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Organometallic Intramolecular-Coordination Compounds Containing a Nitrogen Donor Ligand

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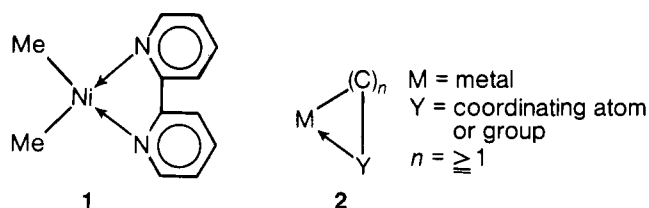
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I. Introduction

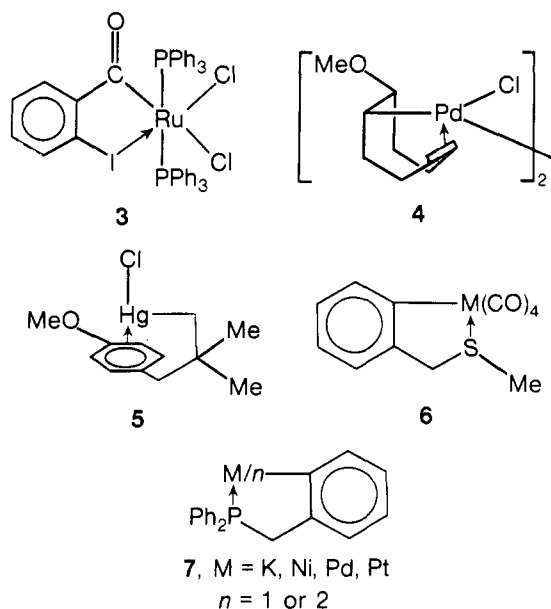
Articles concerning organometallic intramolecular-coordination compounds are on the increase owing to the progress of analytical instruments; especially a great many articles concerning olefin π -complexes are reported. Furthermore, it seems to be obvious that studies concerning orthometalated compounds in addition to the above-mentioned olefin π -complexes have rapidly become the object of investigation in recent years. However, very few reviews¹⁻³ on organometallic intramolecular-coordination compounds have been published.

Organometallic intramolecular-coordination compounds are, in a general sense, those which have at least one M-C bond and at least one group forming an intramolecular coordination bond. The compound⁴ **1**, for example, belongs to this group. However,

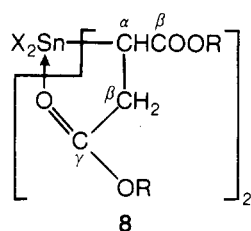


the present review is limited to articles on compounds such as the inner complexes of the Bähr definition⁵ in which the coordination group comprises the M-C bond and the coordinating atom or group. Hence, intramolecular-coordination compounds such as **1** which have a coordination group without the M-C bond do not belong to this group (present review). The coordination is usually formed using a lone pair of an atom or the π electrons of a multibond such as C=C or phenyl.

In the previous review,¹ the organometallic intramolecular-coordination compounds were classified for the first time into the following four groups with respect to the ligand group: (i) carbonyl, (ii) amino, (iii) alkenyl, and (iv) halogen, phenyl, etc.; and the carbonyl group¹ was discussed mainly in relation to organotin compounds in the previous review. This review reports on the second group. This classification must be revised in view of the large number of recent articles as follows: (i) oxygen donor ligand (carbonyl,¹ ethers, etc.); (ii) nitrogen donor ligand (this review); (iii) multibond donor ligand (alkenyl, phenyl, etc.); and (iv) other donor ligands such as halogen, sulfur, phosphorus, etc. The organometallic intramolecular-coordination compounds having a ligand group such as halogen,⁶ alkenyl,⁷ phenyl,⁸ sulfur,⁹ and phosphorus¹⁰ are, e.g., as follows:



In 1966, Matsuda, Kikkawa, and Omae, in reporting the compounds **8**,¹¹ proposed the five-membered ring structure theory. These compounds were obtained by the direct reaction of tin with halosuccinic acid dialkyl esters. They have two different C=O absorptions; one shows a large lower shift and the other shows a smaller shift. It was suggested from this evidence that one carbonyl group (at the γ position in **8**) forms an intramolecular coordination bond and the other (at the β position) is essentially in a free state. The theory, very simply, is as follows: organometallic intramolecular-coordination compounds tend to form five-membered ring structures because the five-mem-



R = alkyl group
X = halogen atom

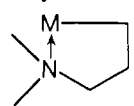
bered ring of the organometallic intramolecular-coordination compounds, when compared with other membered rings (except compounds having multibond donor ligands such as alkenyl and phenyl), can generally be formed sterically free from strain owing to the bond length and the bond angle of each member since the metal generally forms four- (square-planar), five- (bipyramidal) and six- (octahedral) coordination structures and the bond angle made by two bonds containing the metal in the center of two atoms is closer to 90° than to $109^\circ 28'$ (sp^3) or to 120° (sp^2). The metal bonded by the more electronegative atoms or groups can form the stronger intramolecular coordination bond.

Matsuda and co-workers¹ have synthesized more than 150 novel organotin intramolecular-coordination compounds having the five-membered ring structure. The structure of compounds **8**¹¹ have been confirmed by the X-ray diffraction studies.^{12,13}

Recently, a large number of organometallic intramolecular-coordination compounds have been reported, and many chelate ring structures of them also have been confirmed subsequently by X-ray diffraction studies.

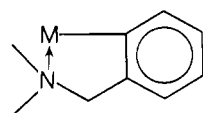
The third class contains chelate compounds of the metal- π -complex type which have reported in several reviews.¹⁴⁻¹⁸ This group can form multimembered rings and complex rings

Alkylamines



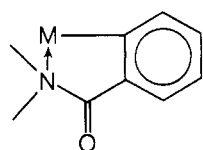
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Benzylamines



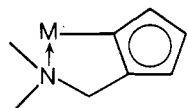
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Benzoylamines



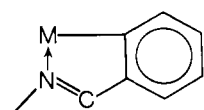
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Aminoferrrocenes



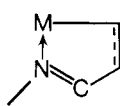
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Benzylideneamines



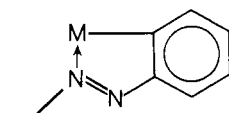
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Imines



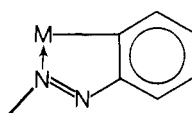
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Azobenzenes



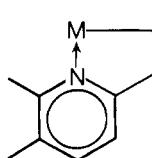
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Phenyldiimides



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Heteroaromatic Compounds



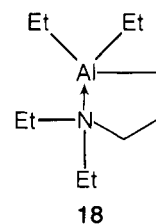
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since the coordination of the ligand to the metal is π -bonded, whereas other groups may form the five-membered ring mainly by coordination of a lone pair of the ligand atom. One of the objects of the present review is to show that almost all of the organometallic compounds of the second group having a nitrogen donor ligand have the five-membered ring structure as shown in **9-17**; these structures have been confirmed by X-ray diffraction data. The other object of the present review is to discuss the optical data, the reaction derivatives of these compounds, etc.

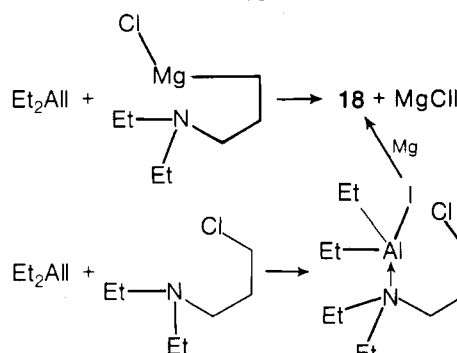
II. Organometallic Intramolecular-Coordination Compounds Containing a Nitrogen Donor Ligand

A. Alkylamines

In 1955, Bähr and Müller⁵ first reported the organometallic intramolecular-coordination compound **18** having the five-membered ring structure. The structure was inferred from the following reactions since suitable analytical techniques were not yet developed at that time. Compound **18** is obtained by two



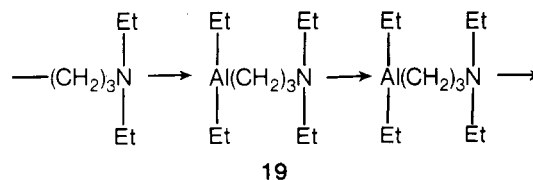
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(1)



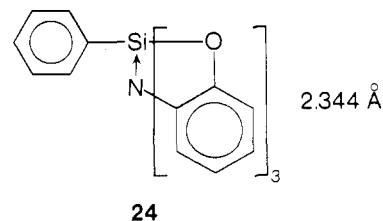
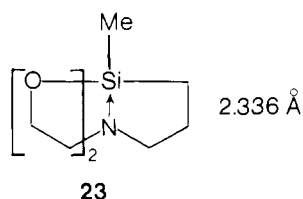
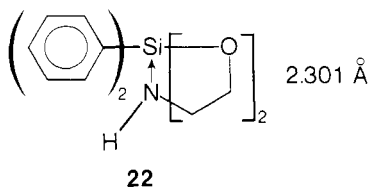
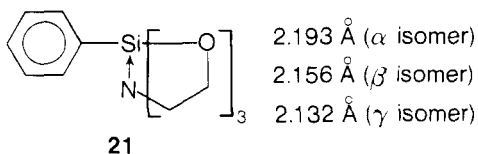
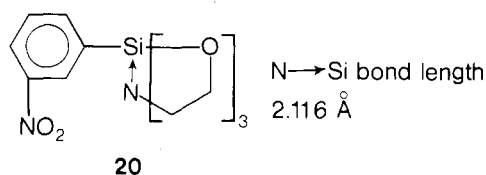
reaction routes (eq 1), and the hydrolysis of the product affords the components showing the decomposition of the coordination compound **18** (eq 2). Compound **18** is a colorless liquid, mp -2°C , bp 97°C (2 mmHg). It has a monomeric structure, not a polymeric structure **19**.



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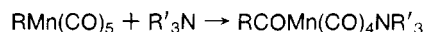
The five-membered ring structure theory suggests that the ring structure is generally strengthened by electronegative groups bonded to the metal since the electrophilicity of the metal to the ligand atom is enhanced by the electron-withdrawing group. Hence, it is considered that the coordination in **18** is weak.

Recently, Parkanyi and co-workers¹⁹ have precisely reported the relation between the bond strength of the coordination and the number of the electron-withdrawing groups concerning organosilicon compounds **20-24**: only **23** is one of the organometallic intramolecular-coordination compounds included in our definition;^{1,5} however, the five silatranes **20-24** will illustrate

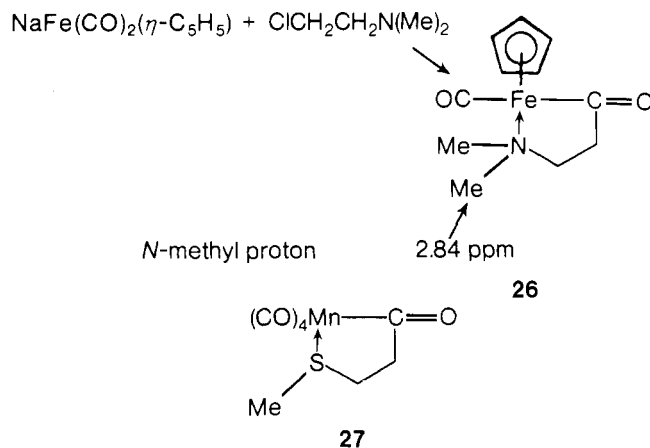
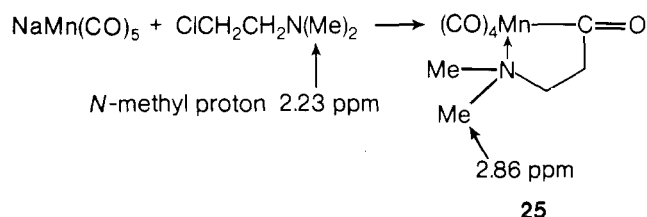


clearly the relation between Si-N bond length and the electro-negative groups bonded to the Si metal. The formation of the characteristic silatrane structure may be depicted clearly by considering a positively charged silicon atom acting as a Lewis acid under the influence of three oxygen atoms. The positive silicon readily interacts with the appropriate Lewis bases, i.e., the lone pair of the nitrogen atom. The resulting dative $N \rightarrow Si$ bond leads to a relatively large electron density on the silicon atom. The length and strength of this "hypervalent"²⁰ bond are very sensitive to electronic interaction, and to steric effects. The electron-withdrawing *m*-nitro group attached to the phenyl substituent further increases the positive charge on the silicon and so a strong dative bond is formed in **20**. In compounds **22** and **23**, there are only two oxygens bound to the silicon atom, and so a weaker $N \rightarrow Si$ bond results. The five-membered ring in **24** is planar, and the phenoxy groups inductively reduce the basicity of the nitrogen atom.²¹ A weak $N \rightarrow Si$ bond is thus formed.

The metal bonded by a carbonyl group as the electron-withdrawing group can easily form the five-membered ring structure, and the nitrogen atom bonded by alkyl groups such as methyl and ethyl, which are electron-donating groups, increases the strength of the donation to the metal. The reaction of 2-chloroethylidimethylamine²² with $NaMn(CO)_5$ or $NaFe(CO)_2(\eta-C_5H_5)$ affords cyclic acyl derivatives having the five-membered ring structure **25** or **26** by the intramolecular Kebllys-Filbey reaction.²³

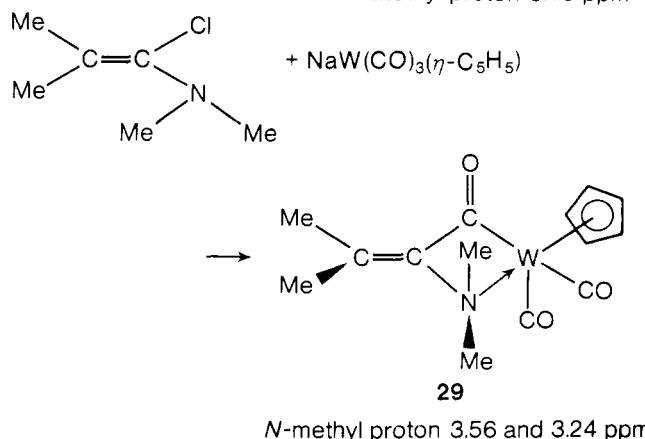
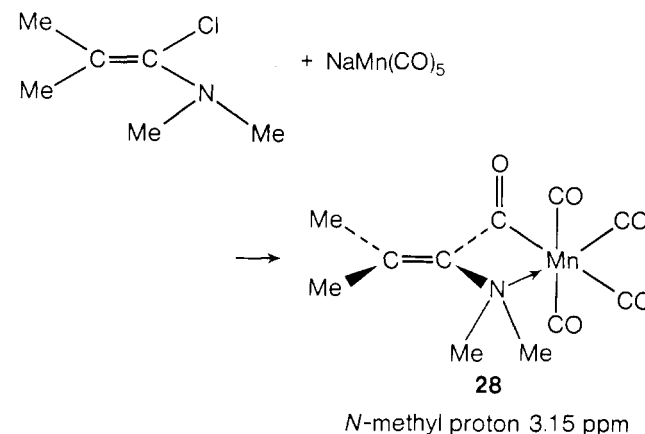


King and co-workers²² assume from IR data that the intramolecular-coordination structures **25** and **26** are very similar to **27** from the carbonyl frequencies.²⁴ However, it should be considered that the NMR spectra of the methyl protons of these products show more direct evidence of nitrogen coordination



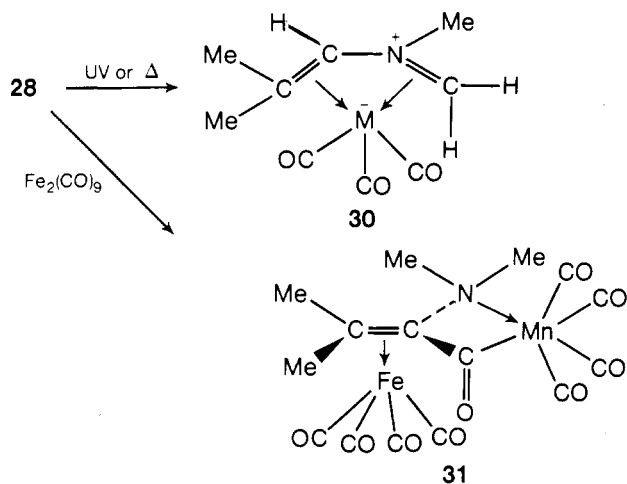
to the metal atom, because the *N*-methyl proton of the raw material and the coordinated metal complexes generally show ca. 2.2 ppm and shifted 2.3–3.6 ppm in a $CDCl_3$ solution, respectively.

