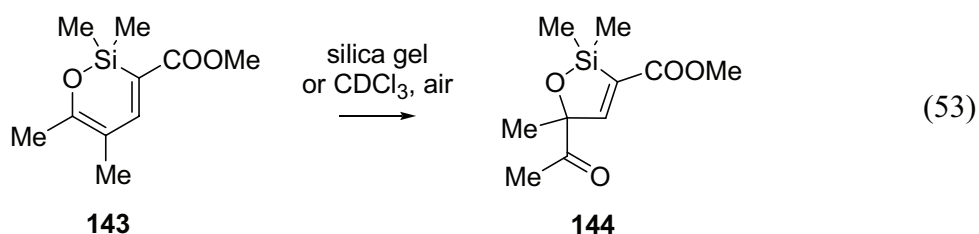
Analogously, intramolecular hydrosilation reactions have been carried out with olefins: cyclisation of alkenyloxysilanes catalysed by thiols <1998JCS(P1)467> and by Pt <1996TL827> have been described. In addition, intramolecular temporary silicon-tethered rhodium catalysed [4+2+2] cycloisomerisation reactions have been carried out by Evans *et al.* (Equation 50) <2004JA11150>.



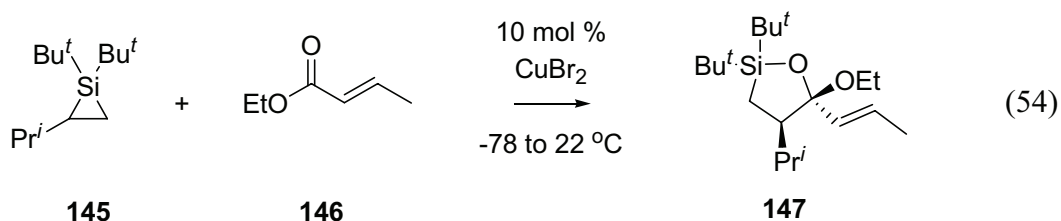
Silicon-oxygen heterocycles from thermal <2004CC122, 2004JOM1739>, photochemical <1999EJO1939>, transition-metal-catalysed and radical <2004PS955> reactions have been extensively described from 1995 to 2005. Woerpel and coworkers have studied many different strategies to obtain oxasilacyclopentanes <2002JA6524, 2002JA12648, 2003OL4325>. Particularly, they reported the reaction of α,β -unsaturated (or not) alkenes with silacyclopropanes: ZnBr_2 <2000AG(E)4295>, CuBr_2 <2000AG(E)4295>, AgOTf <2004JOC4007>, $\text{AgOTf} / \text{ZnBr}_2$ <2002JA9370, 2004JOC4007>, $\text{AgOTf} / \text{CuI}$ <2004JOC4007>, AgOCOCF_3 <2005JA2046>, $\text{AgOCOCF}_3 / \text{ZnBr}_2$ <2004JOC4007> - catalysed reactions have been reported.

Another way to synthesise oxacyclopentanes is the thermal insertion reaction of 1-formylpyrrolidine **138** into silirane *trans*-**139** which proceeded cleanly in hexanes at 120 °C

Oxasilines have generally been found to be of limited stability <1999EJO1213>. Indeed, by passing through a silica gel column or in CDCl_3 solution, **143** was converted, by ring contraction and incorporation of an oxygen atom, into 5-acetyl-2,5-dihydro-1,2-oxasilole **144** (Equation (53)).



Oxasilacyclopentanes have been synthesised by insertion reactions of silacyclopropanes with carbonyl compounds <1997T16597, 2002JA9370, 2004JOC4007, 2005JA2046>. For example, copper-catalysed insertion into silacyclopropane **145** is described in Equation (54) <2000AG(E)4295>.

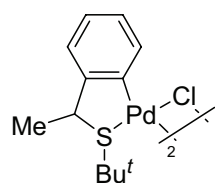


4.19.11 SYNTHESIS OF PARTICULAR CLASSES OF COMPOUNDS AND CRITICAL COMPARISON OF THE VARIOUS ROUTES AVAILABLE

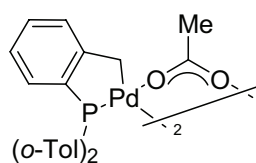
No update of this section, described in the previous edition of *Comprehensive Heterocyclic Chemistry* <96CHECII(3)783>, has been found necessary as no new classes of compounds have been described over the period review. Syntheses of various heterocycles have been developed in section 4.19.9.

4.19.12 IMPORTANT COMPOUNDS AND APPLICATIONS

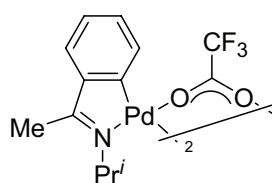
Cyclopalladated compounds have been found to be excellent catalysts, particularly effective for sp^2 - sp^2 carbon coupling processes such as Heck <2000CR3009, 2001T7449> and Suzuki reactions <2002JOM83, 2002JOM54>.



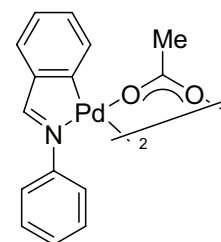
Dupont catalyst
<2000OL2881>



Hermann/Beller catalyst
<1999JOM23>



Milstein catalyst
<1999CC357>



Blackmond/Pfaltz catalyst
<1999OPRD275>

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4.19

Two Adjacent Heteroatoms with at least One Other Element

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4.19.1 INTRODUCTION

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4.19.1 INTRODUCTION

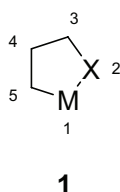
Ring systems with two adjacent heteroatoms and at least one other element were reviewed in the first and second editions of *Comprehensive Heterocyclic Chemistry* (CHEC-I <84CHECI(1)665> and CHEC-II <96CHECII(3)783>). This chapter covers reports up to the end of 2005. The literature was searched by groups within the periodic table.

4.19.1.1 Scope

Contrary to the second edition of *Comprehensive Heterocyclic Chemistry* (CHEC-II) where only rings which have relatively strong σ -bonds between adjacent atoms were reviewed, syntheses of heterocyclic complexes will also be described in this chapter. The chemistry of such “chelates” or “coordination compounds” is very interesting as the carbon-metal bond is labile and subject to various reactions such as insertion, protonation or substitution. However, even though the synthesis of these intramolecular complexes will be described in section 4.19.9, their physical properties will not be reported in this chapter. As the cyclic complex is in equilibrium with its open-chain form, the structural properties of such compounds may not be indicative of the heterocycle ring at all.

4.19.1.2 Nomenclature

IUPAC nomenclature is generally followed using the numbering shown in **1**. The cyclic structure, when X is a non-metallic heteroatom and M is a metal, is called a metallaheterocycle or a cyclometallic compound. Most metallaheterocyclopentanes have a stabilizing aromatic ring fused to the five-membered ring but a few cases of unfused stable metallaheterocyclopentanes are known.



4.19.2 THEORETICAL METHODS

There are no reports of *ab initio* or semi-empirical methods being used on five-membered ring heterocycles of this class.

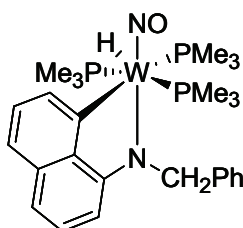
4.19.3 EXPERIMENTAL STRUCTURAL METHODS

4.19.3.1 X-ray Diffraction Studies

X-ray diffraction data have focussed on determining the conformation of the five-membered ring or substituents, or the geometry around the metal atom. Over the past ten years, X-ray crystallography has been used routinely and most of the new heterocycles

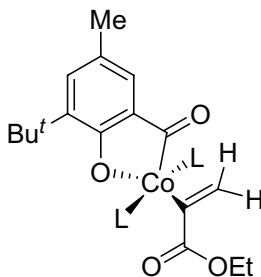
synthesised have been examined by this method. Mention of these results is made in the appropriate sections dealing with the synthesis of the heterocycle.

The crystals of **2** were submitted to single-crystal X-ray diffraction and the structure revealed a distorted pentagonal bipyramidal geometry around the tungsten center bearing one nitrosyl group, one hydride ligand, three PMe₃ ligands, and the bidendate η²-benzyl-naphthylamide ligand <2005JCS(D)580>.



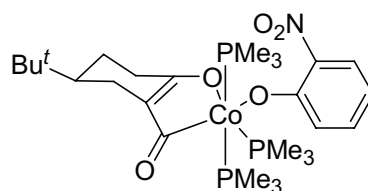
2

The structure of the pentacoordinate vinylcobalt(III) **3** (L = trimethylphosphine) has been determined by an X-ray diffraction analysis <2005ZAAC1929>. The cobalt atom is located above the base of a square pyramid and attains penta-coordination with two equatorial phosphorus atoms of *trans*-trimethylphosphine ligands, a carbon atom of the vinyl group, and an oxygen atom of the phenoxy group. The carbon atom of the acyl group is located at the apex of the square pyramid.



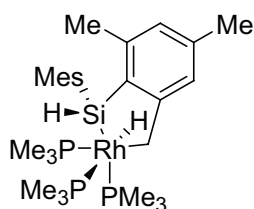
3

The molecular structure structure of **4** showed a hexacoordinate cobalt and three *P*-donor atoms lying in a plane, and two phenolate-*O* donors and an acyl group arranged in a plane perpendicular to the first <2003ICA179>.



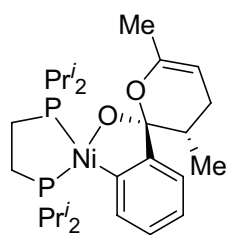
4

The structure of **5** was also determined by X-ray diffraction. The Rh-Si distance was 2.365(7) Å, hydrogen atoms on rhodium and silicon were located and refined to provide Rh-H and Si-H distances of 1.541(3) and 1.456(3) Å. The small Si-Rh-C angle of 80.16(7)° was indicative of some strain in the five-membered ring <1998OM2912>.



5

Conclusive evidence for the structure of **6** was obtained from an X-ray analysis, which confirmed the presence of a spirocyclic unit, with the expected *trans* disposition of C-2 and C-12 <2003CC1742>.

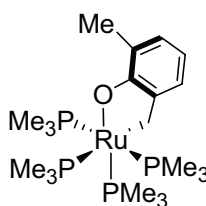


6

4.19.3.2 NMR Studies

Structural characterisation by NMR methods is routine and, in general, mention of the results has been deferred to the sections dealing with the synthesis of particular heterocycles. This section includes results where sufficient work has been performed to suggest patterns and where more unusual techniques have been discussed.

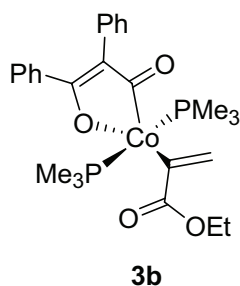
The $^3\text{P}\{^1\text{H}\}$ NMR spectrum of complex **7** showed an AM_2X pattern at -13.8, -0.96 and 10.7 ppm, indicating two *trans* and two *cis* PMe_3 ligands in an octahedral geometry. The ^1H NMR spectrum showed three magnetically inequivalent PMe_3 ligands at δ 0.90, 1.00 and 1.17 ppm <1998OM501>.



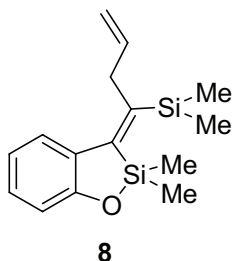
7

The ^1H NMR spectrum of **3b** showed a pseudo triplet at 1.0 ppm with strong coupling ($|^2J_{\text{P,H}} + ^4J_{\text{P,H}}| = 8.1$ Hz) to the *trans* PMe_3 ligands. The signals of the two geminal protons in the alkenyl group were found in the range expected of alkenyl-CH groups, with coupling

constants $^2J = 3$ Hz. In the ^{31}P NMR spectrum at -30 °C, singlet for the *trans* PMe_3 groups were observed. The diamagnetic properties of **3b** were compatible with a square pyramidal configuration <2005ZAAC1929>.



In 1998, the structure of compound **8** was determined by various physical methods, including ^1H - ^1H and ^1H - ^{13}C correlation spectroscopy (COSY), HMBC, nuclear Overhauser and exchange spectroscopy (NOESY) <1998TL6891>.



4.19.3.3 Ultraviolet and Infrared Spectroscopy

Most of the studies have been carried out on non-stable metallacycles with one or more weak bonds in the intended five-membered ring. However, compound **2**, previously described in section 4.19.3.1, has been analysed by IR spectroscopy <2005JCS(D)580>. The spectrum revealed a band at 1535 cm^{-1} , which provided the evidence for the presence of an

NO group in this complex. Complex **3** has also been analysed by IR and its spectrum showed bands at 1659 and 1641 cm^{-1} characteristic of the presence of C=O <2005ZAAC1929>.

4.19.4 THERMODYNAMIC ASPECTS

Because of the wide range of atoms that can occupy sites in the heterocycle ring, it is not possible to make many generalisations about physical and thermodynamical properties. However, it is possible to conclude that many metal-carbon bonds are weak or subject to easy reactions such as protonation, insertion, or redox reactions. Many metal bonds to nitrogen, oxygen, sulfur, silicon, and phosphorus are also labile. Particular attention should be paid to the valence states of heteroatoms: those, whose normal valence state is satisfied without closure of the ring, or those whose valence is exceeded on ring closure, are generally in equilibrium with open-chain or polymeric structures (physical properties of such complexes will not be covered in this section).

4.19.4.1 Physical Properties

A common feature of many metallaheterocyclopentanes is their sensitivity to hydrolysis, insertion of carbon monoxide, or oxidation on exposure to air. Many are subject to dimerisation reactions that are thermally induced or thermally reversed.