The reaction of α -chloroenamines^{25,26} in place of 2-chloroethylidimethylamine with metal carbonyls affords an air-stable cyclic acyl compound having the four-membered ring structures **28** and **29**. In structure **28**, the *C*-methyls are nonequivalent since one is *cis* to the dimethylamino group. However, in structure **28**, the *N*-methyls are equivalent since the symmetry of the $Mn(CO)_4$ unit makes both sides of the four-membered ring identical.



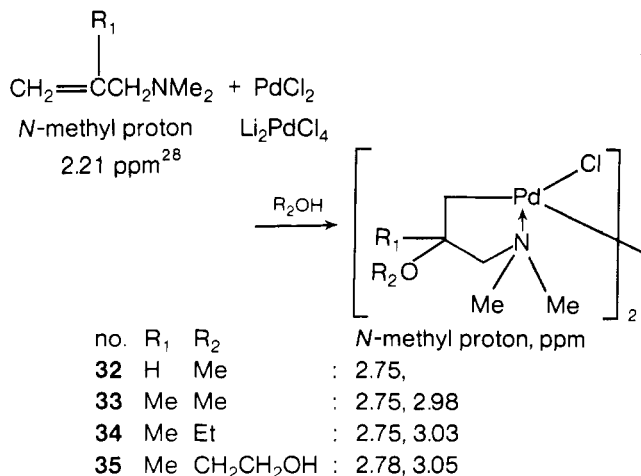
The NMR equivalence of the two *N*-methyl groups in **28** and their nonequivalence in **29** arise from the symmetry of the *cis* Mn(CO)₄ unit and the asymmetry of the W(CO)₂(η -C₅H₅) unit. It should be considered that these four-membered ring structures can be formed by the strong bond strength between the electrophilic metal which is bonded by many electronegative groups and the electron-donating nitrogen atoms which are bonded by two methyls as electron-releasing groups.

Photolysis or pyrolysis of **28** results in the loss of two carbonyl groups to give 2-azabutadiene manganese tricarbonyl derivatives **30**. The single *N*-methyl resonance of **30** at 2.60 ppm is a



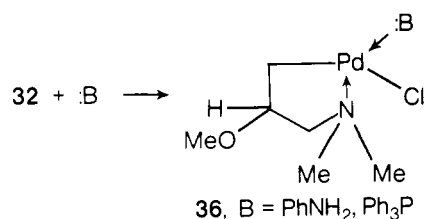
smaller lower field shift than that of **28** (3.15 ppm). This evidence shows that the electron transfer of the *N*-methyl group in **30** is less than that of **28** because the electron transfer from the nitrogen to the metal in **30** is less than that of the nitrogen which directly bonds to the metal in **28** since coordination of **30** is formed by the π bond of the N=C bond. The reaction of **28** with Fe₂(CO)₉ was investigated in an attempt to bond an Fe(CO)₄ unit to the uncomplexed carbon-carbon double bond of the manganese complex to give the bimetallic derivative **31**.

As compounds having halogen atoms of an electron-withdrawing group, Cope and co-workers²⁷ have reported a μ -halo-bridged bond. Palladium(II) chloride or lithium chloropalladate(II) reacts with *N,N*-dimethylallylamine or *N,N*-dimethyl-2-methylallylamine to give di- μ -chloro-bis(2-methoxy-3-*N,N*-dimethylaminopropyl-C¹,*N*)dipalladium(II) (**32**) or di- μ -chloro-bis(2-alkoxy-2-methyl-3-*N,N*-dimethylaminopropyl-C¹,*N*)dipalladium(II) (**33**), respectively. The nonequivalence of these *N*-methyl groups in **33**-**35** is most easily explained

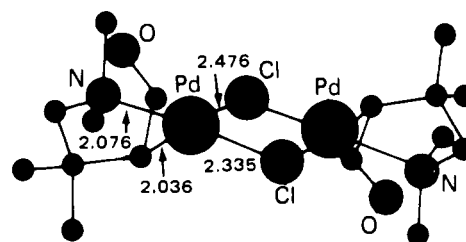


in terms of a cyclic system in which nitrogen is coordinated strongly to the metal to prevent inversion. The strength of this coordinate bond is demonstrated by the observation that the NMR

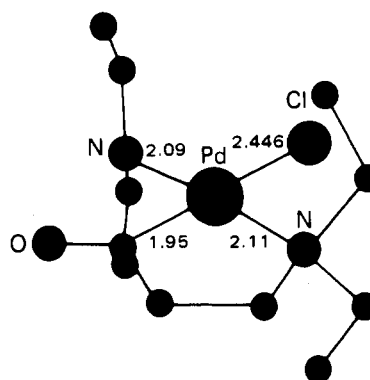
spectrum remains essentially unchanged at temperatures higher than 100 °C. Compound **32** reacts with aniline or triphenylphosphine to give compound **36**.



Recently, similar structures of two kinds of compounds, i.e., the chloro-bridged dimer **32** and the compounds **36**, exchanged the ligand by the cleavage of the bridged structure, have been determined by the X-ray analyses of di- μ -chloro-bis(1-formyl-2,2-dimethyl-3-*N,N*-dimethylaminopropyl-C¹,*N*)dipalladium(II) (**37**)²⁹ and chloro(3-diethylaminopropionyl-C¹,*N*)(diethylamine)palladium(II) (**38**).³⁰ The former compound, **37**, is obtained

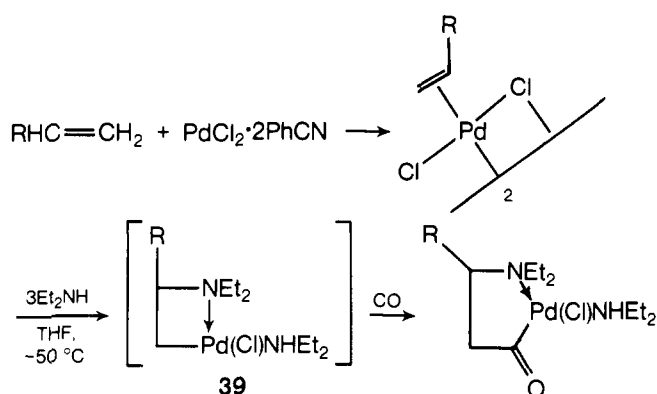
**37**

by reaction of dichloro(2,2-*N,N*-tetramethyl-3-butene-1-amino)palladium(II) with methanol in the presence of base. In the centrosymmetric dimeric molecule, each Pd atom is in a square-planar configuration in the five-membered chelate ring that has an envelope conformation. The latter compound, **38**,^{30,31}

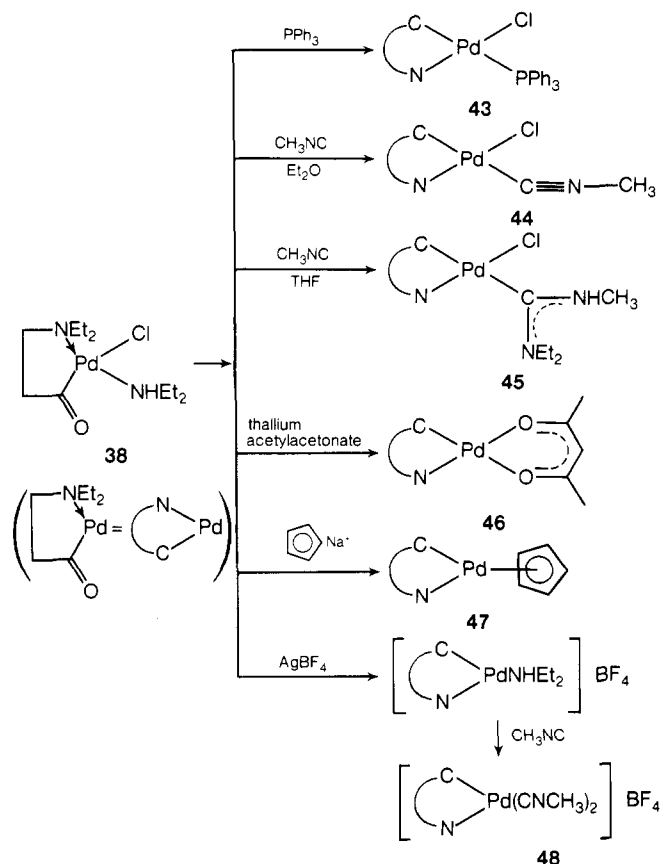
**38**

was prepared by the treatment of the unstable σ -alkylpalladium(II) complexes **39** having the four-membered ring resulting from nucleophilic attack of diethylamine on the palladium(II) chloride complexes of ethene (R = H), [propene (R = CH₃), **40**; 1-butene (R = Et), **41**; 1-hexene (R = *n*-Bu), **42**], with carbon monoxide. The NMR spectra due to the ethyl groups of both amino groups in **38**, which formed intra- and intermolecular coordination to the palladium, indicated the downfield shift of the signals relative to the signals in free diethyl- or triethylamine. Complexes^{30,31} resulting from the replacement of the Et₂NH in **38** by triphenylphosphine (**43**), methyl isocyanide (**44**), and (methylamino)(diethylamino)carbene (**45**), and from the replacement of both Et₂NH and Cl⁻ by acac (**46**), cyclopentadienyl (**47**), and methyl isocyanide (2 equiv) (**48**) were also synthesized.

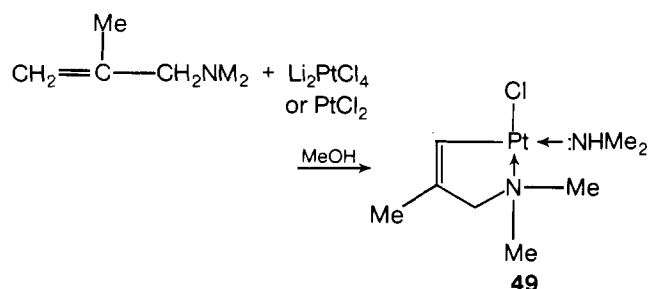
The reaction³² of *N,N*-dimethyl-2-methylallylamine (in excess) with the compounds containing platinum in place of palladium



no.	R	M _p (dec.) °C	Pd←N(CH ₂ CH ₃) ₂ , ppm	H Pd←N(CH ₂ CH ₃) ₂ ppm	Yield, %
38	H	120-130	3.50 (m)	3.08 (m)	73
40	Me	135-140	3.15 (m)	2.06 (m)	72
41	Et	120-130	3.10 (m)	2.65 (m)	65
42	<i>n</i> -Bu	-	-	-	70
Et ₃ N	-	-	2.52 (q)	-	-
Et ₂ NH	-	-	-	2.63 (q)	-



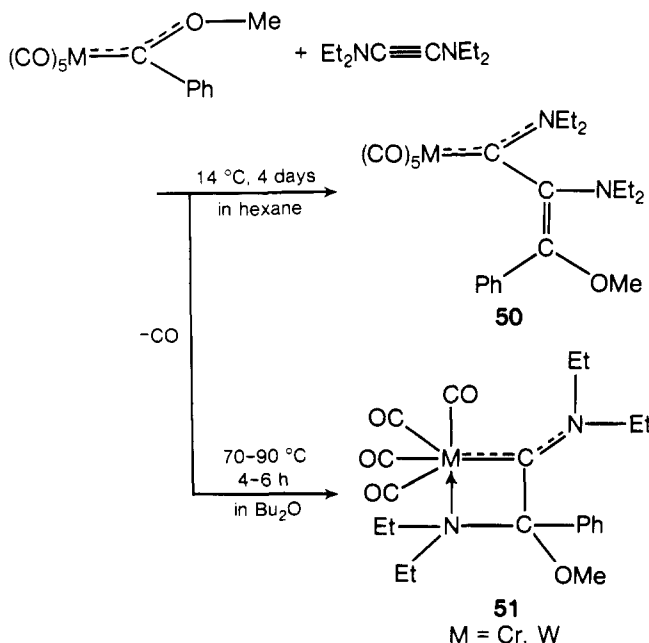
affords [2-methyl-3-(dimethylamino)propenyl-*C',N*]platinum(II) chloride-dimethylamine (**49**) which has the five-membered ring structure containing a double bond. Treatment of **49** either with



triphenylphosphine or aniline causes the elimination of dimethylamine and gives the corresponding triphenylphosphine or anilino complex.

The *N*-methyl proton resonance of the triphenylphosphine derivatives occurs at 2.96 ppm as in **32** and **36**, but the peak is a multiplet, which is due to the *N*-methyl groups coupled to both the platinum (25.0 Hz) and the phosphorus (3.0 Hz) atoms. Cope and Kliegman³² concluded from these couplings with platinum and phosphorus that the unshared pair on nitrogen is truly coordinated with the metal, giving the five-membered ring.

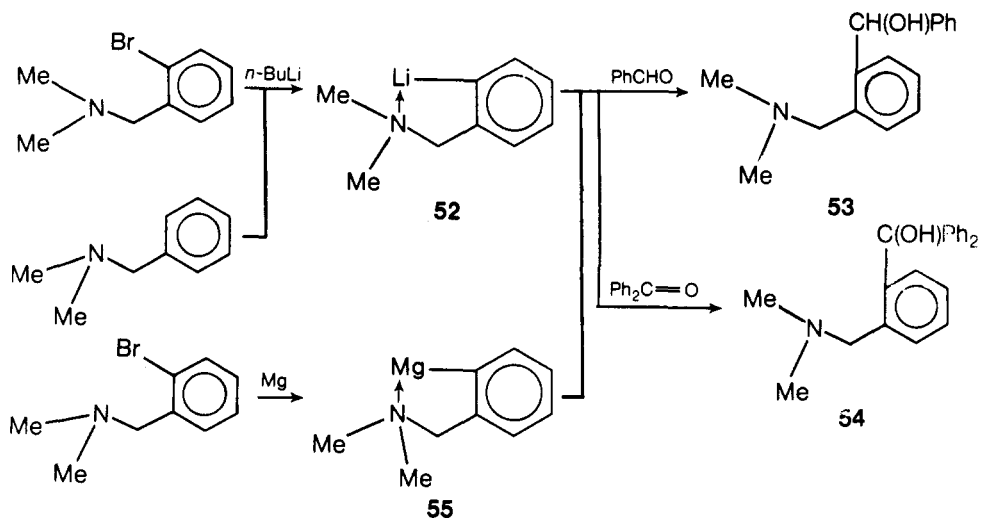
The greater the number of electron-withdrawing groups, the more capability the metal has donated by the ligand group; of course, sexadentate metal is not capable of forming a new coordination bond if the metal has six bonds. However, the reaction with these metal compounds often affords the intramolecular-coordination compounds by the elimination of a group such as CO in the course of the reaction. The reaction³³ between pentacarbonyl(methoxyphenylcarbene)chromium(0) with bis-(diethylamino)acetylene affords pentacarbonyl[diethylamino(α -diethylamino- β -methoxystyryl)carbene]chromium(0) (**50**). On warming **50**, a carbonyl ligand is eliminated and the diethylamino group is coordinated to the metal to form *cis*-tetracarbonyl[diethylamino(α -diethylamino- β -methoxystyryl)carbene-*C',N*]chromium(0) (**51**), and the analogous tungsten complex can be synthesized in a similar manner.



B. Benzylamines

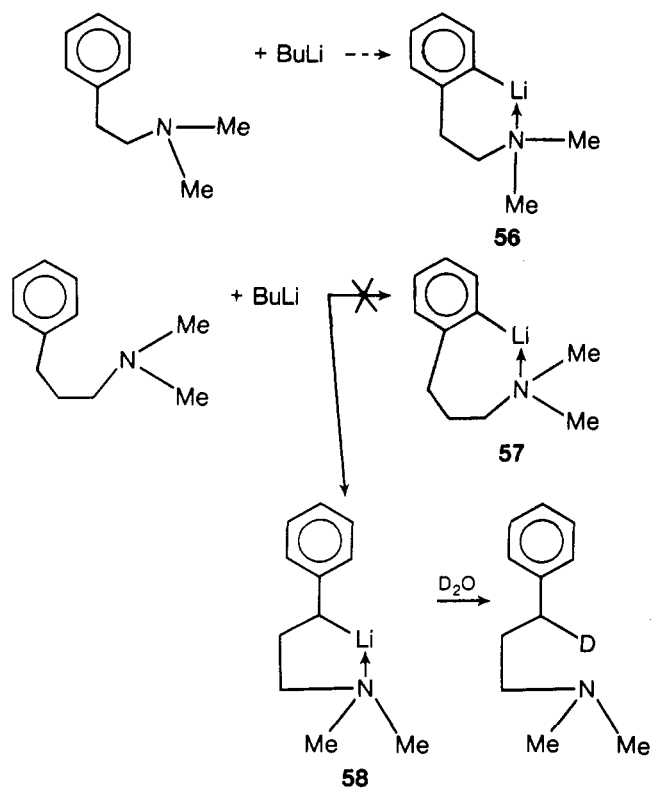
In 1962, Hauser and Jones^{34,35} reported the reaction of butyllithium and benzylidimethylamine or 2-bromobenzylidimethylamine. The reaction product **52** reacted with benzaldehyde or benzophenone to yield the corresponding amino alcohols **53** or **54**, respectively. These authors presumed the intermediacy of an organolithium compound **52** having the five-membered ring structure by considering the structures of **53** and **54**.

Similar to **52**, the intermediate **55** also is obtained from the organomagnesium³⁵ analog. However, 3- and 4-bromobenzylidimethylamine failed to be converted to Grignard reagents under the above reaction conditions. These data show a specificity that the five-membered ring structure can be formed at the ortho position and the orthometalation reactions are useful for the synthesis of various ortho derivatives of amines.³⁶ *o*-Lithiobenzylidimethylamine was condensed not only with aldehydes or ketones, but also with benzonitrile, phenyl isocyanate, cyclohexene oxide, or phenyl benzoate to yield the cor-



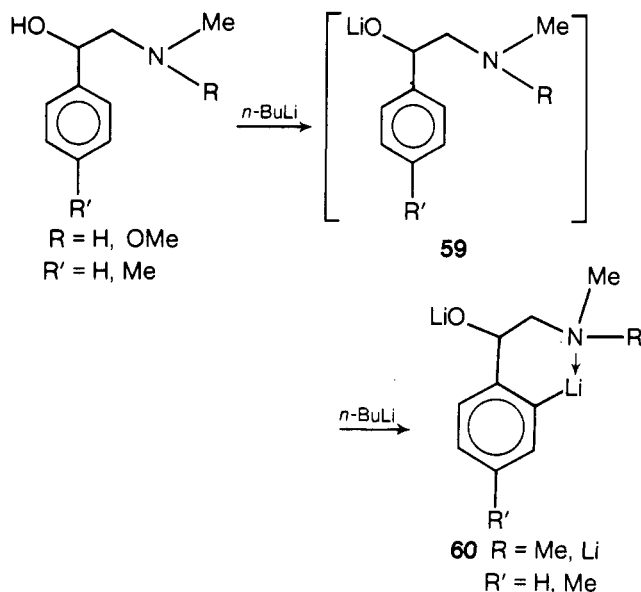
responding aminocarbinols, amino ketone, amino amide, or diaminocarbinol.

Hauser and co-workers³⁷⁻⁴¹ further examined five-membered ring formation in comparison with six- or seven-membered ring formation. That is, the reaction of *n*-butyllithium with *N,N*-dimethylphenylmethylamine yielded the intermediate having the five-membered ring structure; however, the reaction with *N,N*-dimethyl-2-phenylethylamine gave the six-membered ring compound **56** in little or no yield and the reaction of *N,N*-dimethyl-3-phenylpropylamine yielded the five-membered ring compound **58** in place of the seven-membered ring compound **57**. These studies show that the five-membered ring structure

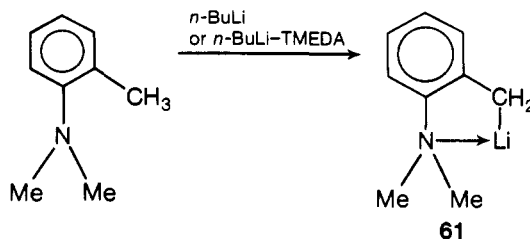


can be easily formed, but formation of the six-membered ring structure is difficult and that of the seven-membered ring structure is almost impossible (see **59** and **60**). The main product^{39,41} of the direct metalation of *N,N*-dimethyl-2-phenylethylamine is polystyrene which presumably arises via base-induced elimination of dimethylamine. However, Slocum and

Achermann⁴² obtained the six-membered ring compounds, avoiding this elimination by the dimetalation of a phenethylamine system containing an acidic α substituent, where the ionization of the proton attached at the oxygen atom would significantly decrease the acidity of the benzylic proton.

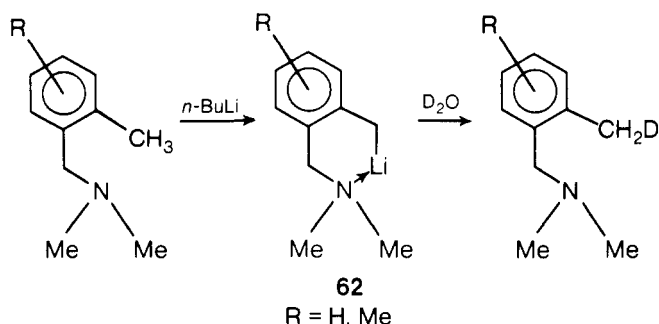


Upon treatment⁴³ with *n*-butyllithium in ether-hexane, *N,N*-dimethyl-*o*-toluidine undergoes metalation predominantly in the 2-methyl position to form lithioamine, **61**; small amounts of ring metalation were also detected. When *n*-butyllithium-TMEDA in hexane was used as a metalating agent, a more rapid and selective metalation occurred to give a better yield of intermediate lithioamine **61**. The metalation of 2-methyl- and 2,3-dimethyl-

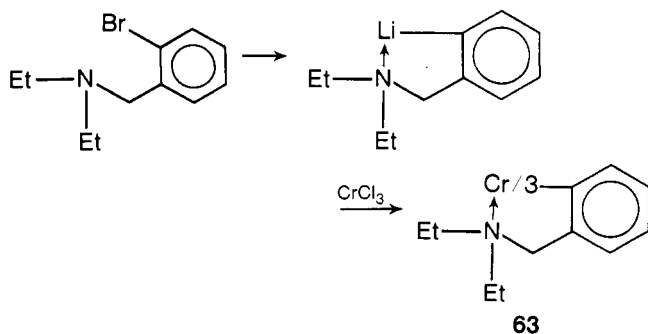


benzyl dimethylamines with *n*-BuLi can afford the intermediates **62** having the six-membered ring which are inferred from their deuterated analogs.

Stable metal-ortho-substituted *N,N*-dialkylbenzylamine derivatives were first prepared from the lithium compound by Bähr

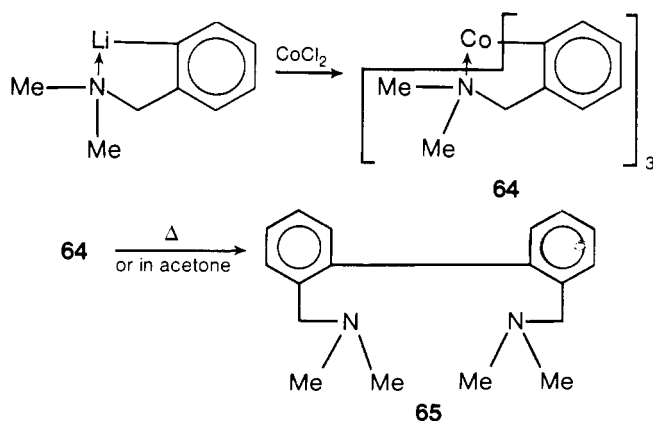


in 1963.⁴⁴ The reaction of *o*-lithiobenzyl-diethylamine with dry chromium(III) chloride affords tris[*o*-(diethylaminomethyl)-phenyl-*C*¹,*N*]chromium (**63**), which has lustrous garnet red crystals and which is extremely sensitive toward atmospheric oxygen.



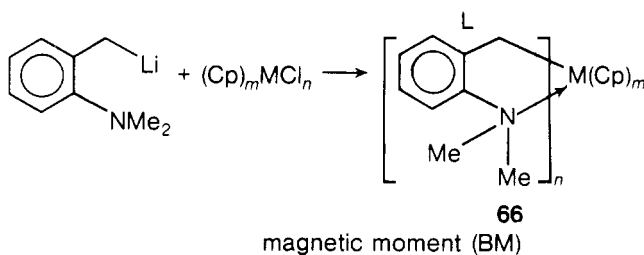
The intramolecular-coordination compounds having the benzylamino ligand are the compounds which contain a benzene ring as the chelate ring components. Recently, many studies on this group have been reported as ortho-metallated complexes have been prepared whose ligands bond not only through the nitrogen atom but also other elements such as phosphorus, **7**, and sulfur, **6**.

Cope and Gourley⁴⁵ obtained the cobalt complex **64** by the reaction of *o*-lithio-*N,N*-dimethylbenzylamine derivatives with anhydrous cobalt chloride. The complex **64** is stable when kept at room temperature in air, but when heated to 120 °C or allowed to remain in solution, especially in acetone, it decomposes to give the crystalline biphenyl derivative **65**.

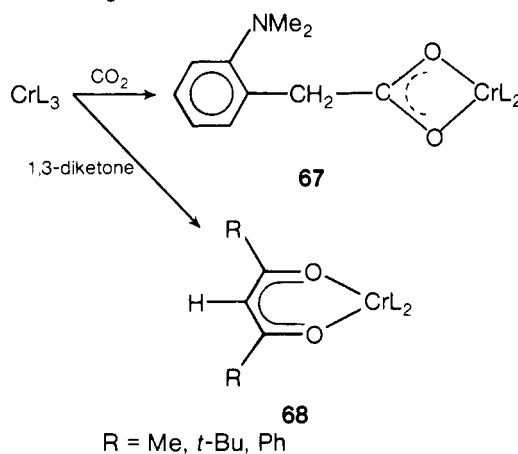


Recently, Manzer^{46,47} reported the transition metal complexes (such as Cr, Ti, V, Mn, and Sc) of **61**. The reaction of $\text{LiCH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2$ with Cp_2MCl ($\text{M} = \text{Ti, V}$; $\text{Cp} = \eta\text{-C}_5\text{H}_5$), CpTiCl_2 , CrCl_3 , ScCl_3 , MnI_2 , or CrCl_2 has led to the isolation of thermal stable, air-sensitive complexes, **66**, whose stability is attributed to chelation. The reaction of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ with CO_2 gave a paramagnetic complex **67** in which CO_2 has

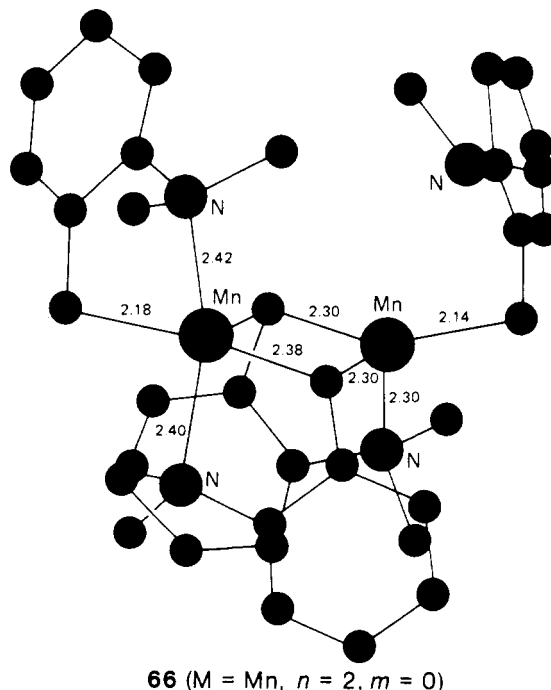
been inserted into only one Cr–C bond and with diketones to give diketonate **68**.



Cp_2TiLi	1.7
Cp_2VL	
CpTiL_2	1.6
CrL_3	3.6
$(\text{MnL}_2)_2$	2.6
CrL_2	2.6

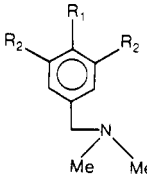
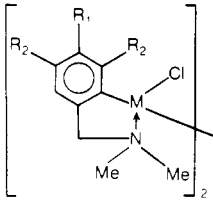


The X-ray crystal structure⁴⁷ of $\text{Mn}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2$, obtained by the reaction of $\text{LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ with MnI_2 , was determined. The molecule is dimeric, containing one bridging and one terminal $\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2$ ligand per metal. The bridging ligand is

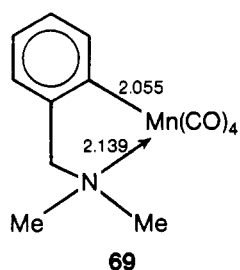


bonded to both manganese atoms through a common $\text{-CH}_2\text{-}$ group. One manganese atom has a bidentate $\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2$ ligand while the other manganese atom has a monodentate *o*-

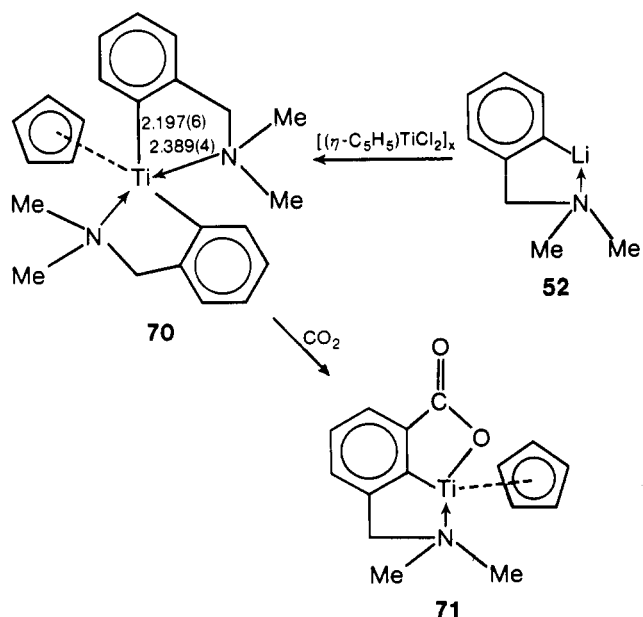
TABLE I. NMR Spectral Data of *N*-Methyl Protons

	R ₁	R ₂	M	<i>N</i> -methyl proton, ppm
	H	H		2.22
	OMe	H		2.22
	H	OMe		2.25
 72	H	H	Pt	3.00
	H	H	Pd	2.83
	OMe	H	Pd	2.83
	H	OMe	Pd	2.70

dimethylaminobenzyl ligand. It should be considered that one free nitrogen in **66** is formed because the coordination capability of the metal is weak since the metal has no electronegative group. This evidence shows that the bond length (2.30–2.42 Å) between the nitrogen atom and the metal in **66** is much longer than that (2.07 Å) of tetracarbonyl(*N,N*-dimethylbenzylamine-*C*²,*N*)manganese (**69**)⁴⁸ which has four electronegative carbonyl group.