4.19.4.2 Conformational Studies

There have been no conformational studies on metallaheterocyclopentanes over the period of this review.

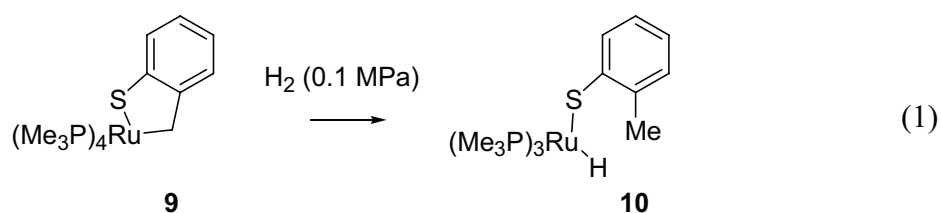
4.19.5 REACTIVITY OF FULLY CONJUGATED RINGS

Metallaheterocycles with the metal atom capable of supporting a carbon-metal double bond, and with oxygen, nitrogen, sulfur, or selenium as the second heteroatom are the only structures capable of full conjugation. These compounds show furan-like aromaticity with the heteroatom *p*-electrons participating. No examples of this type of ring system were uncovered, undoubtedly due to the stability of the metalla-carbon double bonds required for their formation.

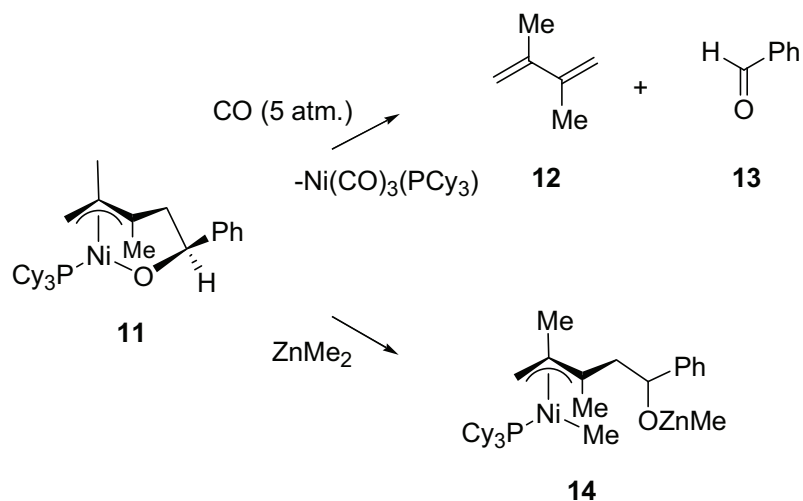
4.19.6 REACTIVITY OF NON-CONJUGATED RINGS

This section considers both reduced or partially reduced metallaheterocycles, i.e. means with one or no double bonds.

Exposure of the thiaruthenacycle **9** to hydrogen gas (0.1 MPa) in C₆D₆ led to hydrogenolysis (Equation (1)) <2005OM4799>.

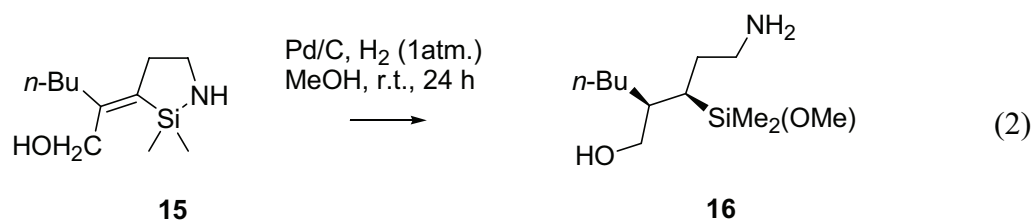


Treatment of the nickel complex **11** with carbon monoxide (5 atm.) led to the formation of butadiene **12** and aldehyde **13** with the formation of $\text{Ni}(\text{CO})_3(\text{PCy}_3)$ <2006JA7077>. The scission of the nickel-oxygen bond of the alkoxy complex **11** was also achieved with ZnMe_2 to afford **14** in very good yield (Scheme 1).

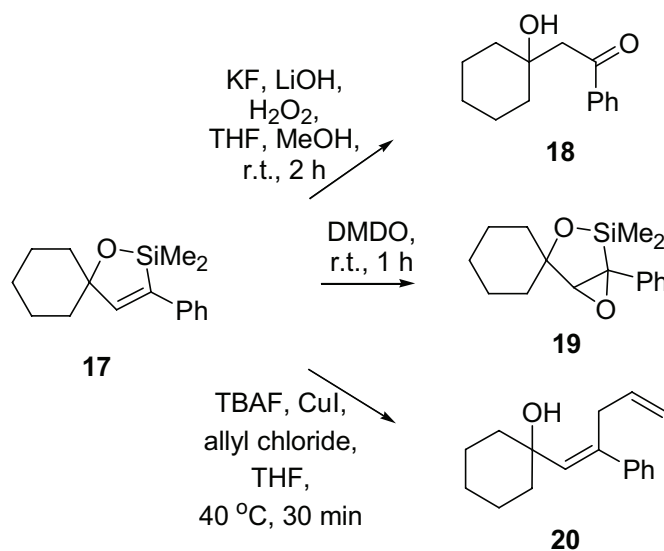


Scheme 1

Ring opening of azasilacycle **15** has also been observed (Equation (2)) <1999OM5103>.

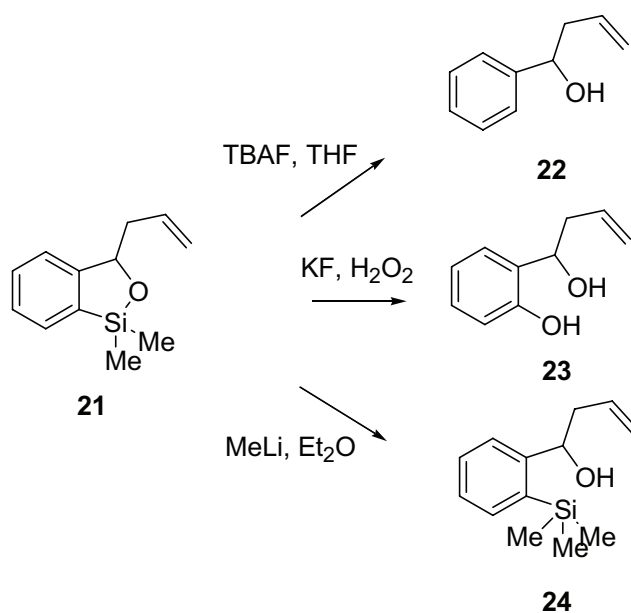


Oxacyclopentene **17** underwent a variety of transformations, like Tamao oxidation, yielding the β -hydroxy ketone **18** efficiently, an epoxidation reaction, and transformation into 1,4-diene **20** (Scheme 2) <2005OL4995>.



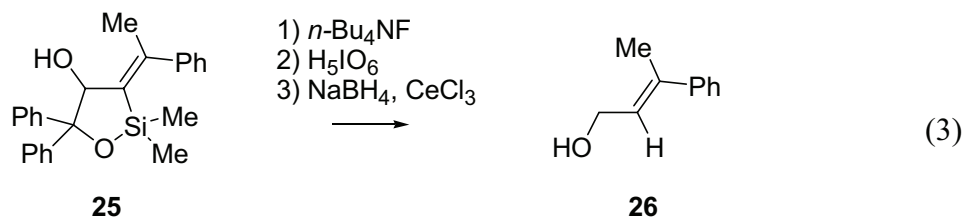
Scheme 2

Reactivity of benzo[1,2]oxasilole **21** was also studied <2004CC122>. Homoallylic alcohol **22**, was obtained by treatment with TBAF. Tamao reaction provided the desilylated *ortho*-phenolic benzyl alcohol **23**. Finally, treatment with methyllithium resulted in nucleophilic methylation on silicon and opening of the Si-O bond (Scheme 3).



Scheme 2

Instead of using Tamao conditions, Woerpel *et al.* have oxidised the C-Si bond with *t*-BuOOH, cesium hydroxide and cesium fluoride <1997T16597, 2002JA6524>. Oxidation of oxasilacyclopentanes with alkyl hydroperoxides to provide 1,3-diols was also described <2002JA12648>. Silicon-tethered ynals were converted into allylic alcohols *via* a cleavage process that involved stereospecific protodesilylation of the vinyl functionality (Equation (3)) <2001TL3259>.

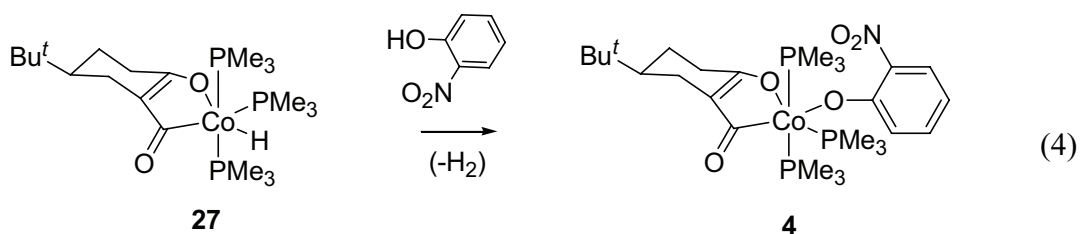


4.19.7 REACTIVITY OF SUBSTITUENTS ATTACHED TO RING CARBON ATOMS

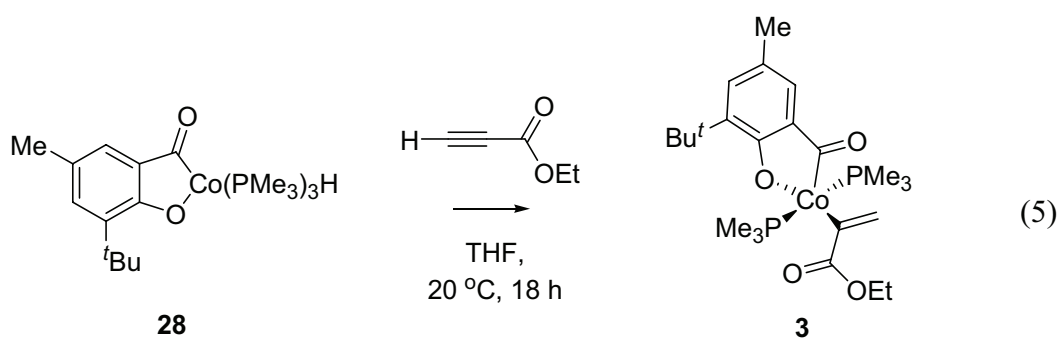
Substituent chemistry is that expected from analogous reactions of those substituents on saturated cyclic hydrocarbons or on aromatic heterocycles.

4.19.8 REACTIVITY OF SUBSTITUENTS ATTACHED TO RING HETEROATOMS

Acylphenolato(hydrido)cobalt(III) complexes were found to react smoothly with 2-nitrophenol, according to Equation (4) <2003ICA179>.



Formal insertion of propynoic acid ethyl ester into Co-H functions afforded pentacoordinate vinylcobalt(III) **3** (Equation (5)) <2005ZAAC1929>.



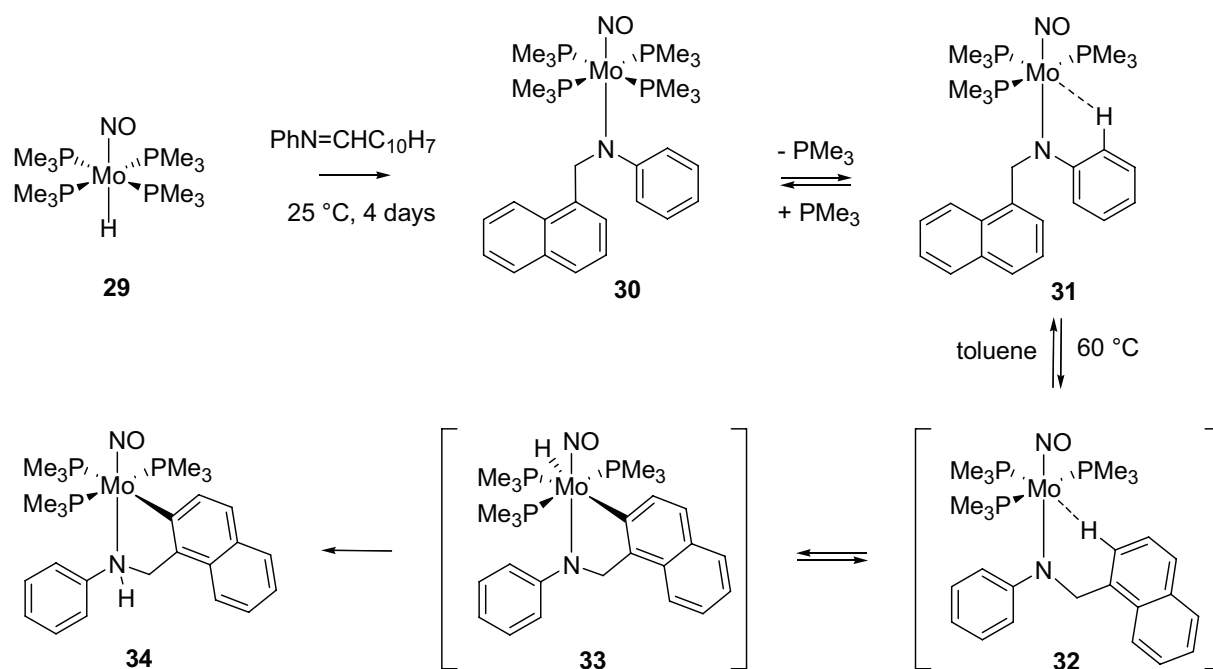
4.19.9 RING SYNTHESSES - FULLY SATURATED OR PARTIALLY SATURATED DERIVATIVES

In general, ring-forming reactions which result in hypervalent heteroatoms give complexes, where one of the ring bonds is weaker than the other ring bonds, i.e., the intended ring bond, between the metal atom and the heteroatom, generates a formal charge on one or more atomic centers. As such, these complexes are in equilibrium with their open-chain and polymeric structures. Contrary to the second edition of *Comprehensive Heterocyclic Chemistry* (CHEC-II) where only rings which have relatively strong σ -bonds between adjacent atoms were reviewed, the syntheses of heterocyclic complexes are also described in this section.