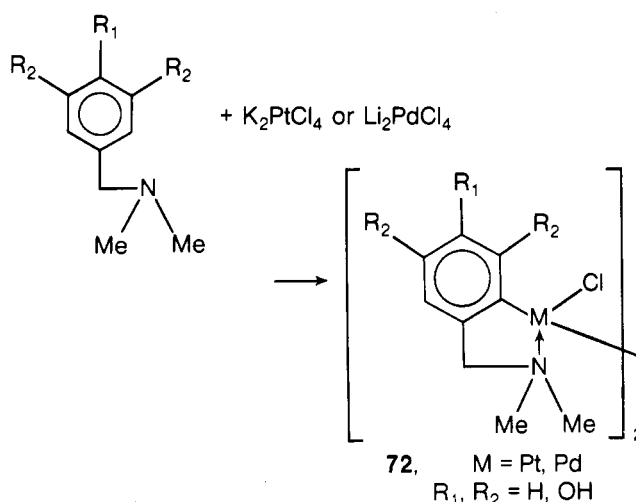


The reaction⁴⁹ of *o*-lithiobenzylamine with $(\eta\text{-C}_5\text{H}_5)\text{TiCl}_2$ gives an air-sensitive, paramagnetic complex, **70** (1.7 BM), whose crystal structure has been determined by X-ray diffraction studies. The two five-membered rings are planar and the Ti–N



distance is very long for a single bond. It is noteworthy that two bidentate dimethylaminomethylphenyl ligands adopt roughly a trans configuration about titanium. This titanium complex reacts

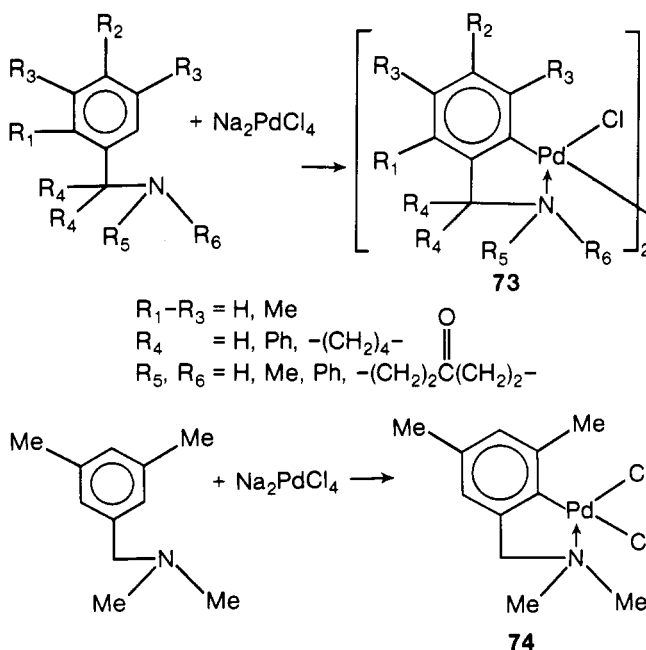
with carbon dioxide to give red-brown crystals, which show a strong sharp IR band at 1710 cm^{-1} to which Manzer et al.⁴⁹ have tentatively assigned the structure **71**.



Potassium tetrachloroplatinate(II)⁵⁰ and lithium tetrachloropalladate(II) react readily with *N,N*-dimethylbenzylamine to give di- μ -chloro-bis(*N,N*-dimethylbenzylamine-*C*²,*N*)diplatinum(II) and -dipalladium(II) (**72**), respectively. Similar bond formation by palladium(II) is observed in its complexes with the *p*-methoxy and 3,5-dimethoxy derivatives of *N,N*-dimethylbenzylamine. A summary of the NMR spectral data is given in Table I. The *N*-methyl proton resonance of the starting materials is seen at about 2.2 ppm and those of the metal complexes **72** are shifted downfield to 2.70–3.00 ppm, as shown previously in alkylamine complexes.

The NMR spectrum of the platinum-*N,N*-dimethylbenzylamine complexes also provides precisely the evidence that, in these materials, nitrogen is coordinated through its unshared pair of electrons to the metal: the methyl proton and methylene proton signals in the spectrum of **72** were observed as triplets due to coupling with ¹⁹⁵Pt (spin 1/2) isotope (R₁, R₂ = H; $J^{195\text{Pt},\text{NCH}_3} = 48\text{ Hz}$, $J^{195\text{Pt},\text{NCH}_2\text{Ph}} = 55\text{ Hz}$). The *N*-methyl and benzylmethylene of the ¹³C NMR (**72**, M = Pd)⁵¹ spectrum are seen at 52.6 and 73.1 ppm, respectively.

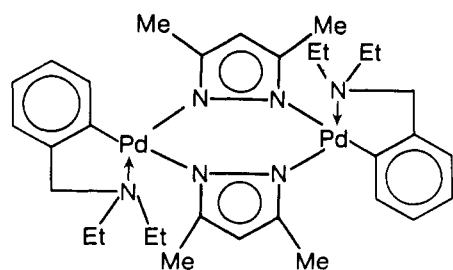
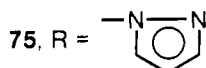
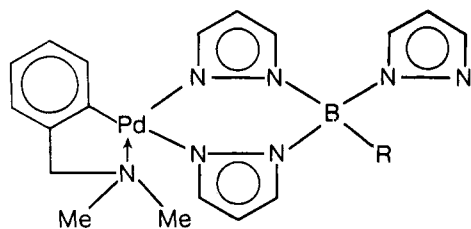
The slightly activated *N,N*-2- and *N,N*-4-trimethylbenzylamines⁵² both react with sodium chloropalladate to give complexes **73** which are similar to **72**. The reaction of the highly hindered



N,N-3,5-tetramethylbenzylamine, however, yields **74** in place of the chloro-bridged dimer **72** and **73**. This behavior contrasts with that of the similarly hindered but more highly activated *N,N*-dimethyl-3,5-dimethoxybenzylamine, which forms **72** and **73**. Both *N*-methyl-*N*-phenylbenzylamine and *N*-benzylpiperidin-4-one react with Na_2PdCl_4 to give **73**-like compounds which have the chloro-bridged bond. The substitution of the α -benzyl position with bulky groups, however, favors the formation of **73** complexes. Not only does the tertiary amine, 1-phenyl-*N,N*-dimethylcyclohexylamine, form palladium complexes corresponding to **73**, but also the primary and secondary amines, triphenylmethylamine and *N*-methyltriphenylmethylamine, react. These are the first examples of primary and secondary amines forming such complexes with palladium.

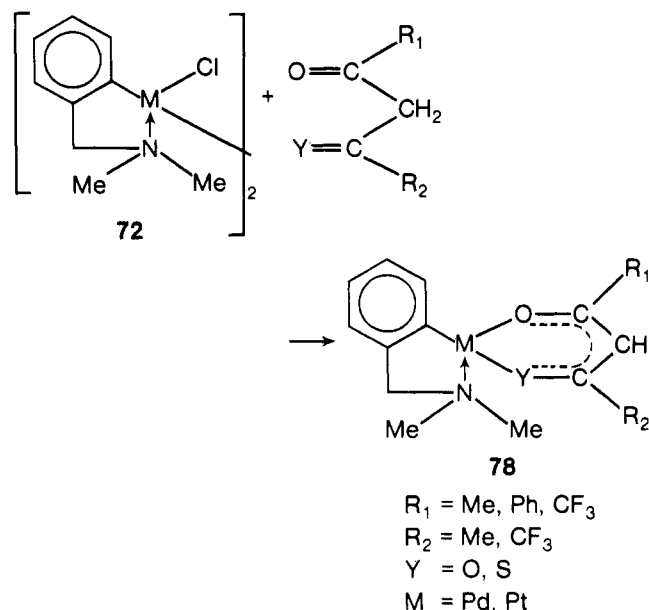
In 1968, Cope and Friedrich⁵⁰ interpreted the reaction mechanism of the benzylamines as follows. The reaction of the palladium(II) chloride with *N,N*-dimethylbenzylamine probably occurs by an initial rapid coordination of the nitrogen to the metal. This process is then followed by attack of the metal at an ortho position on the ring. Apparently, the favorable entropy factors for electrophilic attack by the coordinated palladium via the five-membered ring transition state are necessary to facilitate the aromatic substitution. No products containing palladium-carbon bonds were obtained from the deactivated *p*-nitro-*N,N*-dimethylbenzylamine, or from the *N,N*-dimethyl-2-phenylethyl- and 3-phenylpropylamine which would have to react via six- and seven-membered ring transition states. Similar conclusions may be drawn by analogy for the reaction of potassium tetrachloroplatinate(II) with *N,N*-dimethylbenzylamine. The reasons for the difference observed in the reactions of the platinum(II) and palladium(II) chlorides with the tertiary *N,N*-dimethylbenzylamine and with the primary and secondary benzylamines are not entirely clear. In the complex and formation, the initial step must involve coordination of the metal to nitrogen followed by attack on the ring. Since one would expect for steric reasons that the primary and secondary amines should coordinate more strongly to the metal than do the tertiary amines, this stronger coordination may decrease the electrophilic character of the metal sufficiently to prevent later attack upon the phenyl ring.

A number of the halogen-bridged dimers (**72**, **73**) easily undergo cleavage reactions with ligand compounds such as pyridine, phosphines,⁵³ triphenylarsine, triphenylstibine, sodium tetrakis(1-pyrazolylborate)⁵⁴ (**75**, **76**) to produce, generally, the

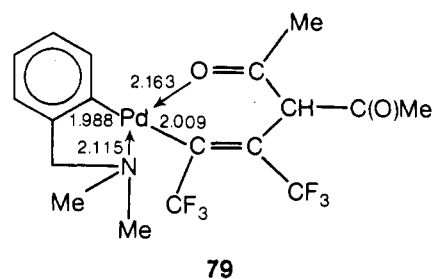


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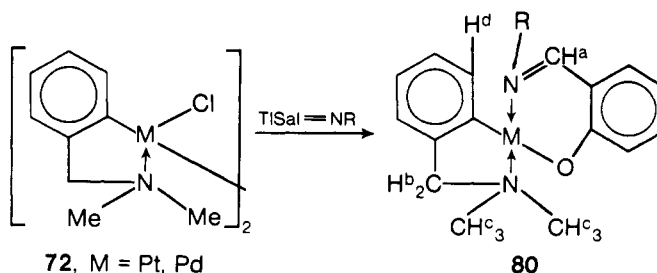
monomeric species which are more soluble than the corresponding dimeric compounds; however, the reaction of potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate⁵⁵ with **72** and **73** gave the 3,5-dimethylpyrazolylene bridged dimer, **77**. The cleavage reaction⁵⁶ of **72** with β -ketones was also studied. For example, di- μ -chloro-bis(*N,N*-dimethylbenzylamine- C^2, N)metal was dissolved in the solution of β -diketones such as acacH or in thio- β -ketones containing KOH to give the β -diketonates or thio- β -ketonates as complexes **78**. The chemical shifts of the



N-methyl proton of above two compounds appear at 2.76–3.00 ppm and the coupling constant of $J^{195\text{Pt-NCH}_2}$ and $J^{195\text{Pt-NCH}_3}$ is found to be 36.5–55.3 and 29.1–47 Hz, respectively. The acetylacetonate complex **78**⁵⁷ reacts with hexafluoro-2-butyne to produce the inserted complex *ab*-[1,2-bis(trifluoromethyl)-3-acetyl-4-oxopent-1-enyl- O, C^1]-*cd*-[2-[(dimethylamino)methyl]phenyl- C^1, N]palladium(II) (**79**) whose structure has been determined by the X-ray diffraction study.⁵⁸



Reaction⁵⁹ of the dichloro-bridged dimer di- μ -chloro-bis[*N,N*-dimethylbenzyl- C^2, N]metal (= Pd or Pt) with the thallium(I) derivatives of alkyl- and arylsalicylaldehydes (Tl-Sal=NR)⁶⁰ gives the complexes **80** (see Table II).

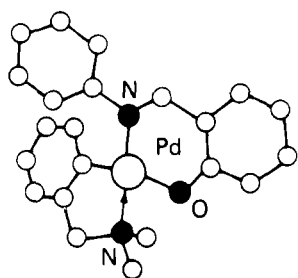


In comparison to compound **80** (M = Pt), the above coupling constants⁵⁰ in **72** are $^3J_{\text{Pt-H}^b} = 55$ and $^3J_{\text{Pt-H}^c} = 48$ Hz, values which are appreciably higher than those found in the complexes

TABLE II. ^{195}Pt - ^1H Coupling Constants for **80**

complex R	$^3J(^{195}\text{Pt}-^1\text{H})$ values, Hz				R
	H ^a	H ^b	H ^c	H ^d	
Me	81.6	41.5	33.3		CH ₃ 42.1
Et	82.3	41.7	33.0		CH ₂ 47.7
C ₆ H ₁₁	87.3	41.9	33.0		
Ph	78.4	44.4	34.9	41.4	
<i>p</i> -ClC ₆ H ₄	77.3	44.6	35.2	41.8	

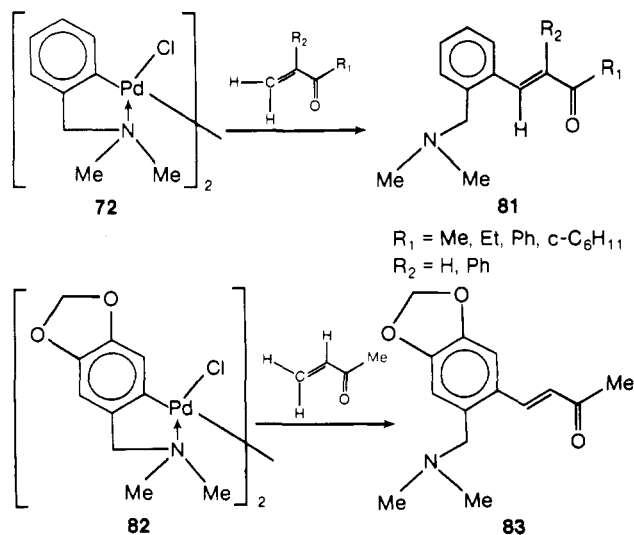
studied here. The reduced coupling constant in these complexes was considered⁵⁹ to be due to the coordination of dimethylamine nitrogen being weakened by the more strongly coordinating Schiff base. Hence, the value of this coupling constant may be useful as a measure of a *trans* effect of a ligand opposite the nitrogen atom in (*N,N*-dimethylbenzylamine-*C*²,*N*)platinum complexes. The increase in these couplings when R changes from alkyl to the less electropositive aryl groups is consistent with this view. The structure of (*N,N*-dimethylbenzylamine-*C*²,*N*)(*N*-phenylsalicylaldiminato)palladium(II), **80** (R = Ph) was determined from diffractometer data.⁶¹



Pd-N(amine) : 2.090 Å
 Pd-N(imine) : 2.037 Å
 Pd-C : 1.981 Å
 Pd-O : 2.094 Å

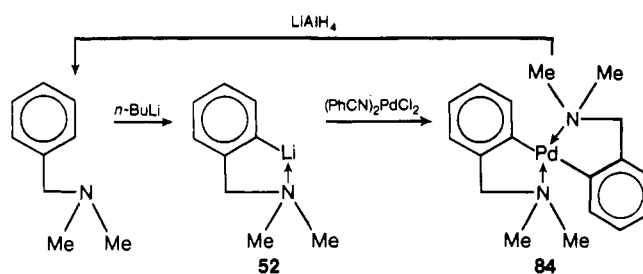
80 (M = Pd, R = Ph)

The palladium complexes **72** react with vinyl ketone⁶² to afford the ring cleavage adduct in high yield. For example, the treatment of the complexes **72** with methyl vinyl ketone containing excess of triethylamine gives rise to metallic palladium and the adduct **81**. The palladium complex **82**, prepared from dimethylpiperonylamine and lithium tetrachloropalladate, also gives the adduct **83** similar to **81**.

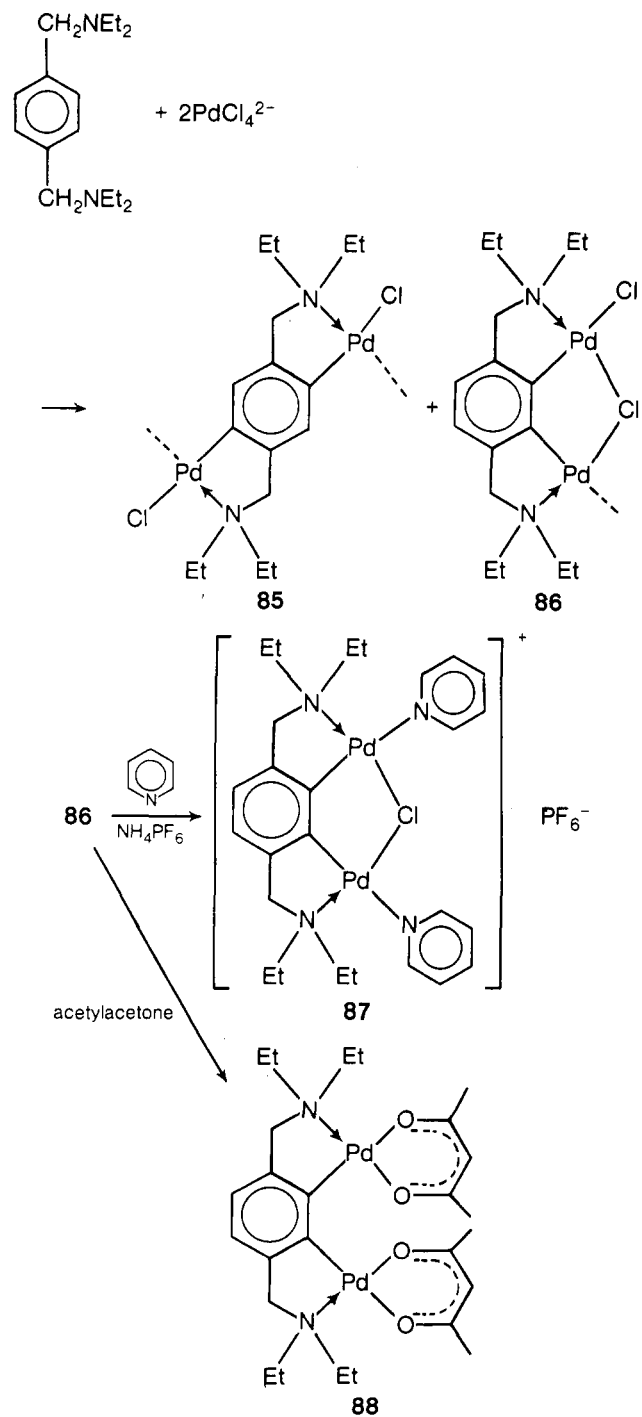


The reaction⁶³ of *N,N*-dimethylbenzylamine with Li_2PdCl_4 affords the μ -chloro complex **72**; however, the reaction of σ -lithio-*N,N*-dimethylbenzylamine with dibenzonitrile-dichloropalladium affords the dimeric compound **84** having the two

five-membered rings which show nonequivalent *N*-methyl protons (2.48 and 3.44 ppm) and nonequivalent benzylmethylene protons (2.96 and 3.80 ppm).

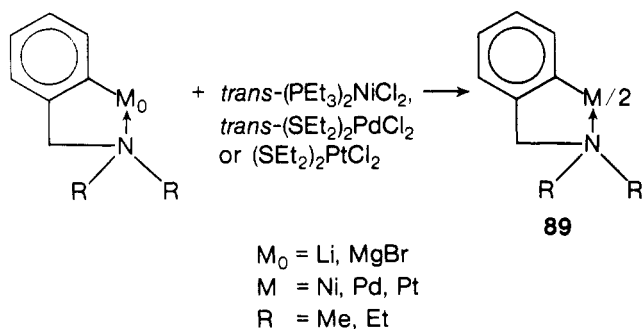


Trofimenko^{64,65} has reported the di-ortho-metalation reaction of palladium compounds. The reaction of *N,N,N',N'*-tetraethyl-*p*-xylenediamine with tetrachloropalladate ion in the presence

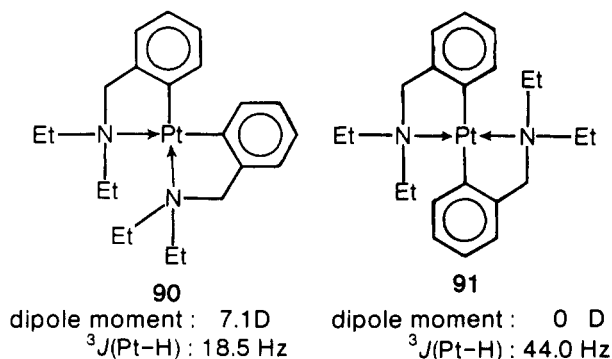


of a hindered tertiary amine gave a mixture of **85** and **86** (the ratio is 7:3), whose structures have been inferred from their solubility, pyridine derivatives (**87**) or acetylacetonate derivatives (**88**), and X-ray photoelectron spectroscopy (ESCA). The presence of two different types of chlorine in **86**, one being tightly bound (bridging) and the other loosely bound and reactive, was indicated by ESCA which showed a Cl peak width of 3.2 eV, a peak broadening consistent with the presence of two types of chlorine in the molecule, and by the reaction of **86** with pyridine which resulted in replacement of only one chlorine and formation of a monocation **87** containing only one pyridine per palladium, instead of two, as found customarily in monopalladio systems or dipalladiobenzenes containing nonadjacent Pd atoms. The 1,2-bis-(chloropalladio) compound **86** contains a relatively inert intramolecular Pd-Cl-Pd bridge.

Longoni and co-workers⁶⁶ have reported the following cis and trans isomers (**89-97**) having two chelated five-membered rings. The reactions of 2-[(dialkylamino)methyl]phenyllithium with *trans*-(PEt₃)₂NiCl₂ gave the trans complex **89** containing two chelate five-membered rings. However, the reaction of 2-

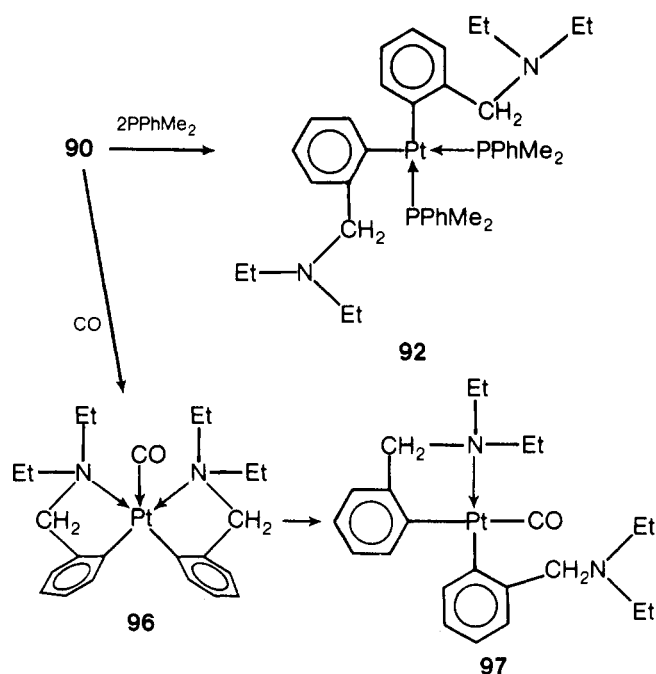


[(dialkylamino)methyl]phenyllithium with *trans*-[(SEt₂)₂PdCl₂] gave the cis isomer, and the reaction with [(SEt₂)₂PtCl₂] gave the cis (**90**) and trans (**91**) isomers.



The platinum compounds are monomeric, and dipole moment measurements and the coupling constant (³J(Pt-H)) of the benzyl proton show **90** to be the cis square-planar isomer and **91** to be the trans isomer. The palladium compounds (**89**) are also monomeric. The dipole moment (μ 6.8 D) and the NMR spectrum in which both the methylene and the methyl protons are equivalent, are consistent with a cis square-planar structure. These results are in contrast to those of **84**⁶³ whose structure is formulated as tetrahedral on the basis of its NMR spectrum shown above. The platinum derivatives are stable to air, protic solvents, and perdeuteriopyridine; however, the reaction with dimethylphenylphosphine gave complex **92**. The cis structure of **92** is shown by the NMR spectrum, in which the methyl groups of the phosphine appear as a doublet split by ¹⁹⁵Pt.⁶⁷

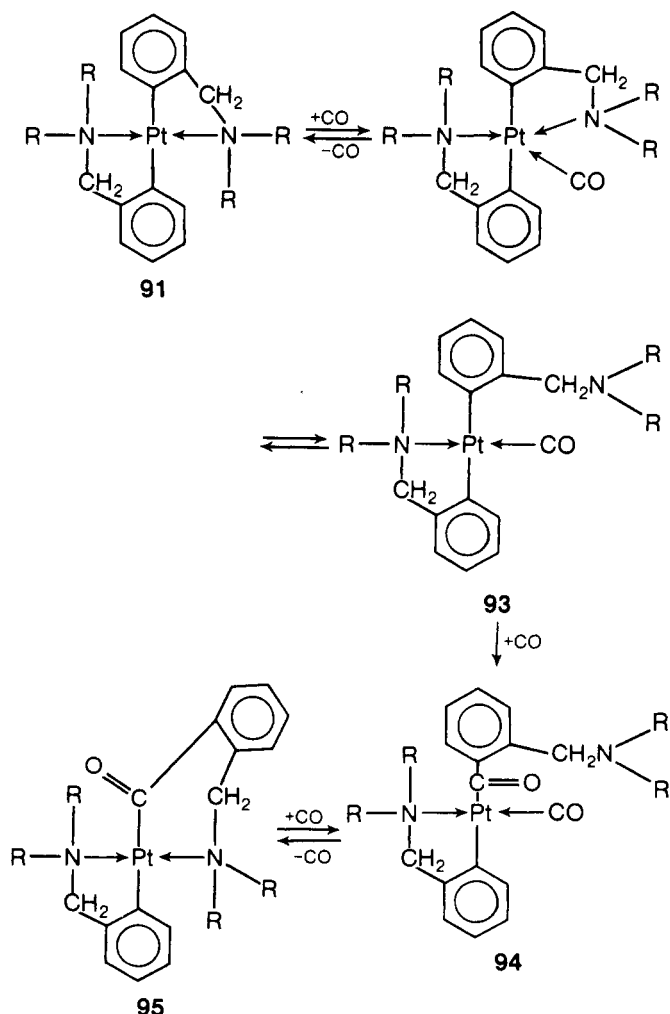
The nickel complex of **89** is rapidly converted by carbon monoxide into Ni(CO)₄ (2055 cm⁻¹). On the other hand, the palladium complexes are converted into palladium complexes of **89**; however, the trans platinum derivatives of **91** react with



CO to give the carbonyl complexes (**94**, **95**) with insertion in the metal-phenyl carbon bond as shown in Scheme I.

The NMR spectrum of **94** shows that both the methyl and benzyl protons of one nitrogen ligand are still coupled with platinum atom (³J(Pt-H) = 14.6 and 18.5 Hz), while the protons

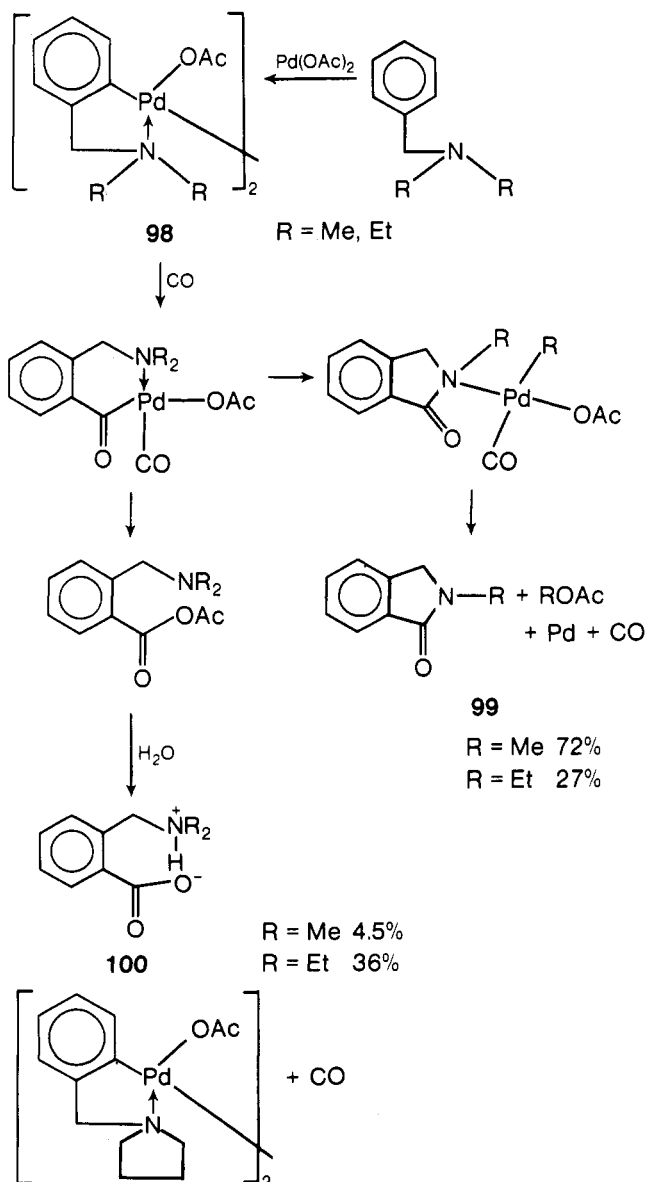
SCHEME I. Reaction of Trans Derivative **91** of Platinum with CO.



of the second nonchelate ligand show a chemical shift similar to that of the free ligand and are not coupled with the platinum atom.