4.19.9.1 Group 6: Chromium, Molybdenum, and Tungsten

Only one example of a chelated tetracarbonyl chromium-containing complex has been reported during the period under review <1997T17297>. Molybdenum, and tungsten-containing complexes have also been studied.

Imine insertion into the Mo-H bond of the tetrakis(trimethylphosphine)-molybdenum nitrosyl hydrido complex **29** was performed by Berke and coworkers <2006JCS(D)73>. Treatment of **29** with an equimolar amount of *N*-naphthylideneaniline in toluene- d_8 , at room temperature during 4 days afforded the amido complex **30** as the only product (Scheme 3). When the reaction was carried out at 60 °C, with one equivalent of *N*-naphthylideneaniline, the amino complex **34** was obtained within 2 weeks.

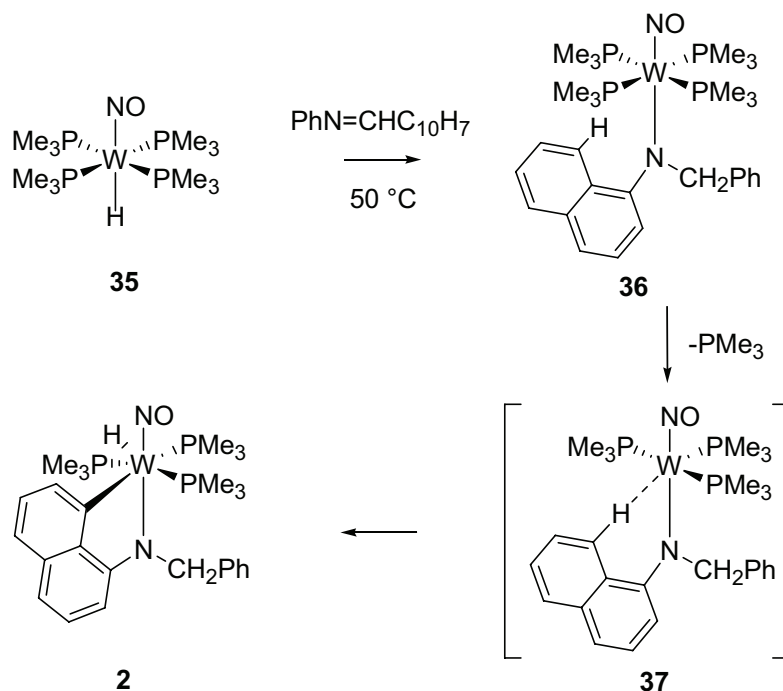


Scheme 3

Scheme 3 presents a plausible pathway for the formation of **34**. The first step is the imine insertion into the Mo-H bond to form the amido complex **30**, which subsequently loses one PMe_3 ligand and establishes an equilibrium with the agostic complex **31**. When the system is heated to $60\text{ }^\circ\text{C}$, other equilibria are assumed to come into play leading to the agostic species **32**. Oxidative addition of the agostic C-H bond produces **33** and proton transfer to the amide ligand eventually gives **34**.

Similar studies have been investigated by the same research group, by replacing the molybdenum by a tungsten atom <2005JCS(D)580>. Indeed, an insertion reaction of the imine $\text{C}_{10}\text{H}_7\text{N=CHPh}$ into the W-H bond of the hydridonitrosyltetrakis(trimethylphosphine)-tungsten(0) **35**, followed by an oxidative addition of the C-H bond to the tungsten center gave

the complex $[W(NO)(H)(PMe_3)_3(C_{10}H_6NCH_2Ph)]$ **2**, which structure was studied by X-ray diffraction (Scheme 4).



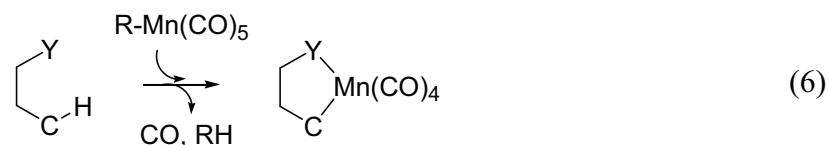
Scheme 4

The insertion of imine into the M-H bond transition metal hydride is believed to be an important step in the catalytic hydrogenation of such substrates. The reaction was observed when a toluene- d_8 solution of **35** was heated at 50 °C during 20 days with *N*-benzylidene-1-naphthylamine affording **2** in 78% yield.

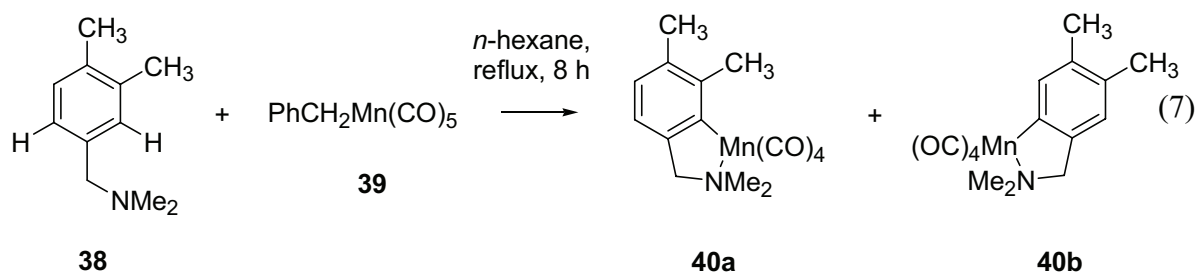
4.19.9.2 Group 7: Manganese, Technetium, and Rhenium

Many types of aromatic substrates are known to undergo a cyclometallation reaction when exposed to alkylpentacarbonylmanganese complexes under thermal conditions. It is well established that the treatment of ligand appended arenes with

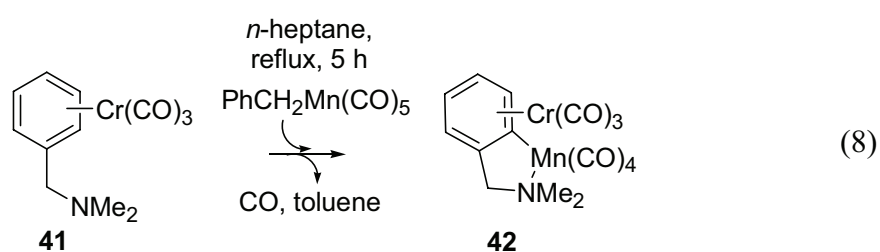
alkylmanganesepentacarbonyl complexes can lead to the formation of [C,Y] heterochelates of $\text{Mn}(\text{CO})_4$ (Y being a two electron donor ligand) (Equation (6)).



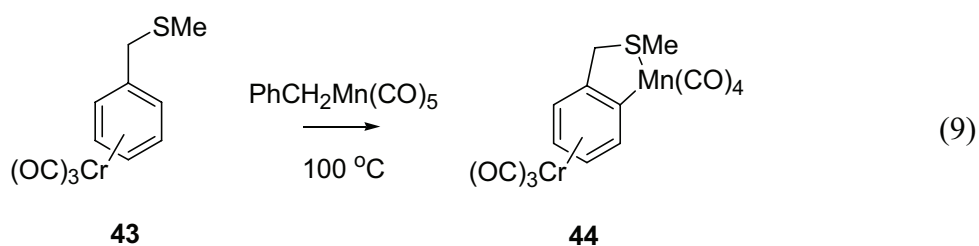
For instance, aromatic compounds such as *N,N*-dimethylbenzylamine, alkyl benzyl thioethers, 2-phenylpyridine, acetophenone, benzaldehyde and diazobenzene can be readily transformed into the corresponding cyclomanganated products when treated with alkyl-pentacarbonylmanganese complexes <1995COMCII(6)21>. The reaction of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ with the tertiary amine 3,4- $\text{Me}_2\text{C}_6\text{H}_3\text{CH}_2\text{NMe}_2$ **38** in refluxing *n*-hexane, afforded the corresponding neutral *C,N*-cyclometalated Mn(I) compounds of stoichiometry $\text{Mn}(\text{C-N})(\text{CO})_4$ **40a** and **40b** (Equation (7)). The net yield was 88% and the relative **40a:40b** ratio was 1:2 <1995IC643>. In this reaction, with two potential cyclometallation sites, the observed orientational preference was to avoid a steric interaction between the methyl group *ortho* to the Mn-C bond and a CO unit.



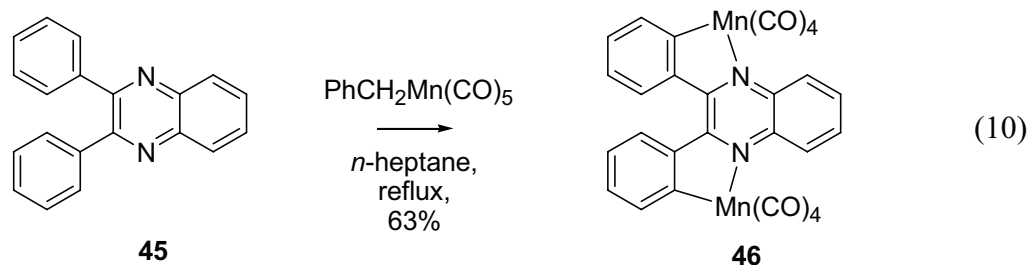
Cyclomanganation reactions of (η^6 -acylaryl)tricarbonylchromium complexes have been investigated and the novel heterobimetallic complexes synthesized characterised by X-ray crystallography <1996JOM109>. Complementary studies have been carried by Djukic *et al.* <1997OM657, 1998JOM65>, who studied the metallation with (η^6 -arene)tricarbonylchromium substrates taking as a model the *ortho*-manganation reaction promoted by benzylpentacarbonylmanganese (Equation (8)).



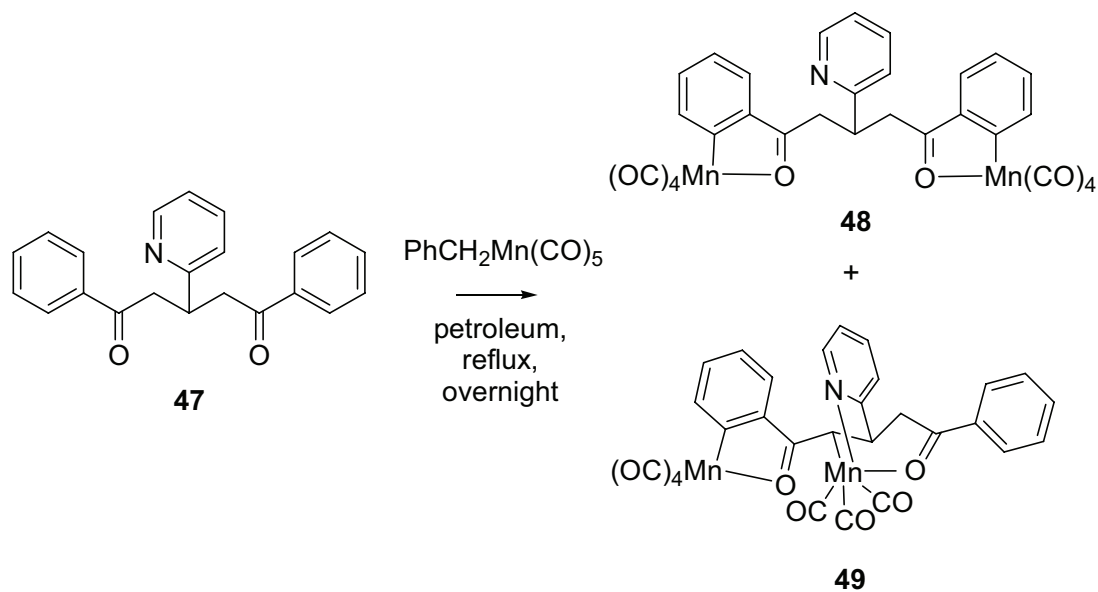
A thioether such as **43** also afforded a cyclomanganated product **44** (Equation (9)).



Some examples of bis-cyclomanganation have also been reported <2002OM3519, 2002TL5241, 2005JOM4822>. For example, the reaction of 2,3-diphenylquinoxaline **46** with $\text{PhCH}_2\text{Mn(CO)}_5$ afforded the dinuclear complex **47** <2002CC638> (Equation (10)).