A solution of **94** in THF, on standing in nitrogen atmosphere, gave **95**, whose structure was determined by IR spectrum. But, it should be considered that **95** may be a polymeric complex because it has a very low solubility and the six-membered ring of **95** has more strain than that of the five-membered ring. Reaction of the *cis*-platinum derivatives, **90**, with carbon monoxide gives the adduct **96** whose square-pyramidal structure is in agreement with the NMR spectrum, which indicates that all the *N*-alkyl and benzyl protons are still coupled with the platinum atom, with a $[\delta^3 J(\text{Pt-H})]$ similar to that of **90**. The unstable complex **96** is slowly transformed to complex **97** similar to **93**.

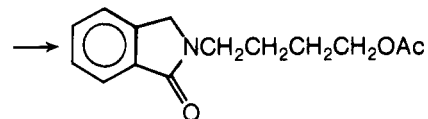
The acetoxy bridged dimers **98**⁶⁸ were prepared by the reaction of *N,N*-dialkylbenzylamine or *N*-benzylpyrrolidine with palladium acetate. Although the carbonylation of the complex **98** ($R = \text{Me, Et}$) was expected to produce only mixed anhydrides and ketones, as is observed in carbonylation of simple arylpalladium acetate derivatives^{69,70} such as **95**, ketones were not observed; however, hydrolysis products of the mixed anhydride were an unexpected third type of product, which was formed in both reactions, so that a phthalimidine **99** was produced by cyclization and loss of one of the *N*-alkyl group. Compound **100**



was obtained presumably by hydrolysis during isolation of an initially formed mixed anhydride with acetic acid.

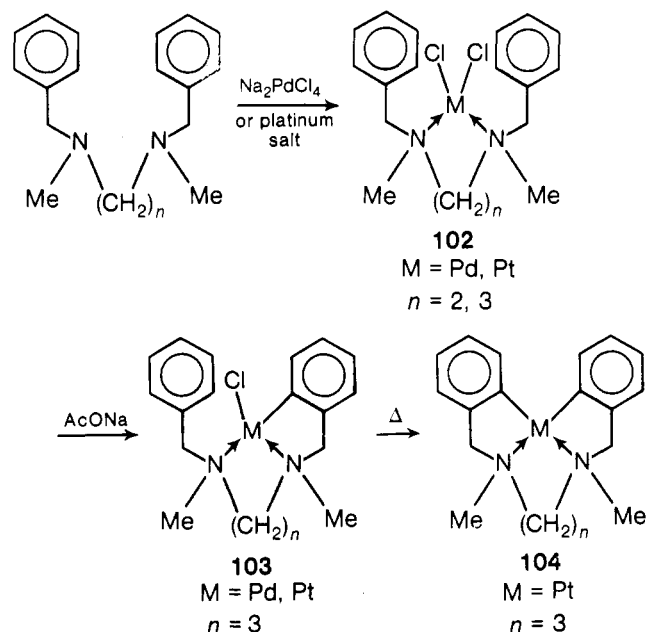
The carbonylation⁶⁸ of **98** [$-\text{R}-\text{R}- = -(\text{CH}_2)_4-$] also was investigated in the palladium acetate-*N*-benzylpyrrolidine complex, where the "second alkyl group" could not be lost as a low molecular weight fragment. The carbonylation gave only one significant product, 2-(4'-acetoxybutyl)phthalimidine (**101**).

98 ($-\text{R}-\text{R}- = -(\text{CH}_2)_4-$)

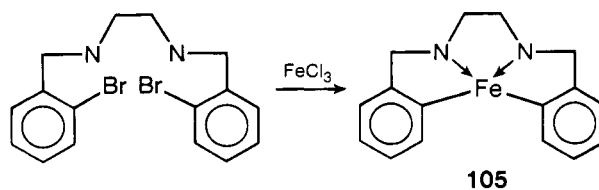


101

Compounds $\text{PhCH}_2(\text{Me})\text{N}(\text{CH}_2)_n\text{N}(\text{Me})\text{CH}_2\text{Ph}$ ($n = 2, 3$)⁷¹ react with Na_2PdCl_4 or platinum salt to give the bidentate di-*N*-donor complexes **102**, and then, by heating with sodium acetate which promotes internal metalation,⁷² **102** are converted into the orthometalated compound **103**. It is expected that the greater flexibility of the six-membered ring in **102** would enable the benzyl group to approach the metal and become metalated more easily. Further, prolonged (10 days) reflux of **103** ($M = \text{Pt}, n = 3$) in xylene, gave the di-orthometalated compound **104** in low yield. It should be considered that the intramolecular dimetalation from **102** to **104** is extremely limited not only sterically but also electrically because **104** has no electronegative group even though the formation of stable chelate ring requires more electronegative atoms than in **102**.



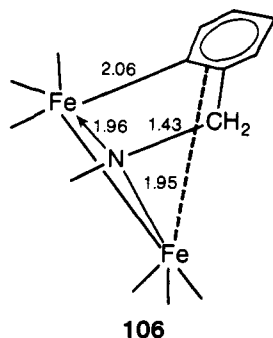
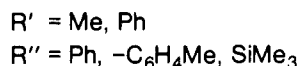
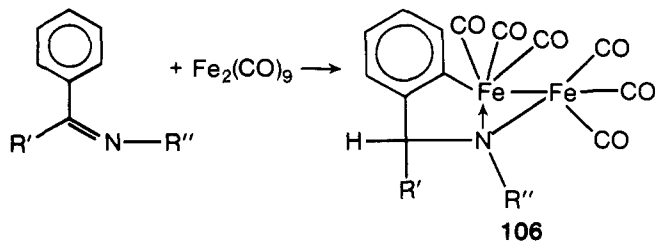
The reaction⁷³ of *N,N*-dimethyl-*N,N'*-bis(*o*-bromobenzyl)-ethylenediamine with anhydrous iron(II) chloride gave the internal dimetalation compound **105** whose magnetic moment is 4.45 BM.



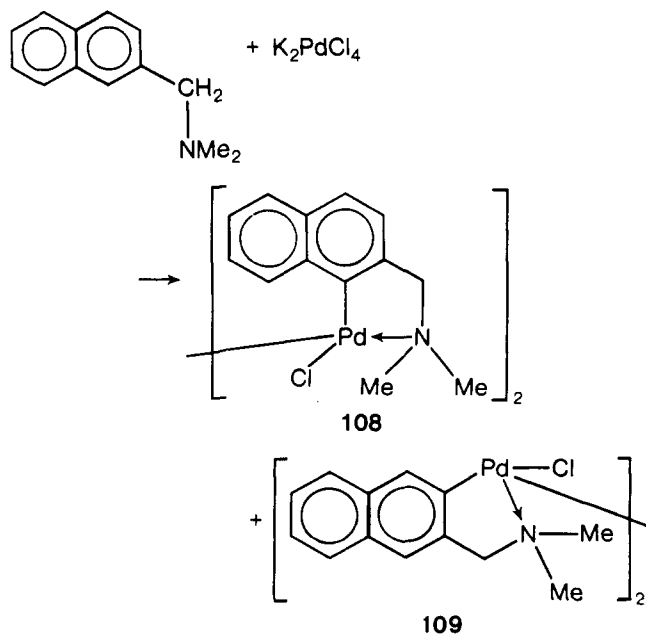
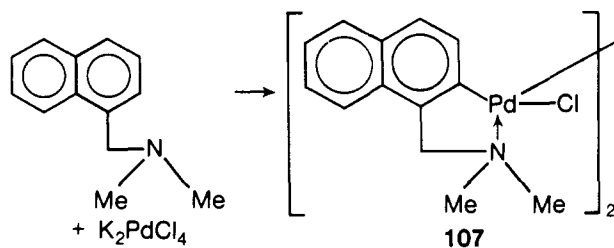
105

The reaction of diiron nonacarbonyl⁷⁴⁻⁷⁶ with Schiff bases affords hexacarbonyldiiron complexes **106** having the five-membered ring structure. This structure has been determined by an X-ray diffraction study. Although the carbons of the phenyl

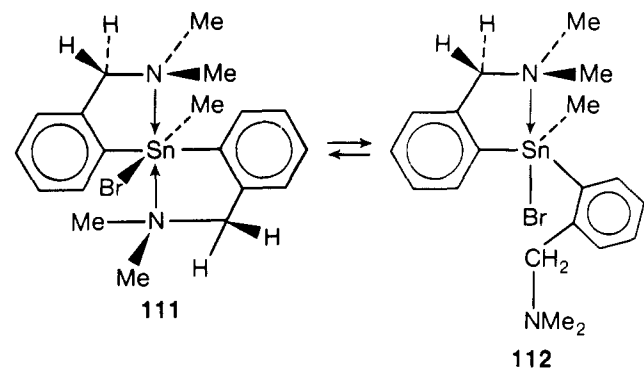
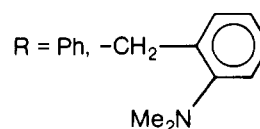
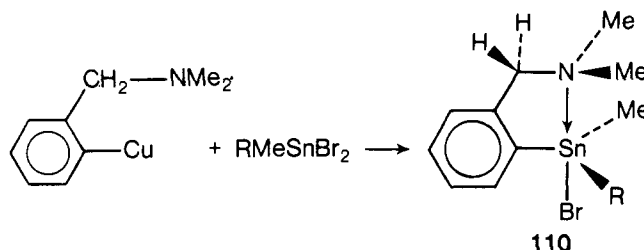
group which form part of the ring are equidistant from the iron (2.3 Å), the methylene group, which cannot participate in bonding with the metal, is bent away (2.6 Å) while the nitrogen moves toward the iron so that it lies equidistant from both iron atoms (1.96, 1.95 Å).



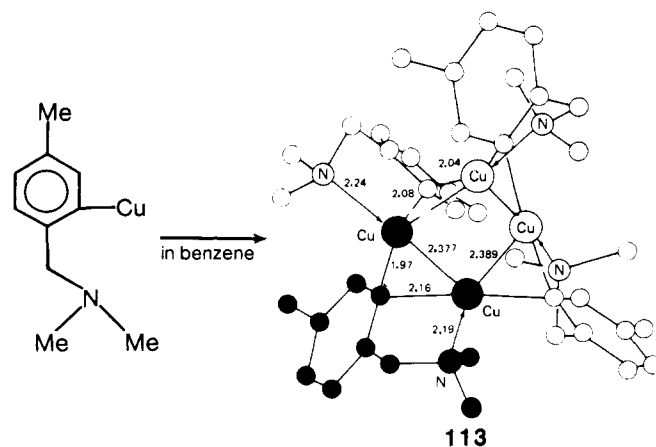
The palladation⁷⁷ of 1-dimethylaminomethylnaphthalene takes place only on the 2 position (**107**), whereas reactions of the 2-isomer occur on the 1 and 3 positions (**108/109**, 66/33% yield). *N*-Methyl- and -benzylmethylene resonances of ¹³C NMR (**107**) are at 51.5 and 70.0 ppm, being almost the same as those of the benzyl complexes **72**, respectively.



The reaction⁷⁸ of alkylaryltin dibromide with 2-(*N,N*-dimethylaminomethyl)phenylcopper gives a chiral triorganotin halide **110** which has a stable chiral tin atom by the intramolecular coordination. The tin atom is an optically active center, and **110** ($R = \text{Ph}$) is stable at 30 °C; however, the rate-determining step from **111** to **112** occurs at -10 °C. As for the difference of the stability between **110** ($R = \text{Ph}$) and **111**, it should be considered that the coordination capability of the tin atom in **111** is weaker than that of **110** because **111** has one electron-withdrawing group to the two ligand groups.



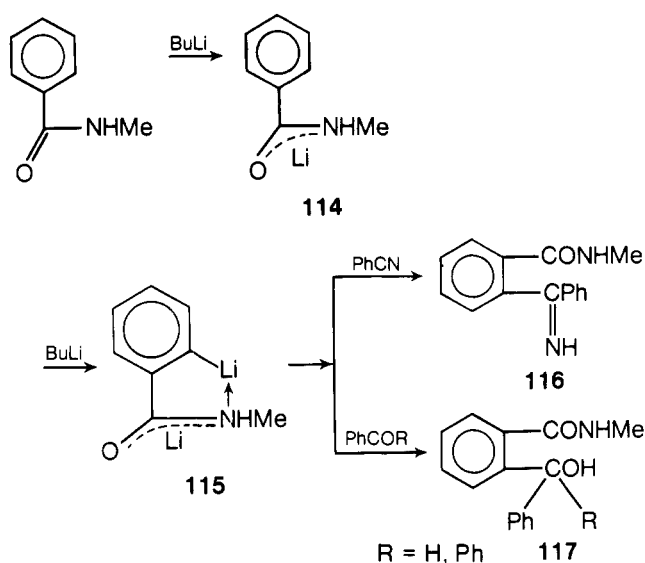
The cooling⁷⁹ of 5-methyl-2-[(dimethylamino)methyl]phenyl-copper(II) in a saturated benzene solution from 60 to 20 °C at a rate of 2 °C per day gives a single crystal. This structure is tetrameric in the solid state and possesses the five-membered ring, as determined by X-ray analysis. The Cu-N distances of 2.21 Å, as well as the observed stereochemistry around copper, indicate that Cu-N coordination occurs. The most remarkable feature is the presence of bridging phenyl groups. The bonds from the aryl ligands to the respective copper atoms are either symmetric, 2.04 and 2.08 Å, or asymmetric, 2.16 and 1.97 Å. Mass spectra of **113**, 5-methyl-2-[(dimethylamino)methyl]phenylcopper (=R)₄Cu₄ (**113**), reveal that the Cu₄ cluster has considerable stability. Although the R₄Cu₄⁺ ion is very abundant, R₃Cu₄⁺ forms the base peak.



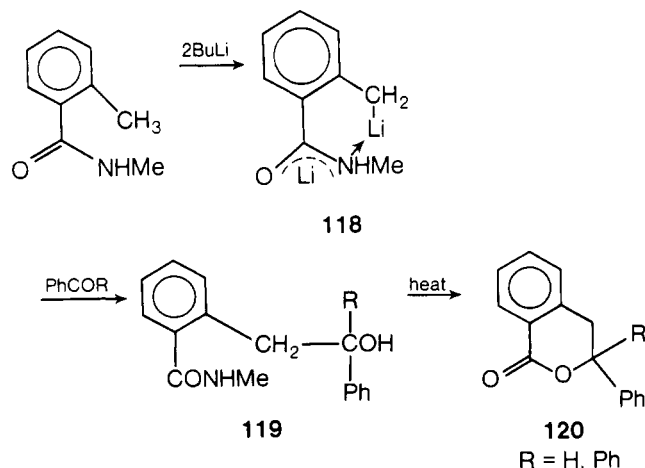
Other complexes such as boron complexes⁸⁰ having benzylamine groups, lithium complexes⁸¹ having dimethylaminomethylpyridine groups, etc., have been reported.

C. Benzoylamines

It is well known that *N,N*-dialkylamides undergo addition reactions with Grignard⁸² and lithium reagents⁸³ leading to the formation of ketones. The reaction of *N,N*-dimethylbenzamide with *n*-butyllithium is observed to form valerophenone in high yield.⁸⁴ However, Hauser and Puterbaugh⁸⁴ presumed that *N*-methylbenzamide,⁸⁴ which would undergo an initial *N*-metalation with *n*-butyllithium to form monolithioamide **114**, might exhibit ortho metalation with excess of this reagent to give dilithioamide **115** having the five-membered ring structure similar to the benzamide metal complex, since the carbonyl group in **114** should be deactivated for additional reaction. The formation of the *o,N*-dilithioamide **115** is established by condensation with electrophilic compounds such as benzophenone and benzonitrile to form the corresponding ortho-substituted amides **116** and **117**, respectively.