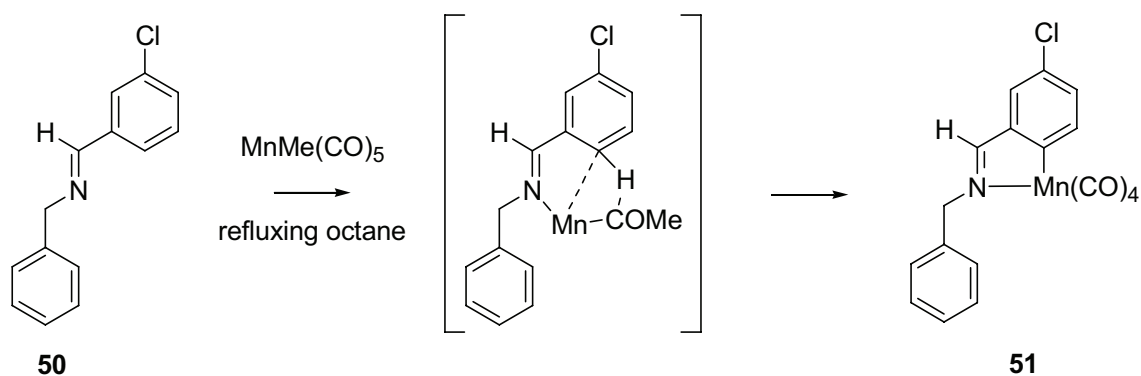


Reaction of the 1,5-diphenyl-3-(2-pyridyl)pentane-1,5-dione **47** with 2.5 equivalents of benzylpentacarbonylmanganese in petroleum under reflux gave a small amount of the symmetrical di-aryl-manganated product **48** but mostly the complex **49**, which is manganated at only one aryl carbon (by Mn(CO)_4) but also (by Mn(CO)_3 with *N* and *O* coordination) at the methylene carbon adjacent to the Mn(CO)_4 -coordinated ketone carbonyl (Scheme 5). The latter is a rare example of direct cyclomanganation at a saturated carbon and the only known case adjacent to carbonyl <2005JOM3348>.



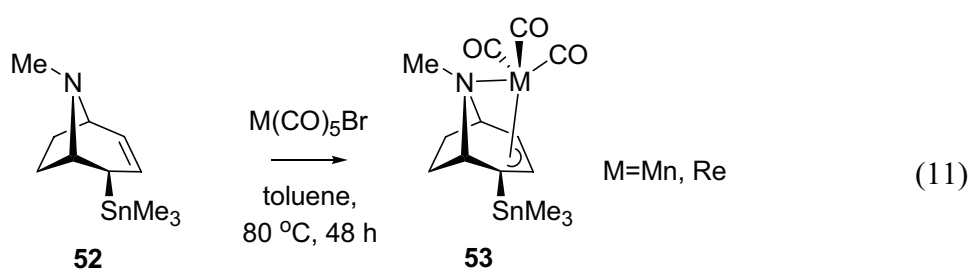
Scheme 5

The synthesis of cyclomanganated metallocycles has also been carried out by reaction between Benzyl-benzylidene imines and the metallating agent MnMe(CO)_5 <2004JOM4889>. Complex **51** has been characterised by FABMS and NMR analysis. The proton spectrum provided conclusive evidence on the metallation position: the methinic proton signal in **51** appeared at a δ value close to that of the methinic proton of the free imines, in agreement with an *E*-configuration for this ligand (Scheme 6).

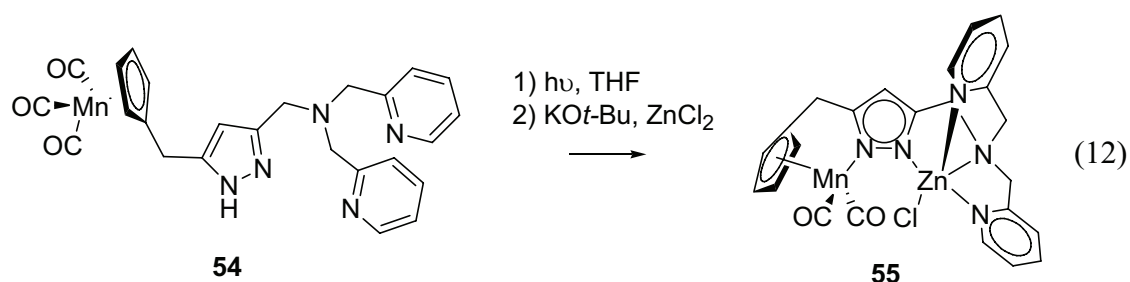


Scheme 6

The preparation of tropidinyll transition metal complex **53** was achieved by reaction of 4-trimethylstannyltropidine **52** with $M(\text{CO})_5\text{Br}$, $M=\text{Mn}$, Re <2003ZAAC(629)2408>. In complex **53**, the tropidinyll ligand is coordinated through the three-carbon allylic system which serves as a $2\sigma/4\pi$ -electron donor. It has been characterised by single-crystal X-ray diffraction analysis (Equation (11)).

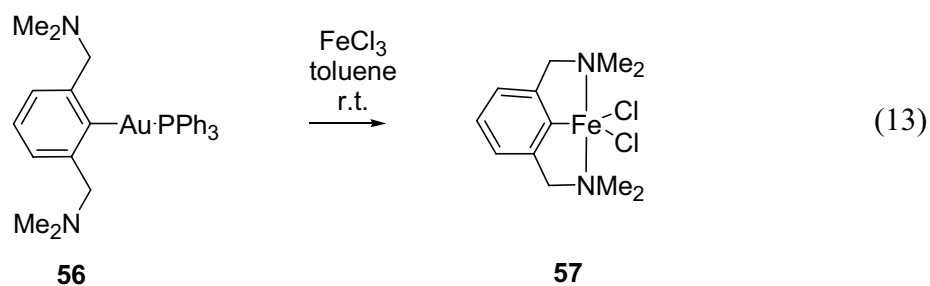


Finally, pyrazole, binding to manganese(I) has been achieved by photoinduced substitution of CO, and the adjacent N_4 -coordination pocket is suited to accommodate a second metal ion (Equation (12)). The heterodinuclear MnZn complex **55** was characterised crystallographically and its redox chemistry investigated by spectroelectrochemical methods <2002JOM113, 2005IC3863>.

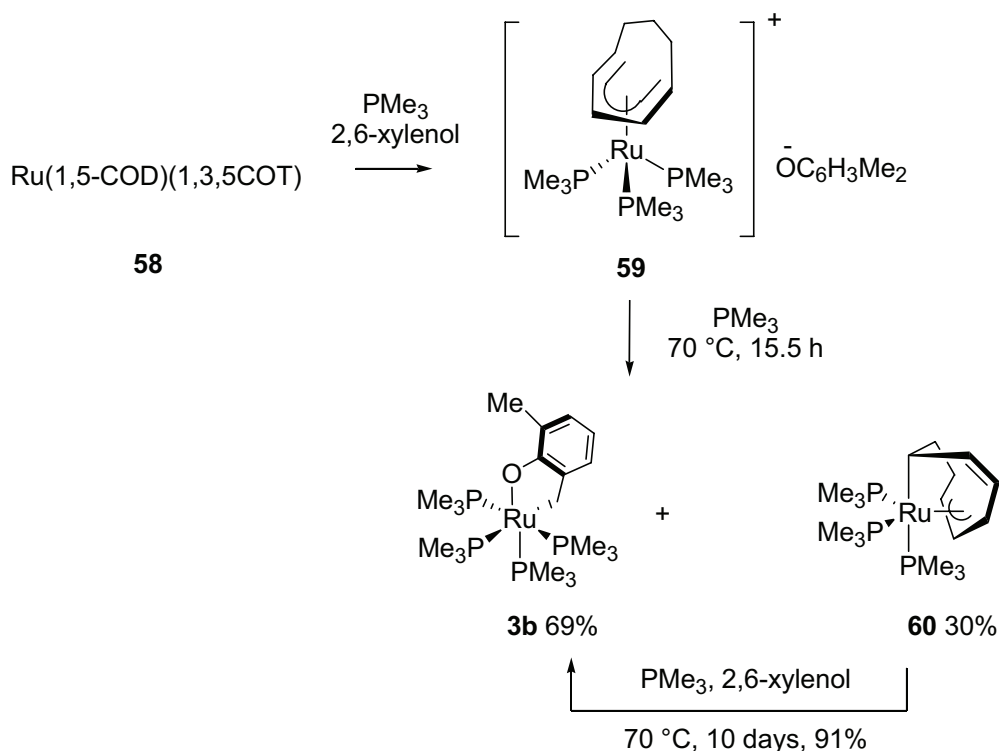


4.19.9.3 Group 8: Iron, Ruthenium and Osmium

The synthesis of only one iron-containing heterocycle was described between 1995 and 2006. The formation of paramagnetic **57** from a stable arylgold(I) phosphine, [Au(η^1 -C-NCN)(PPh₃)] **56** and anhydrous FeCl₃ in toluene at room temperature was confirmed by X-ray diffraction techniques <2002OM4556>. The reaction was carried out on millimolar scale and **57** was obtained in good yield. Moreover, the reaction was performed at room temperature, which underlines the nonreductive character of **56** giving an easy access to the formation of C-Fe^{III} bonds (Equation (13)).



Komiya and coworkers have studied the successive O-H and sp³ C-H bond activation of *ortho*-substituted phenols by a ruthenium(0) complex <1998OM501>.

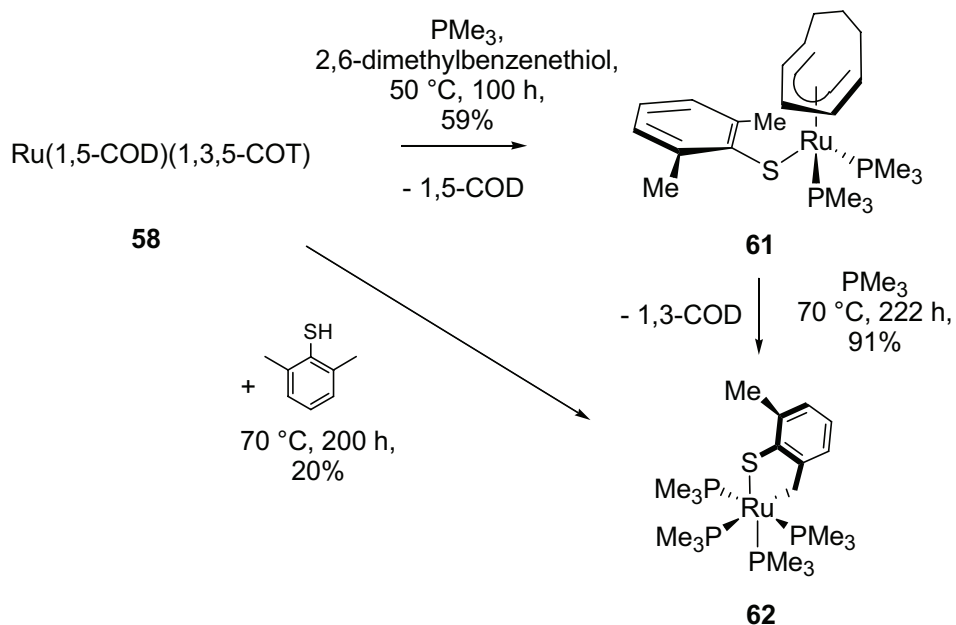


Scheme 7

The reaction of Ru(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) **58** with PMe₃ and 2,6-xyleneol in hexane caused immediate precipitation of [Ru(η⁵-C₈H₃-2,6)]⁺[OC₆H₃Me₂-2,6]⁻ **59** as a white powder (Scheme 7) <2000JOM18>. Treatment of **59** with PMe₃ at 70 °C for 15.5 hours resulted in sp³ C-H bond cleavage of the *ortho* methyl group in the aryloxo anion giving an oxaruthenacycle complex $\text{cis-Ru}[\text{OC}_6\text{H}_3(2\text{-CH}_2)(6\text{-Me})](\text{PMe}_3)_4$ **3b** in 69% yield with concomitant formation of 1,3-cyclooctadiene and 2,6-xyleneol. A small amount of **60** was also formed in the reaction. The η⁵-C₈H₁₁ moiety was considered to act as the hydrogen acceptor for the C-H bond activation liberating 1,3-cyclooctadiene. Complex **3b** has been characterised by NMR, IR and elemental analysis.

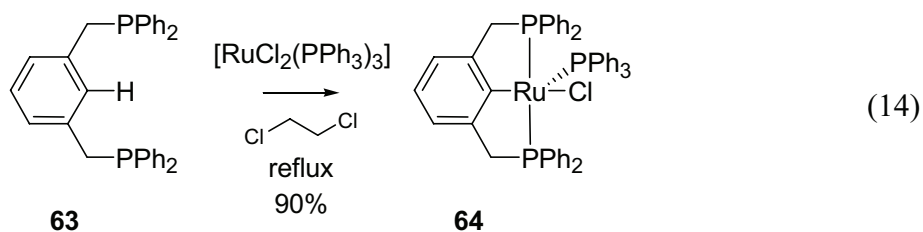
With the O-H and sp³ C-H bond activation of *ortho*-substituted phenols methodology in hand, Komiya and coworkers carried their research forward by synthesising a divalent

thiaruthenacycle complex, the *cis*-Ru[SC₆H₃(2-CH₂)(6-Me)-κ²S,C](PMe₃)₄ **62** (Scheme 8) <2005OM4799>.

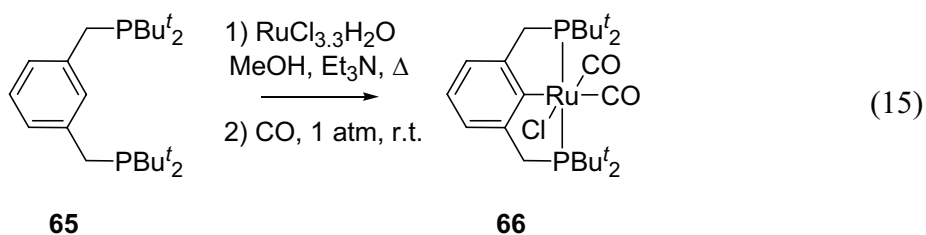


Scheme 8

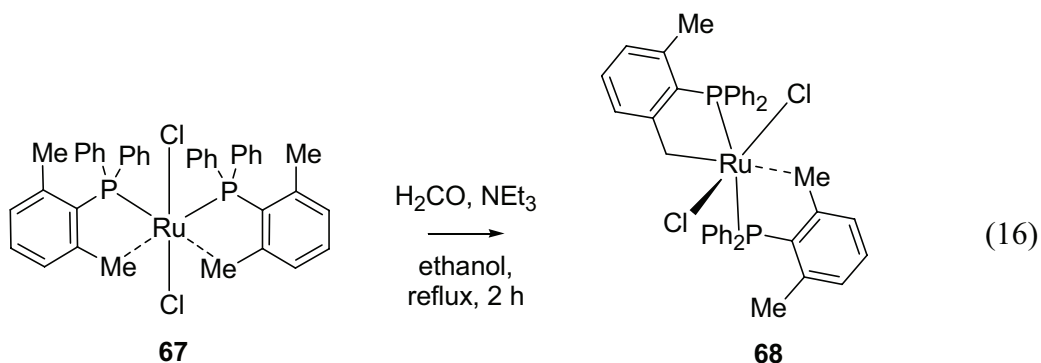
The synthesis, characterisation and reactivity of various ruthenium(II) complexes has been studied extensively by Koten and coworkers (Equation (14)) <1996OM5687, 1997JA11317, 2000OM5287, 2001EJI125, 2004OM5833>.



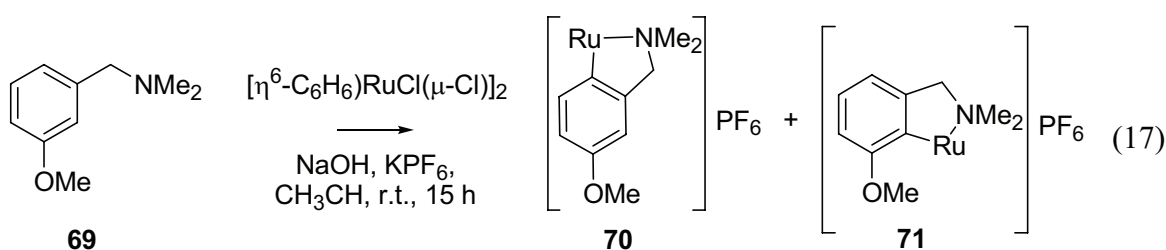
Treatment of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ with an equimolar amount of the bisphosphine ligand [2,6-($\text{CH}_2\text{P}^t\text{Bu}_2$) $_2$ - C_6H_4] **65** in methanol at 80 °C in a pressure vessel followed by reaction with carbon monoxide (1 atm) at room temperature resulted in the formation of the saturated complex **66** (Equation (15)) <2004ICA1854>.



In 2004, Baratta *et al.* achieved the synthesis of the five-coordinate complex $\text{RuCl}[2\text{-CH}_2\text{-6-MeC}_6\text{H}_3\text{PPh}_2][(\text{CO})(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{-PPh}_2]$ **68**, according to Equation (16) <2004OM6264>. The reaction of the 14-electron complex $\text{RuCl}_2[(\text{CO})(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{-PPh}_2]_2$ **67** with formaldehyde in presence of triethylamine proceeded in high yield *via* cyclometalation of an *ortho* methyl group and aldehyde decarbonylation.

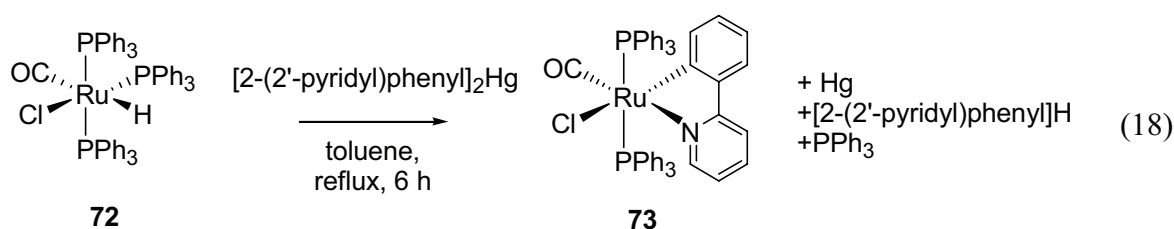


The cycloruthenation of substituted *N,N*-dimethylbenzylamines by $[\eta^6\text{-C}_6\text{H}_6]\text{RuCl}(\mu\text{-Cl})_2$ in acetonitrile in the presence of NaOH and KPF_6 , which led to the formation of corresponding cycloruthenated complexes in good to moderate yields has also been studied <1999OM2390>. For example, the work of Le Lagadec *et al.* is illustrated in Equation (17) <2004JOM4820>.

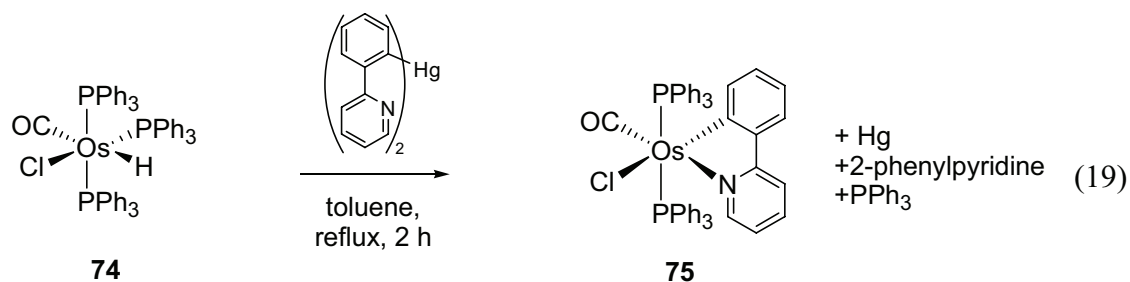


As shown in Equation (17), the cycloruthenation of the 3-substituted *N,N*-dimethylbenzylamine **69** afforded two positional isomers as a result of the Ru(II) attack at the C-2 or C-6 aromatic carbons.

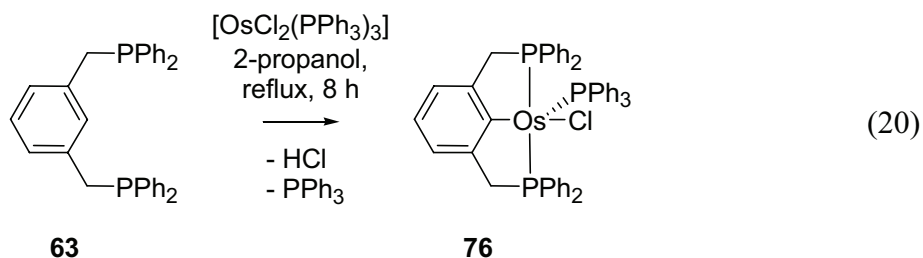
Treatment of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with $[\text{2}-(\text{2}'\text{-pyridyl})\text{phenyl}]_2\text{Hg}$ proceeded smoothly to form $[\text{Ru}(\eta^2\text{-}[\text{2}-(\text{2}'\text{-pyridyl})\text{phenyl}])\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ <1999OM2813>. In this complex, the $[\text{2}-(\text{2}'\text{-pyridyl})\text{phenyl}]$ ligand is bound as a stable five-membered chelate ring (Equation (18)).



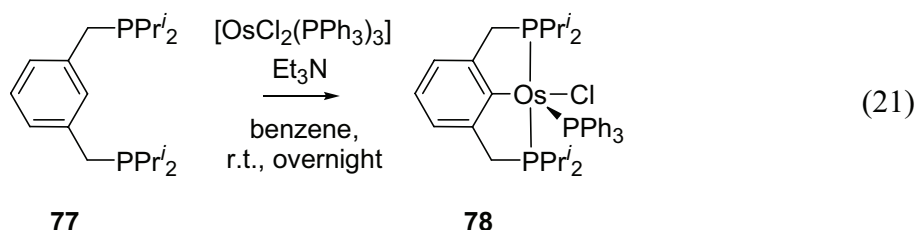
Similar transmetallation reactions using mercury reagents of the form Ar_2Hg have been performed by Clark *et al.* to deliver osmium complexes $\text{Os}[\eta^2\text{-C,N-(2-phenylpyridyl)Cl(CO)(PPh}_3)_2]$ **75** (Equation (19)) <1999OM2813, 2000JOM262>.



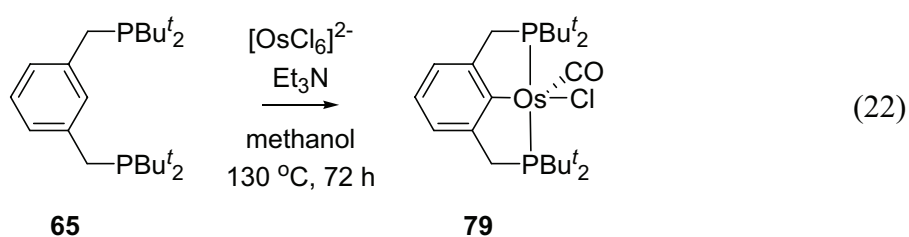
Preparation and spectroscopic characterisation of $\text{OsCl(PPh}_3)_3(\text{PCP})$ **76** ($\text{PCP} = 2,6\text{-Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3$) has been performed by Jia and coworkers <2000OM3803>. Treatment of $\text{OsCl}_2(\text{PPh}_3)_3$ with 1,3-($\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ **63** in 2-propanol indeed led to the formation of the coordinatively unsaturated complex **76** (Equation (20)). The spectroscopic data of the green compound **76** were consistent with a square-pyramidal complex with PPh_3 occupying the apical position.



An analogous complex **78** has been synthesised by Gauvin *et al.* <2001OM1719>, by reaction between the diphosphine **77**, $\text{OsCl}_2(\text{PPh}_3)_3$ and Et_3N (Equation (21)).

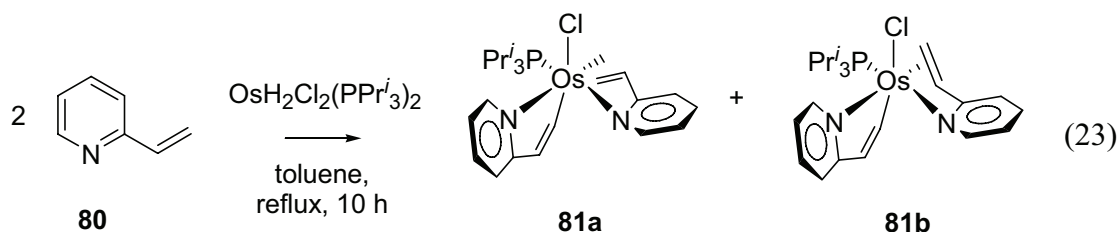


Similar conditions have been used by Gusev *et al.* to synthesise complex **54** <2001OM1001>. From OsCl_6^{2-} , they obtained the 16-electron chloride square-pyramidal compound **54**, using triethylamine and methanol as solvent ((Equation (22)).



More recently, C-H bond activation and subsequent C-C bond formation promoted by osmium have been investigated by Esteruelas *et al.* <2006JA4596>. Treatment of $\text{OsH}_2\text{Cl}_2(\text{P}i\text{-Pr}_3)_2$ with 2 equivalents of 2-vinylpyridine in toluene under reflux gave rise to the

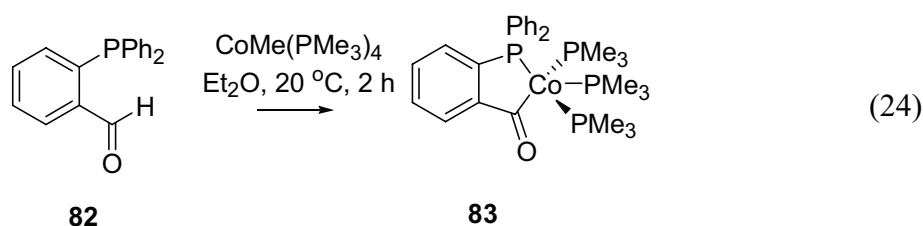
release of H₂ and [*i*-Pr₃PH]Cl and the formation of the red complex **81**, which was isolated in 70% yield as a 6:4 mixture of the isomers **a** and **b** shown in Equation (23).



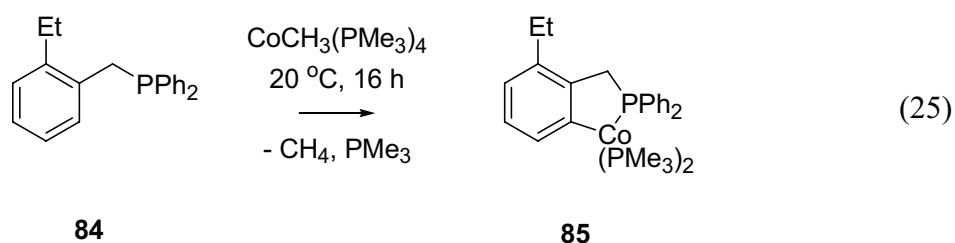
Complex **81** contains two substrate molecules. One of them is metalated, as a consequence of C(sp²)-H bond activation of the CH₂ group of the vinyl substituent, whereas the other one is coordinated to the osmium atom by the nitrogen atom and the C=C double bond of the olefin.