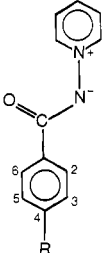
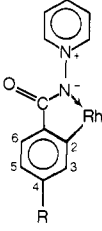


N-Methyl-*o*-toluamide⁸⁵ is also metalated at the 2-methyl group as well as the nitrogen atom with an excess of *n*-butyllithium to form the complexes **118** similar to **62**. The resulting dilithioamide is condensed with ketones and aldehydes to form δ -hydroxyamides **119**. These products are cyclized thermally to afford δ -lactones **120**.



The reaction^{86,87} of various ylides of general formula $\text{ArC}=\text{ON}^-\text{Y}^+$ ($\text{Ar} = \text{Ph}$ or *m*- or *p*- MeC_6H_4 ; $\text{Y} = \text{pyridine}$, NMe_3 , or PPh_3) with halide salts of Pd(II), Pt(II), Rh(III), and Ir(III) affords

TABLE III. ¹³C NMR Data at 25.2 MHz (ppm)

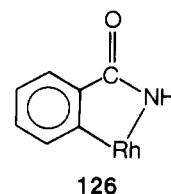
	R	C(2)	C(6)
	H		126.3
	Me		128.5
	H	159.5	129.2
	Me	$J = 32.5$ Hz 160.5	128.5

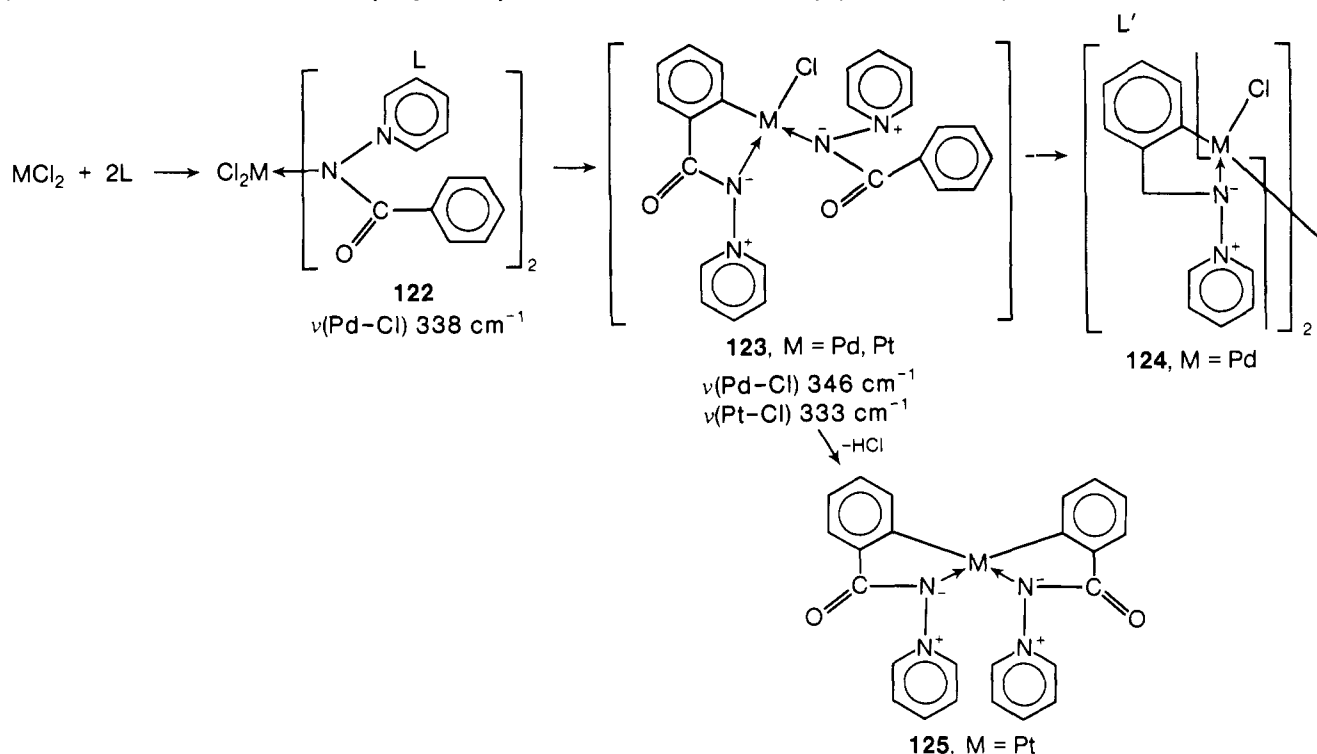
121

products containing metalated betaines. Spectroscopic data show unambiguously that the aryl group Ar has become metalated in a position ortho to the carbonyl group and also that the ylide is bidentate (L') via the group N^- . ¹³C NMR data of C(2) in rhodium complexes having a pyridinium ligand show downfield shifted absorption at about 160 ppm ($J = \sim 33$ Hz) comparable to those of C(6) which are 125–130 ppm as shown in Table III.

In the reaction⁸⁷ with palladium salt, it is possible by slight variation of the experimental conditions to isolate **122** and **123** which may be regarded as intermediates in the path to **124**. Dias and co-workers⁸⁷ suggested, therefore, that the first step is formation of intermolecular coordination compound **122**, in which the nitrogen donor atom is coordinated simply to the metal, and then one orthometalated complex is formed by the metal to attack one benzene ring at the ortho position as shown in Scheme II. They compared the rates of formation of complexes [**124**, $\text{L}' = \text{N}$ -(1-pyridino)benzamidate-, *m*-toluamidate, and *p*-toluamidate- C^2, N] and found the relative rate to be in the following order: *m*-toluamidate \gg benzamidate $>$ *p*-toluamidate. This order strongly suggests that the orthometalation also involves electrophilic attack by the metal on the benzene ring at the ortho position. The structures of **122** and **123** are presumed to be trans by IR data of $\text{M}-\text{Cl}$.⁸⁸ No analog of complex **124** was prepared in the platinum case. They⁸⁷ presumed that **124** arises via nucleophilic displacement of the nonmetalated ligand from **123**; this reaction is likely to be slow for platinum with the result that internal metalation of the second ylide molecule may proceed at a rate which is at least comparable to that of the displacement reaction to give a reasonable yield of this complex, **125**. The structure of **125** is presumed to be cis because the two metalated ligands are equivalent (¹H NMR).

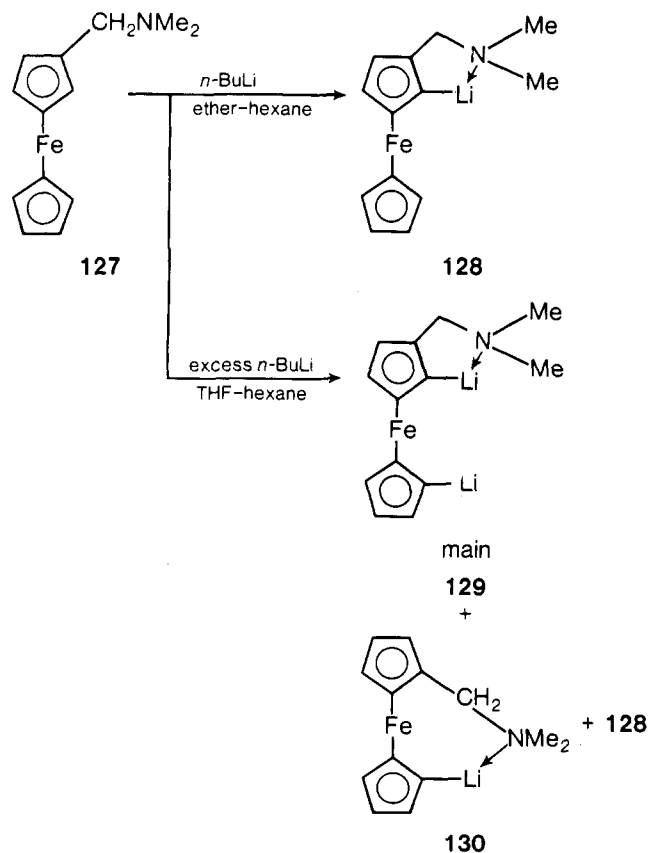
The reaction⁸⁹ of di- μ -chloro-bis(dicarbonylrhodium) with benzoyl azide affords the rhodium metal complex, which apparently has the benzoylimino moiety (**126**) according to structural studies based on its chemical behavior, IR, and NMR data for the adducts with triphenylphosphine, *p*-toluidine, pyridine, and 3,4-lutidine.



SCHEME II. Orthometalation of *N*-(1-Pyridinio)benzamidate with Palladium(II) and Platinum(II)

D. Aminoalkylferrocenes

N,N-Dimethylaminomethylferrocenes, **127**, afford compounds analogous with the *N,N*-dimethylaminomethylbenzenes. For example, *N,N*-dimethylaminomethylferrocene⁹⁰ was metalated with *n*-butyllithium in ether-hexane, and the resulting monolithioamine was condensed with benzophenone, acetone, benzonitrile, and phenyl isocyanate to form the corresponding 2-derivatives such as **53** and **54**. However, when the amine **127**

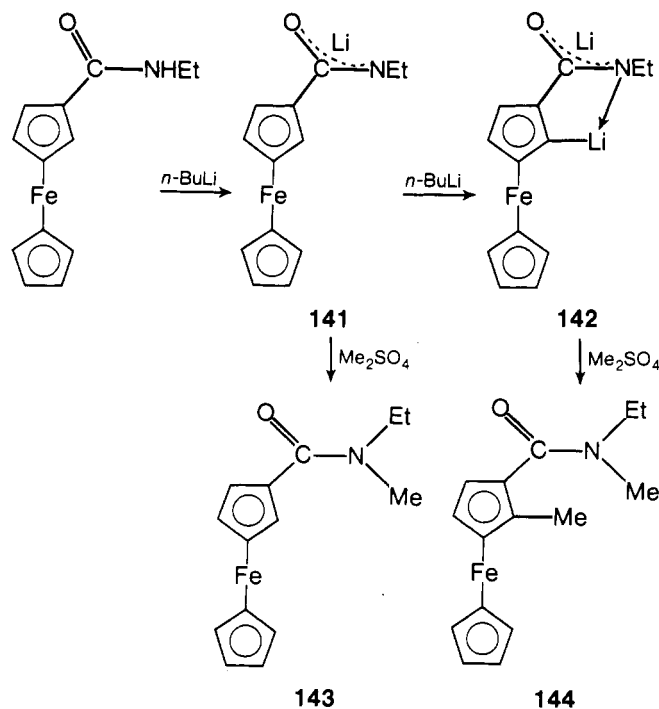


was metalated with excess *n*-butyllithium in THF-hexane, and the resulting intermediate was condensed with benzophenone, the product was mainly the 2,1'-derivative (**129**); also some of the 2- and the 1'-derivatives (**130**) were formed. In THF-hexane, the amine **127** was converted primarily to a dilithioamine. The amine **127** underwent lithiation more readily than ferrocene. The 2-lithio[(dimethylamino)methyl]ferrocene (**128**) was, in fact, isolated by Rausch and co-workers⁹¹ in 1973, as an extremely air-sensitive pink solid.

The lithiation of benzyldimethylamine easily gives a lithio intermediate having a five-membered ring structure; however, the lithiation of phenylethyldimethylamine does not readily yield a lithio intermediate having a six-membered ring structure. Hauser et al.^{37,38} reported a study of the metalation, but they recorded only a tarry product from the reaction of the amine with BuLi followed by treatment with benzophenone. However, Slocum and co-workers⁹² and Narasimhan and Ranade⁶⁰ obtained the six-membered cyclic lithioamine intermediate although the yield of such an intermediate was very low. In contrast to the reaction of the benzene derivatives, *N,N*-dimethylaminoethylferrocene³⁹ was metalated in good yield with *n*-butyllithium in ether-hexane and the intermediate 2-lithioamine was condensed with benzophenone, benzonitrile, phenyl isocyanate, phenyl isothiocyanate, hexachloroethane, or mercuric chloride to form the corresponding 2-derivatives, and, according to Slocum and co-workers,³⁹ the difference in behavior was attributed to the relative acidities of the 2 position and α protons in the corresponding systems. It should be considered that the above difference is mainly caused by the steric factor between the angles made by the ferrocene ring to the methylene and the metal and the angles made by the benzene ring to the methylene and the metal; namely, the steric hindrance of the six-membered ring containing the ferrocene must be less than that containing the benzene.

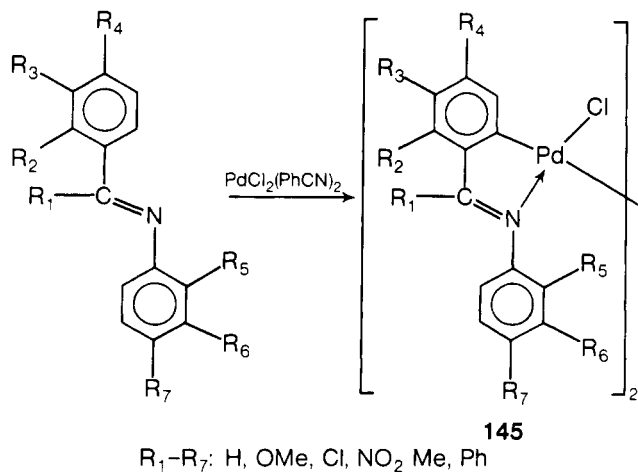
The lithiation reaction of the ferrocenes is used for the syntheses of 1,2-disubstituted derivatives. For example,⁹³ 2-chloromethylferrocene (**131**) and 2-(methoxymethyl)methoxyferrocene (**132**) were prepared from [(*N,N*-dimethylamino)methyl]ferrocene, and the carbinol ether ferrocene **133**⁹⁴ was obtained via the reaction of lithium ferrocene with a ketone

boxylamide with butyllithium similar to the N-metalation and orthometalation of *N*-methylbenzamide shown above (**114**, **115**). The alkylation of **141** and **142** with dimethyl sulfate gave the methylated products **143** and **144**, respectively. These reactions are also useful for the preparation of ferrocenecarboxylic acid derivatives (ferrocenecarboxylic acid and 2-methylferrocenecarboxylic acid) by hydrolysis of the amides, **143** and **144**.