4.19.9.4 Group 9: Cobalt, Rhodium, and Iridium

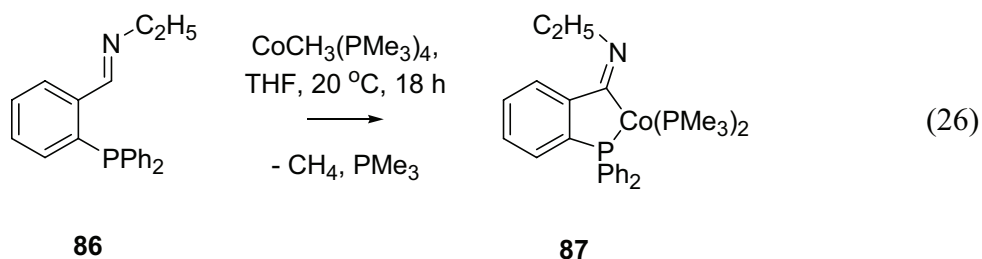
Only a few syntheses of cobalt-containing metalacycles have been carried out over the period under review. In 1998, Klein and coworkers reported the synthesis of the 18-electron cobalt(I) complex **83**, smoothly formed by an aldehyde reaction with a suitable methylcobalt(I) according to Equation (24) <1998OM4196>.



From 1996 to 2005, this research group published extensively on the synthesis of such cobaltacycles <2000EJI2295, 2002EJI3305, 2003EJI853, 2005OM2612>. They notably described the reaction between the benzyldiphenylphosphane **84** with $[\text{CoMe}(\text{PMe}_3)_4]$ at -70 °C in THF affording the selectively *ortho*-metalated complex **85** (Equation (25)).



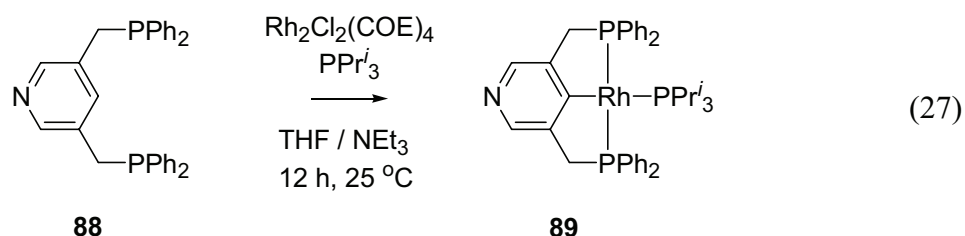
Analogously, the formation of the *C*-metalated complex **87** occurred at -70 °C according to Equation (26).



Rhodium-containing complexes have been extensively studied over the period review. Particularly, chelating ligand systems based on 1,3-disubstituted benzenes have been used to

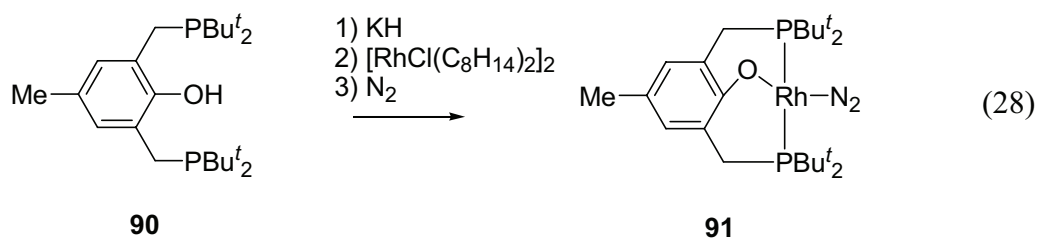
obtain the *ortho*-metalated complexes <1998CC917, 1998JA13415, 1999JA4528, 1999JA6652, 2000JA7723, 2003JA6532, 2003JA11041, 2005CEJ2319, 2006OM2292>.

The reaction of the chelating bis(phosphine)-3,5-bis((diphenylphosphino)-methyl)pyridine **88** with $\text{Rh}_2\text{Cl}_2(\text{COE})_4$ (COE = cyclooctene) and $\text{P}i\text{-Pr}_3$ in THF / Et_3N (3 : 1) led to the formation of the mononuclear Rh(I) complex **89** (Equation (27)) <1996IC1792>.

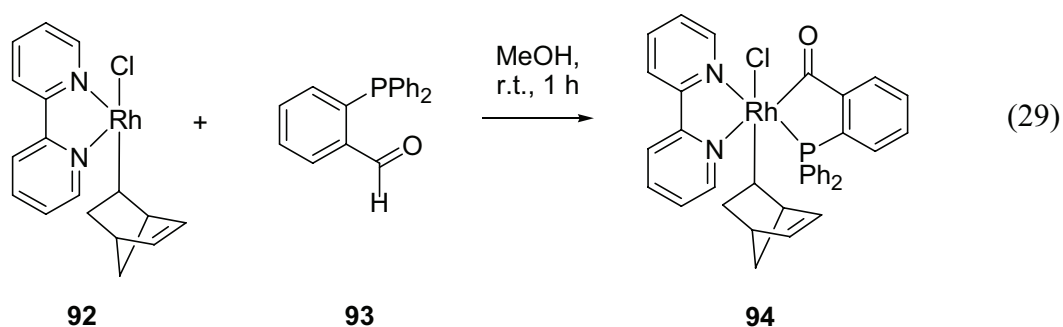


As expected, **89** exhibited two signals in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum (intensity ratio 2 : 1) in accord with the X-ray structure determination (*vide infra*).

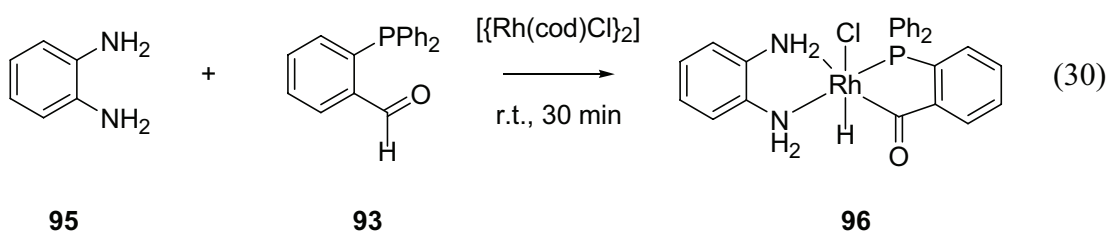
A similar reaction has been carried out between the aromatic phosphine alcohol **90** and $[\text{RhCl}(\text{C}_8\text{H}_{14})_3]_2$ in THF under a nitrogen atmosphere at room temperature affording the complex **91**, as proved spectroscopically by ^1H , $^1\text{H}\{-^{31}\text{P}\}$ and $^{31}\text{P}\{\text{H}\}$ NMR, IR and FD-MS measurements (Equation (28)) <1998JA6531>.



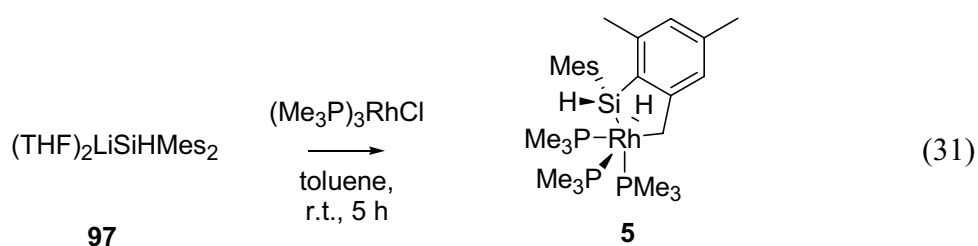
When $[\text{Rh}(\text{Cl})(\text{Nbd})(\text{bipy})]$ (Nbd = norbornadiene) **92**, prepared *in situ* was treated with $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{CHO})$ **93** in methanol, oxidative addition of aldehyde to rhodium followed by insertion of norbornadiene into the Rh-H bond occurred (Equation (29)) <2005EJI1671>. NMR spectroscopy, including 2D experiments allowed complete characterisation of complex **94**.



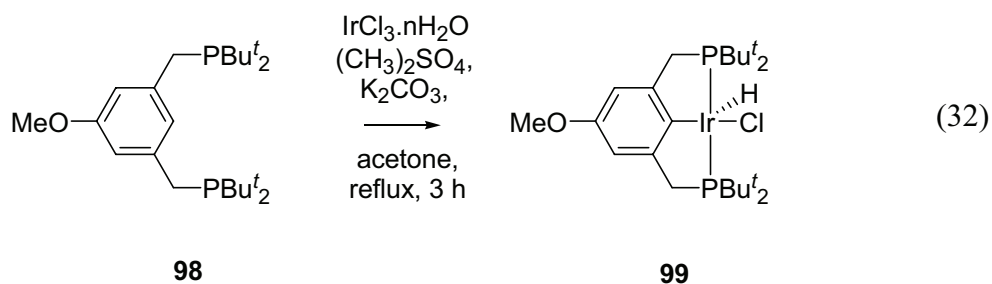
In addition, the reaction of $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ (cod = 1,5-cyclooctadiene) with $\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4\text{CHO})$ **93** in the presence of 1,2-phenylenediamine(daphen) **95** led to the formation of the chelate-assisted oxidative addition product $[\text{Rh}(\text{Cl})(\text{H})[\text{PPh}_2(o\text{-C}_6\text{H}_4\text{CO})](\text{daphen})]$ **96** with displacement of 1,5-cyclooctadiene as shown in Equation (30) <2004ICA2818>.



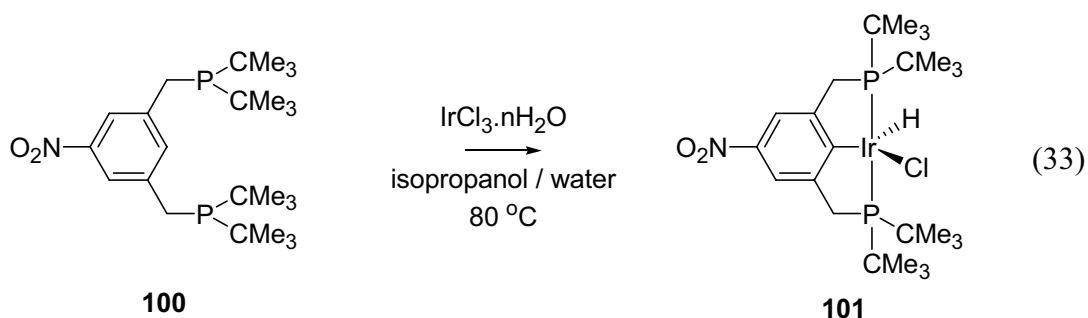
In 1998, Mitchell *et al.* described the synthesis of a new rhodium silyl complex <1998OM2912>. Reaction of $(\text{Me}_3\text{P})_3\text{RhCl}$ with $(\text{THF})_2\text{LiSiHMe}_2$ (Mes = 2,4,6-trimethylphenyl) in toluene resulted in formation of a light yellow solution, from which colorless crystals of **5** were isolated after work-up. The presence of both Rh-H ($\delta = -9.90$) and Si-H ($\delta = 5.76$) resonances in the ^1H NMR spectrum of **5**, and five separate methyl signals suggested the structure shown in Equation (31).



Iridium-containing complexes have also been studied over the period review <2000ICC511, 2002OM5775>. Treatment of the methoxy functionalised ligand **98** with $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ in 2-propanol / water gave the chlorohydrido complex **99** (Equation (32)).

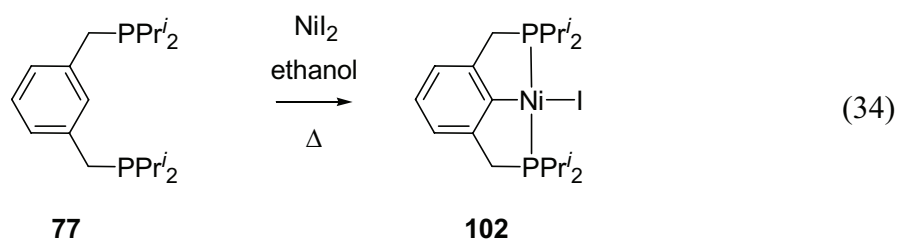


In a similar way, Grimm *et al.* isolated the iridium hydrochloride complex **101**, obtained by heating an isopropanol / water solution of the ligand **100** in the presence of iridium(III)chloride to 80 °C (Equation (33)). The red complex **101** dissolved well in polar organic solvents and was air-sensitive in solution, whereas in the solid state, no decomposition was observed while handling in air.

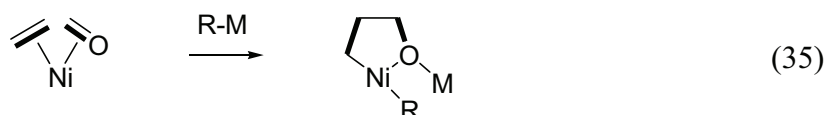


4.19.9.5 Group 10: Nickel, Palladium, and Platinum

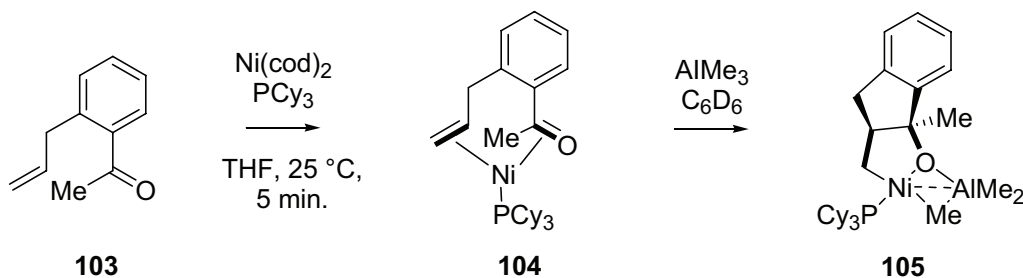
From 1996 to 2005, the synthesis of pincer nickel complexes has been widely described <1999OM277, 2000JA12112, 2002OM4556, 2004JCS(D)2957, 2004OM5653>. For example, reaction of **77** with a stoichiometric amount of NiI₂ in ethanol at 130 °C in a sealed pressure vessel led to the formation of the aryl-nickel complex **102** as shown in Equation (34) <2004ICA4015>. Similar reactions were achieved by Castonguay *et al.* using different nickel halides (Cl and Br) <2006OM602>.



Kurosawa and coworkers have been studying the oxidative cyclisation of an $\eta^2:\eta^2$ -2-allylbenzophenone nickel complexes leading to the formation of nickelhydrofurans (Equation (35)) <2004JA11802, 2006JA7077>.

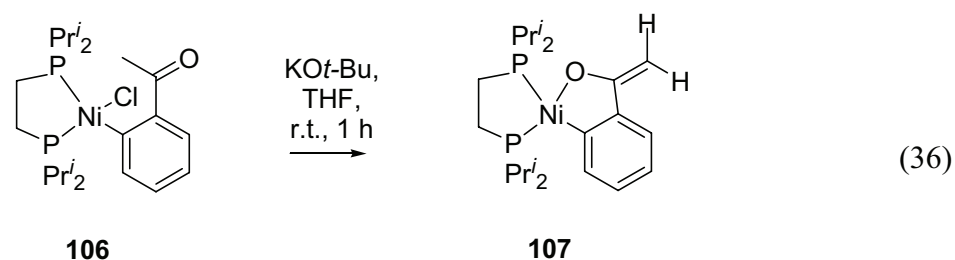


The reaction of 2-allylacetophenone **103** with $\text{Ni}(\text{cod})_2$ and PCy_3 gave an $\eta^2:\eta^2$ -1,5-enone nickel complex **104** quantitatively (Scheme 9). The following reaction of **104** with AlMe_3 in C_6D_6 proceeded very rapidly to give a deep-orange solution of cyclized compound **105**. Its structure was confirmed by X-ray diffraction analysis, showing a unique nickelacycle with a bridging methyl group <2005JA12810>.

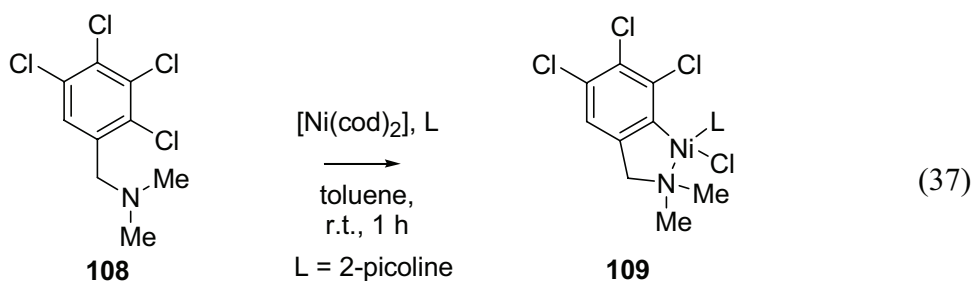


Scheme 9

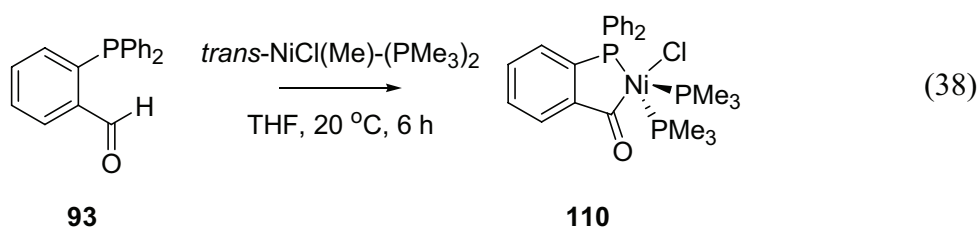
In addition, the synthesis of enolate complexes of nickel has been carried out by Campora and coworkers <2003CC1742, 2003JA1482>. Treatment of a THF solution of Ni(C₆H₄-*o*-C(O)CH₃(Cl)(dippe) **106** with one equivalent of KO*t*-Bu allowed the preparation of the nickel enolate **107** in good isolated yield (60%). *O*-Coordination of the enolate fragment could be proposed on the basis of the NMR spectra. Thus, the terminal methylene group gave rise to two signals in the ¹H spectrum, at δ = 4.62 and 4.79 ppm that correlated (¹H-¹³C HETCOR experiment) with a ¹³C resonance at 75.9 ppm which exhibited no coupling to phosphorus (Equation (36)).



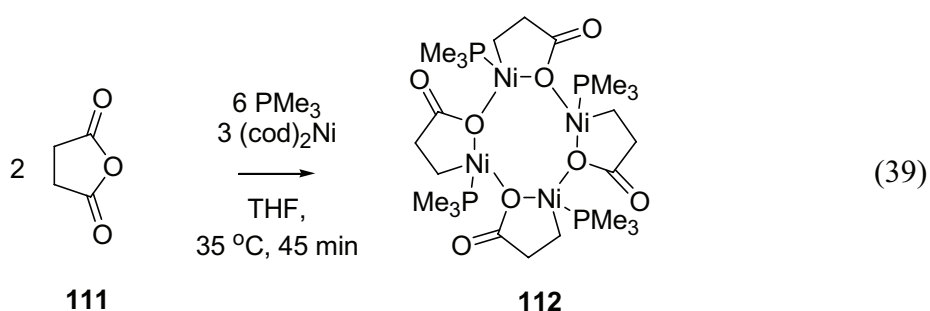
Five-membered nickelacycles have also been investigated by Ceder *et al.* (Equation (37)) <1995OM5544>.



In 1998, Klein *et al.* showed that methylnickel complex activates the C(O)-H function of 2-diphenylphosphinobenzaldehyde **93** to form a five-membered ring Ni(Ph₂PC=O) which occupy OC-axial and P-equatorial positions in the trigonal bipyramidal configuration of nickel compound **110** (Equation (38)) <1998OM4196>.



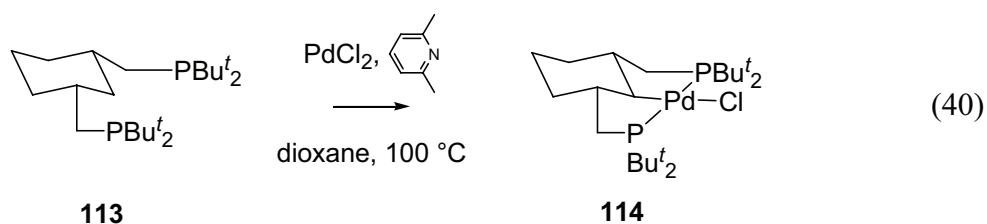
Finally, the reaction of succinic anhydride **111** with a 1:2 mixture of (cod)₂Ni and a monodentate phosphine generated a reactive monomeric nickelalactone, which underwent rapid aggregation to form cyclic oligomer **112** (Equation (39)) <2005OM272>.



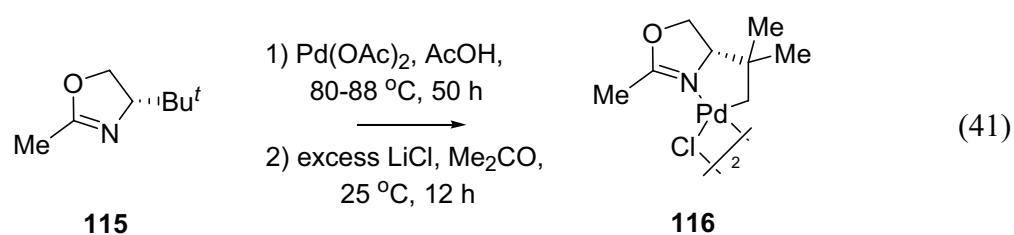
Palladacycles have also been investigated. They are a fascinating family of organometallic complexes with many applications in many areas including total synthesis, materials science and biological and supramolecular chemistry. Moreover, they are often air

stable, are readily synthesised and possess a range of types of metalated carbon and different types of donor groups bound to palladium (P-, N-, S- and O- containing groups).

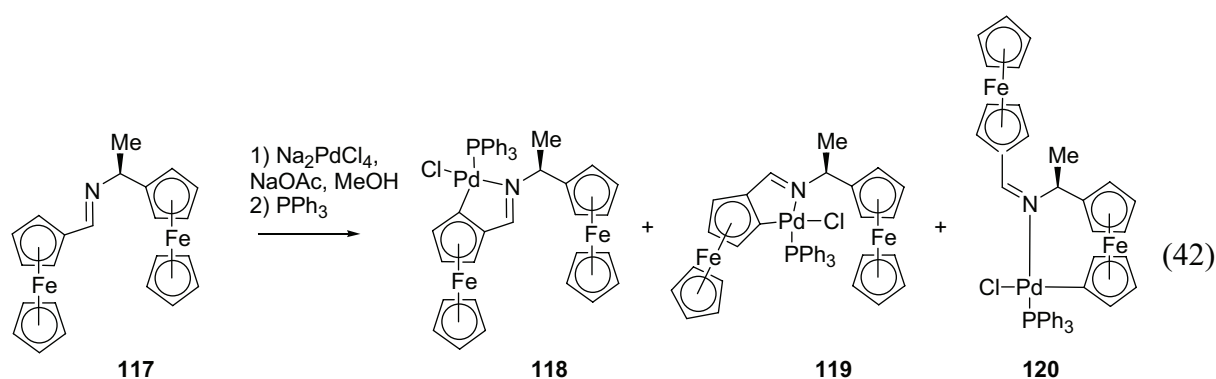
Several pincer complex syntheses have been described over the review period <1995JOM223, 2002OM3221>. The more recent one is the reaction of the *cis*-bis(di-*t*-butylphosphinomethyl)cyclohexane (*cis*-PCyP) **113** with palladium chloride affording C₈ and C₁ symmetrical complex **114**, where the PCyP ligands are coordinated in a meridional fashion through the two phosphorus atoms and the cyclometalated C-1 carbon of the cyclohexane ring (Equation (40)) <2006ICA2806>.



In addition, dimer palladacycles have been extensively studied over the last ten years. Phosphapalladacycles <2000TA3967, 2003CC3002, 2005JA2388, 2005JOM3193> and nitropalladacycles syntheses have been widely described <1995ICA91, 1995JOM215, 1995OM1393, 1995TA2731, 1998TA1917, 1999OM2683, 2000JOM138, 2000OL1823, 2002ICC552, 2002JOM46, 2003JCS(D)3350, 2003OM5243, 2003TA2331, 2004JOC8101, 2004JOM1806, 2005JOC648, 2005OM77, 2005OM5665>. One of many examples is the successful cyclopalladation of compound **115** achieved only using Pd(OAc)₂ as the palladation agent in acetic acid solution, followed by treatment with LiCl (Equation (41)) <2004JOM2382, 2005OM4159>.

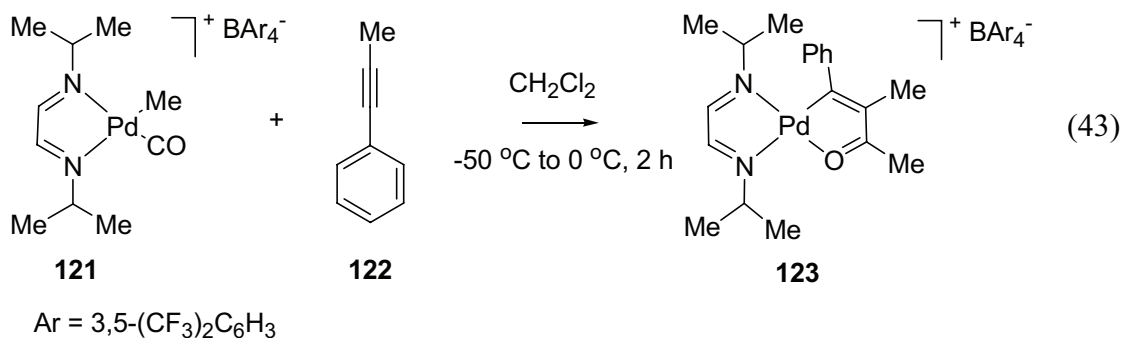


Ferrocene-based palladacycles have also been investigated <1999P2583, 2003OM2396, 2004OM224>. Among several studies, Troitskaya *et al.* achieved the cyclopalladation of the Schiff base **117** with a chiral centre (Equation (42)), leading to a mixture of three products, two of which were planar chiral diastereoisomers formed from homoannular substitution into the aldehyde fragment. The third product was a result of an unusual heteroannular palladation of the nitrogen in starting aldimine <2005JOM3976>.



Cyclopalladated sulfur-containing <1995JOC1005> and oxygen-containing complexes <2003OM3967, 2005CEJ3268> have also been synthesised. The insertion of phenylacetylene

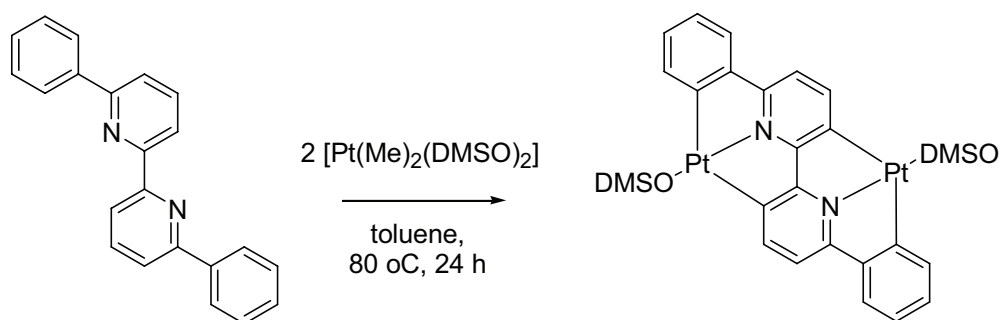
122 into the palladium-carbon bond of complex **121** yielded the palladacycle **123** (Equation (43)).



Similar reactions have been achieved with platinum. Phosphaplatinacycles <2003AG(E)105>, and nitroplatinacycles <2005OM2944> syntheses have been described using PtCl₂(cod) (cod = cyclooctadiene) or PtMeCl(cod).

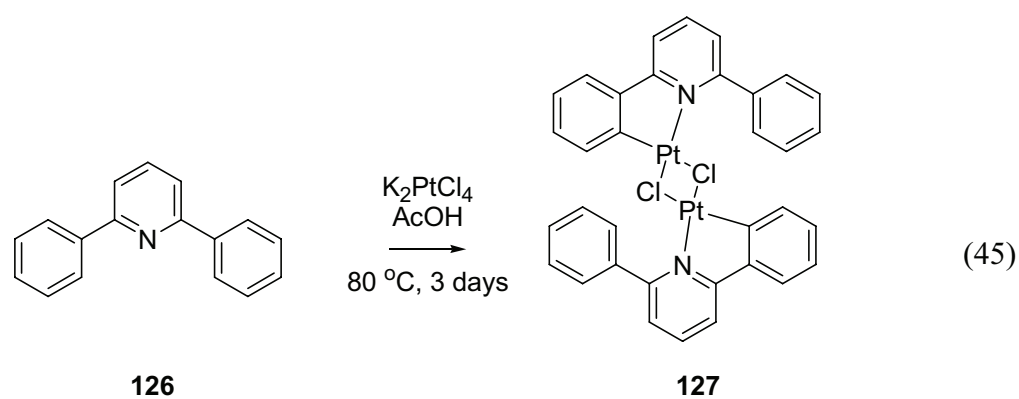
Intramolecular activation of C(aryl)-X bonds (X = Br, Cl, F and H) at platinum(II) has been achieved for amine-imine ligands such as RCH=NCH₂CH₂NMe₂, in which R was an aryl group <1996P1981>.

A series of complexes with bipyridine ligands has also been described <2003EJI2749, 2004EJI4484, 2006OM2074>. The reaction between 6,6'-diphenyl-2,2'-bipyridine **124** and [Pt(Me)₂(DMSO)₂] was carried out with a platinum / ligand ratio of 2 : 1 in toluene at 80 °C (Equation (44)). The reaction was slow and led to the isolation of a yellow product that was insoluble in the reaction medium, was stable in air and had high thermal stability <2006OM2253>.



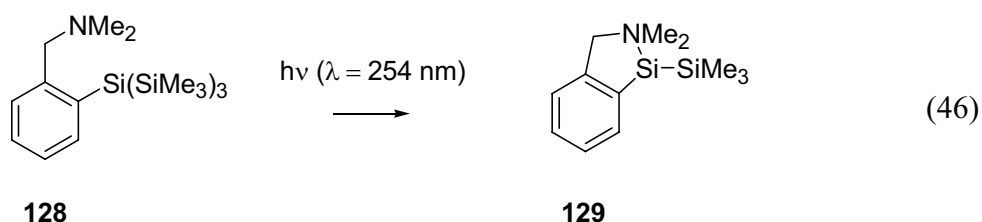
As previously observed for the palladium complexes, pincer ligand systems coordinated to Pt(II) centers have been described in the literature between 1995 and 2005 <2004, IC725, 2004OM5432>.

Platinum-containing dimer compounds have also been synthesised <2003JOM112, 2005IC2443>. Metalation of 2,6-diphenylpyridine **126** by potassium tetrachloroplatinate in acetic acid gave a monocyclometalated chloride-bridged dimer **127** (Equation (45)) <2000OM1355>.

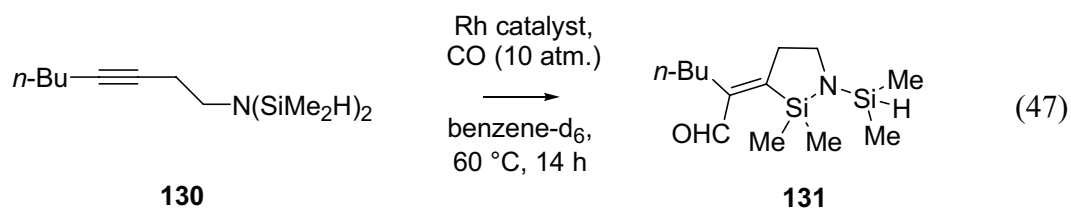


4.19.9.6 Group 14: Silicon-containing Heterocycles

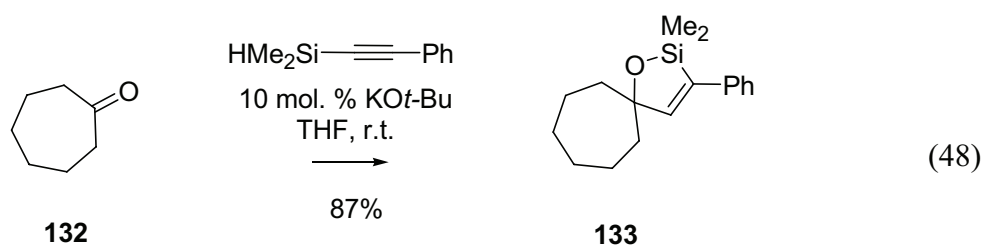
Silicium-containing heterocycles have been widely studied over the period review. Belzer *et al.* have studied nitrogen-containing silacycles <1996JOC3315> and within their research work, they described the photolysis of a trisilane **128** in a hydrocarbon matrix at -196 °C and observed an intense absorption at $\lambda_{\text{max}} = 478$ nm, which was attributed to the intramolecularly coordinated silylene **129** (Equation (46)) <1998CEJ852>.



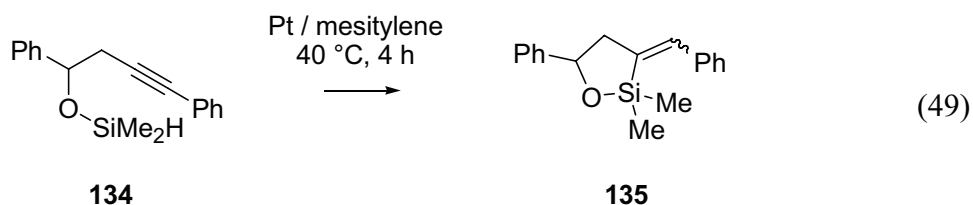
Nitrogen-containing silacycles have also been synthesised by thermolysis of bis(pentacoordinate) silicon compounds in the presence of butyllithium <2003JOM215>, by reaction of various (dichloromethyl)oligosilanes $\text{R}(\text{Me}_3\text{Si})_2\text{-SiCHCl}_2$ with alkyllithium derivatives <2004EJI1538>, and have also been obtained by intramolecular silylformylation of 1-bis(dimethylsilylamino)-3-octyne **130** in the presence of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, in toluene at 60 °C (Equation (47)) <1999OM5103>.



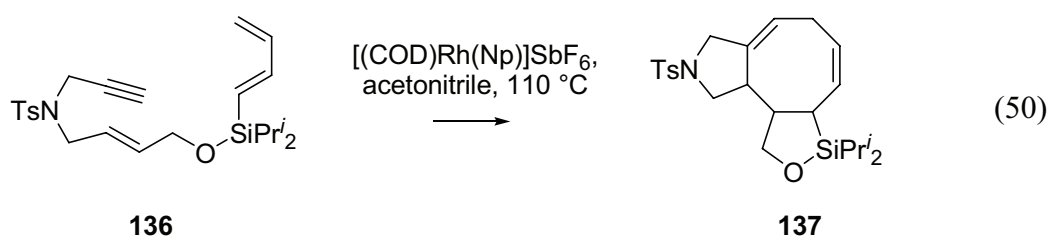
Oxasilacyclopentenes have been synthesised either by silacyclopropenation of alkynes utilizing Ag_3PO_4 as catalyst <2004JA9522>, either by reaction of ketones and alkynylsilanes in the presence of a catalytic amount of a nucleophilic initiator (Equation (48)) <2005OL4995>.



Oxasilacyclopentanes have been extensively studied over the period review and many different methodologies have been developed for their syntheses. Intramolecular radical cyclisations <2001JOC1966>, intramolecular silylformylation of silyloxyalkynes promoted by catalysts such as Rh <2001OL1303>, Ni <2001TL3259>, hydrosilylation of homopropargyl hydrodimethylsilyl ethers promoted by solvated Pt-atoms (Equation 49)) <1998JOM57>, and also photoinduced intramolecular cyclisation of alkynyl-substituted pentamethyldisilanes <1998TL6891> have been reported.



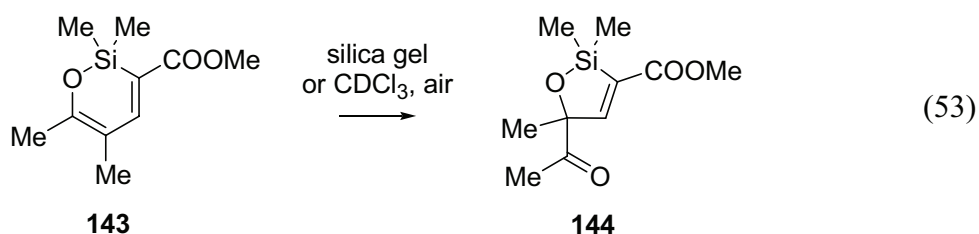
Analogously, intramolecular hydrosilation reactions have been carried out with olefins: cyclisation of alkenyloxysilanes catalysed by thiols <1998JCS(P1)467> and by Pt <1996TL827> have been described. In addition, intramolecular temporary silicon-tethered rhodium catalysed [4+2+2] cycloisomerisation reactions have been carried out by Evans *et al.* (Equation 50) <2004JA11150>.



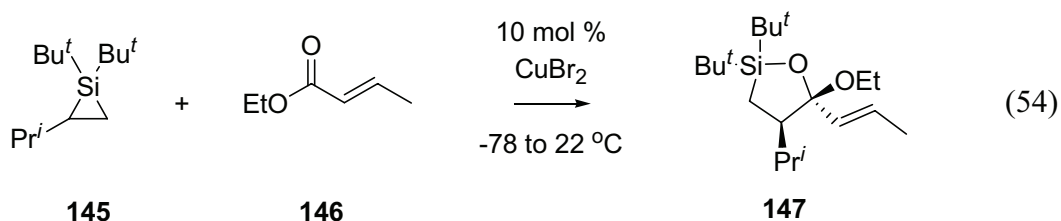
Silicon-oxygen heterocycles from thermal <2004CC122, 2004JOM1739>, photochemical <1999EJO1939>, transition-metal-catalysed and radical <2004PS955> reactions have been extensively described from 1995 to 2005. Woerpel and coworkers have studied many different strategies to obtain oxasilacyclopentanes <2002JA6524, 2002JA12648, 2003OL4325>. Particularly, they reported the reaction of α,β -unsaturated (or not) alkenes with silacyclopropanes: ZnBr_2 <2000AG(E)4295>, CuBr_2 <2000AG(E)4295>, AgOTf <2004JOC4007>, $\text{AgOTf} / \text{ZnBr}_2$ <2002JA9370, 2004JOC4007>, $\text{AgOTf} / \text{CuI}$ <2004JOC4007>, AgOCOCF_3 <2005JA2046>, $\text{AgOCOCF}_3 / \text{ZnBr}_2$ <2004JOC4007> - catalysed reactions have been reported.

Another way to synthesise oxacyclopentanes is the thermal insertion reaction of 1-formylpyrrolidine **138** into silirane *trans*-**139** which proceeded cleanly in hexanes at 120 °C

Oxasilines have generally been found to be of limited stability <1999EJO1213>. Indeed, by passing through a silica gel column or in CDCl₃ solution, **143** was converted, by ring contraction and incorporation of an oxygen atom, into 5-acetyl-2,5-dihydro-1,2-oxasilole **144** (Equation (53)).



Oxasilacyclopentanes have been synthesised by insertion reactions of silacyclopropanes with carbonyl compounds <1997T16597, 2002JA9370, 2004JOC4007, 2005JA2046>. For example, copper-catalysed insertion into silacyclopropane **145** is described in Equation (54) <2000AG(E)4295>.

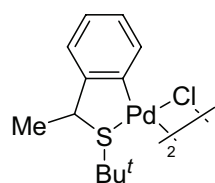


4.19.11 SYNTHESIS OF PARTICULAR CLASSES OF COMPOUNDS AND CRITICAL COMPARISON OF THE VARIOUS ROUTES AVAILABLE

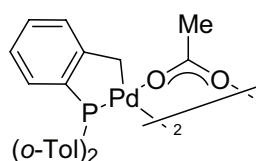
No update of this section, described in the previous edition of *Comprehensive Heterocyclic Chemistry* <96CHECII(3)783>, has been found necessary as no new classes of compounds have been described over the period review. Syntheses of various heterocycles have been developed in section 4.19.9.

4.19.12 IMPORTANT COMPOUNDS AND APPLICATIONS

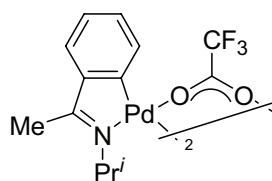
Cyclopalladated compounds have been found to be excellent catalysts, particularly effective for sp^2 - sp^2 carbon coupling processes such as Heck <2000CR3009, 2001T7449> and Suzuki reactions <2002JOM83, 2002JOM54>.



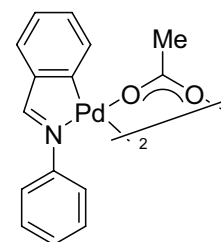
Dupont catalyst
<2000OL2881>



Hermann/Beller catalyst
<1999JOM23>



Milstein catalyst
<1999CC357>



Blackmond/Pfaltz catalyst
<1999OPRD275>

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