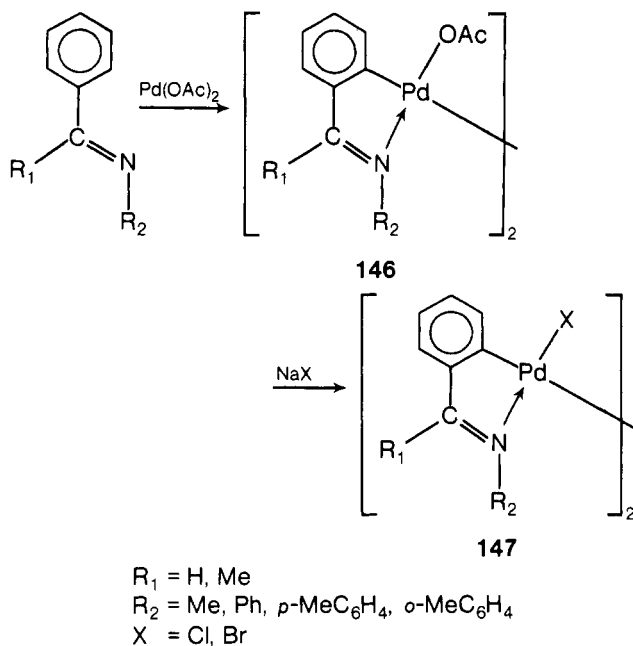


E. Benzylideneamines

Benzylideneamines also afford many kinds of complexes having the five-membered ring structure similar to the benzylamines. Molnar and Orchin¹⁰⁴ first reported these complexes in 1969. The reaction of benzylideneaniline with bis(benzonitrile)palladium(II) dichloride easily affords dichlorobis(benzylideneaniline-*C*²,*N*)palladium(II) and related complexes **145**. The

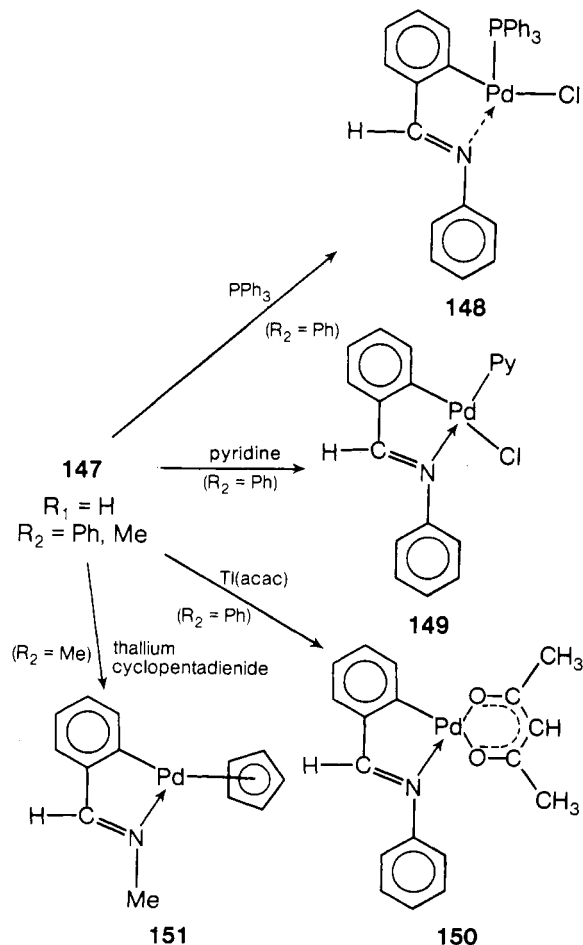


$\nu(\text{C}=\text{N})$ of the free parent benzylideneamines¹⁰⁵ appears two bands at 1600–1650 cm⁻¹.¹⁰⁶ The coordination of benzylideneamines to palladium always results in a shift of the C=N stretching mode to a lower frequency while the stretching frequency of olefins coordinated to Pt or Pd are reduced¹⁰⁷⁻¹⁰⁹ about 150 cm⁻¹. In their series,¹⁰⁵ it is observed that the C=N stretch is reduced on the average only about 26 cm⁻¹ which indicates that the coordination of benzylideneaniline to palladium is almost certainly through the lone pair and not through the azomethine π system.

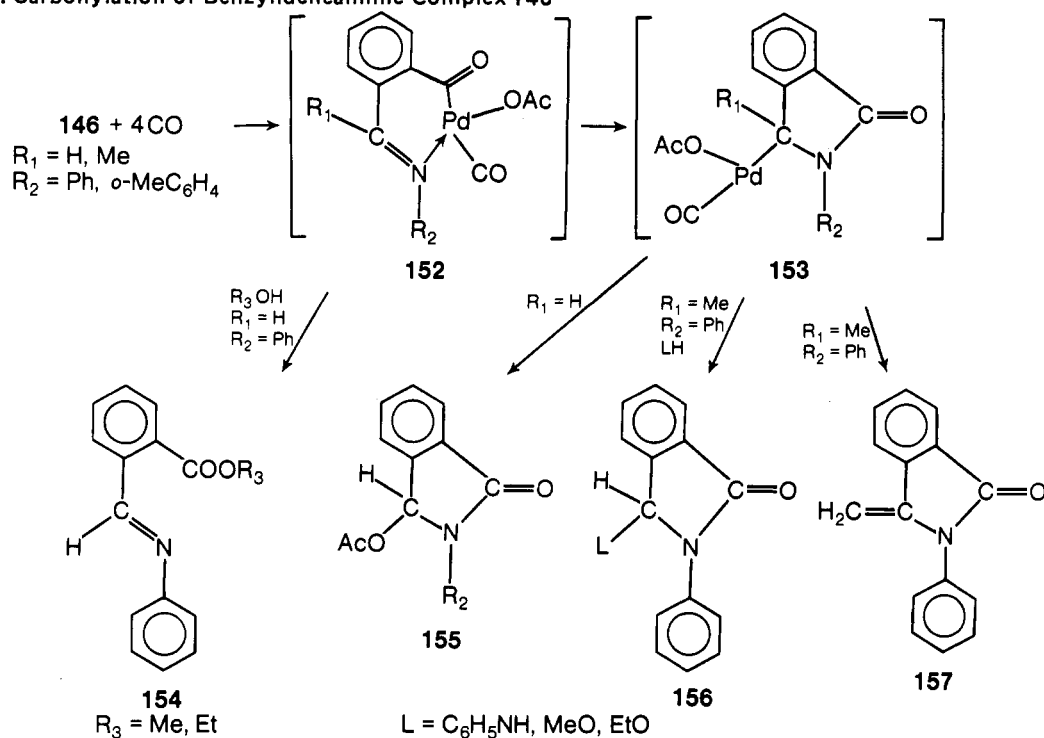


The reaction¹¹⁰ of benzylideneaniline with palladium(II) acetate affords di- μ -acetato-bis(*N*-phenylbenzaldimine-*C*²,*N*)palladium(II) (**146**). The corresponding chloro- and bromo-bridged complexes **147** were obtained by the metathetical reaction of acetyl-bridged complexes **146** with sodium chloride and sodium bromide, respectively. The chloro-bridged complexes **147** react with triphenylphosphine, pyridine, and thallium acetylacetonate to give the corresponding cleavage complexes of the chloro bridge, **148**, **149**, and **150**, respectively.

The NMR spectrum of di- μ -acetato complexes **146** shows a singlet at 7.61 ppm (CH=N), which indicates that the coordi-



SCHEME IV. Carbonylation of Benzylideneaniline Complex 146

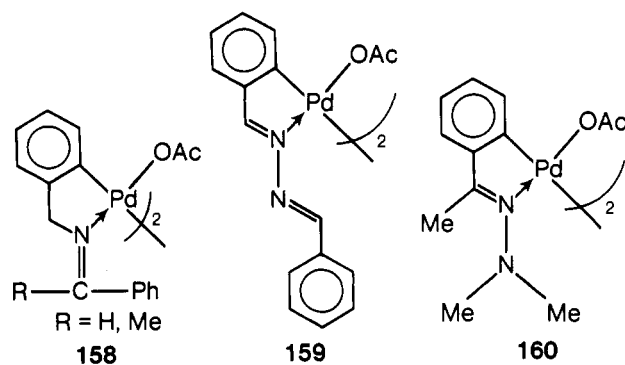


nation to palladium is established through the lone pair of nitrogen and not the C=N double bond as in **30**.²⁶ The acetato-bridged complexes exhibit two strong IR absorptions at ca. 1570 and 1410 cm^{-1} due to the bridging acetato group.¹¹¹ The $\nu(\text{C}=\text{N})$ frequencies show the same low field shift (about 40 cm^{-1}), in comparison with the corresponding frequencies of the starting Schiff bases, which shift also indicates that coordination to palladium is through its lone pair;^{112,113} however, the triphenylphosphine derivatives (**148**) are presumed to have the weak interaction of the azomethine bond with palladium by the presence of only 20 cm^{-1} lower field shifts than the $\nu(\text{C}=\text{N})$ of *N*-phenylbenzaldimine. The palladium(II) chloride of benzylideneaniline (**147** ($R_1 = \text{H}$; $R_2 = \text{Me}$)) is converted to **151** by thallium cyclopentadiene.¹¹⁴

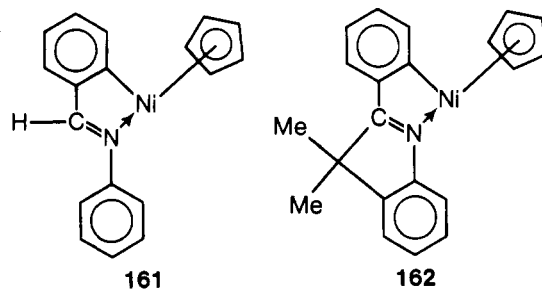
Thompson and Heck⁶⁸ presumed the following carbonylation of benzylideneaniline complex **146** (Scheme IV): initially, CO insertion and bridge breaking likely occur forming intermediate **152**, which then follows two possible reaction paths in alcohol solvents. The alcohol may either attack the carbonyl group and form noncyclized ester **154** or the compound may undergo an internal addition of the acylpalladium group to the nitrogen-carbon double bond to form **153**. A simple reductive elimination of product acetate, **155**, from complex **153**, apparently occurs if R^1 is H. If R^1 is methyl, metal hydride elimination preferably takes place and olefin **157** is formed. When nucleophiles are present, at least when R^1 is H, the palladium group may be also replaced to give **156** by the ligand minus a hydrogen.

The complexes from the benzylamine-Schiff base, **158**, were similarly prepared by heating the Schiff base with palladium acetate. While syn and anti isomers about the C=N double bond are possible, only one, presumably the anti isomer, was found in these complexes. Two varieties of hydrazone complexes were likewise prepared. Benzaldazine gives complex **159**; acetophenone dimethylhydrazone gives complex **160**.

Nickel complexes¹¹⁵ having a cyclopentadiene ring, as in **161** and **162**, were synthesized from the 2-bromobenzalaniline and 2-phenyl-3,3-dimethylindolenine, respectively. The intramolecular coordination structure of **161** is presumed by its NMR signal of the methine (7.68 ppm) which is close to that of benzylideneaniline (8.27 ppm), thus providing strong evidence in favor of the coordination of the azomethine to the nickel atom through

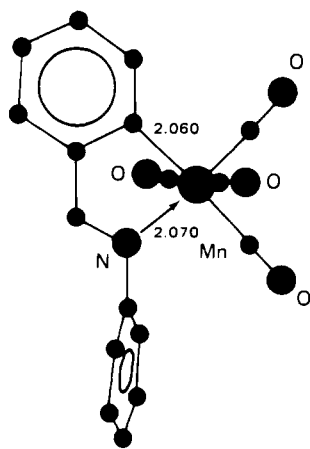


the nitrogen lone pair. If the π electron of the azomethine group had been involved in the coordination process, the azomethine proton would have produced a signal shifted¹¹⁶ upfield by about 2 ppm.

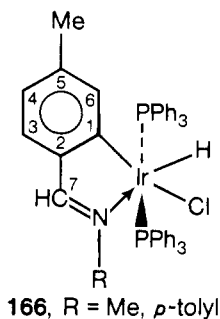
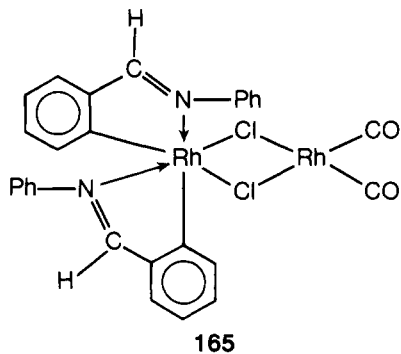
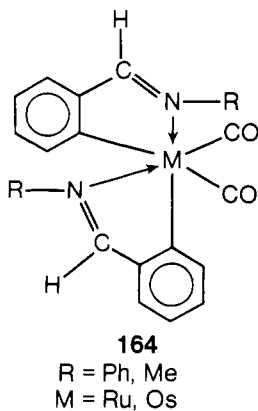
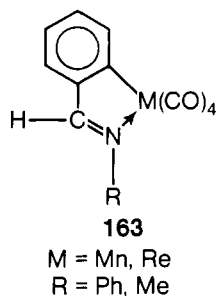


Reactions¹¹⁴ between benzylideneaniline or benzylidene-methylamine and metal carbonyl complexes $[\text{MeM}(\text{CO})_5]$ ($M = \text{Mn, Re}$), $\text{M}_3(\text{CO})_{12}$ ($M = \text{Ru, Os}$),¹¹⁷ and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ afford orthometalated complexes containing the five-membered ring structures **163**, **164**, and **165**, respectively. The crystal structure of tetracarbonyl[2-(*N*-phenylformimidoyl-*C*²,*N*)phenyl]manganese **163** ($M = \text{Mn}$; $R = \text{Ph}$) was determined by X-ray diffraction.^{118,119}

Van Baar and co-workers¹²⁰ have reported NMR spectroscopic studies of the following iridium complexes (**166**): the reaction¹²⁰ of benzylideneamines with *trans*- $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ gave the orthometalated complexes **166** (see Table IV). The *N*-methyl



163



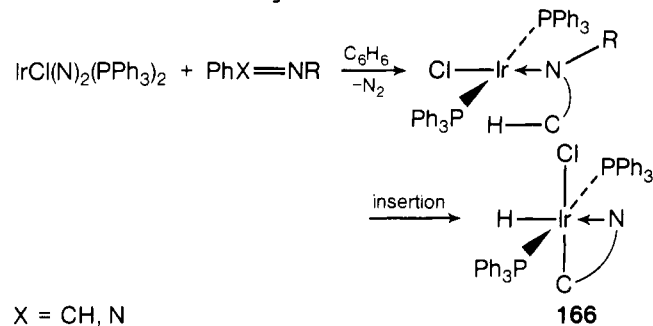
^1H and ^{13}C NMR signals in **166** appear at 2.89 and 44.00 ppm, respectively, which show a similarity to the NMR data of the *N*-benzyl complexes shown above. In ^{13}C NMR the metalated aromatic or olefinic carbon atom resonates at very low field with respect to the corresponding free ligand signals. This phenomenon, which occurs both in the octahedral Ir(III) complexes and the square-planar Pd(II) complexes, has been observed for other metalated aromatic (Ti¹²¹ and Li aryl¹²² compounds) or olefinic (Rh) carbon atoms.¹²³ They¹²⁰ presumed in terms of the paramagnetic shielding¹²⁴ contribution σ_p , of which the main factors are charge polarization effects, variation of π -bond order, and the average excitation energy, ΔE (σ_p varies inversely with ΔE). For both the Li-aryl and Ti-aryl compounds, the shielding of C_1 is dominated by a decrease in the ΔE factor. This might indeed be the main factor contributing to the observed C_1 shift of the Ir(III) and Pd(II) complexes, although charge polarization effects cannot be excluded, as might be concluded from the strikingly large upfield proton and downfield carbon shifts of the $(\text{CH})_1$ moiety of the complex **166**. In this respect, it is noteworthy that the NMR data which are available at present show a remarkable difference between the resonance of the metalated aromatic or olefinic carbon atom and those of methylmetal carbons, which are usually found at very high field.^{121,125} The orthometalation

TABLE IV. ^1H and ^{13}C NMR Spectra of **166** in CDCl_3

R	C_1	C_2	C_3	C_7	NCH_3	NCH_3
Me	152.19	140.92	126.29	173.61	44.00	2.89

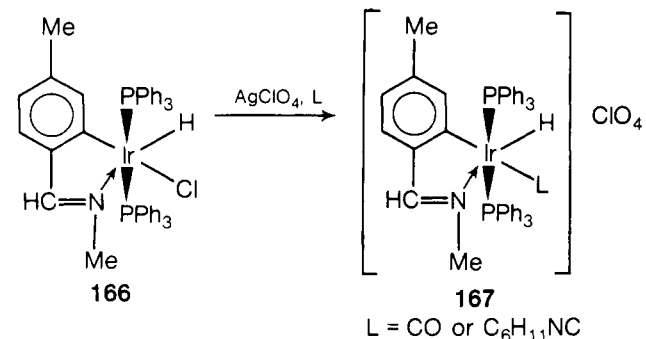
described in benzylamine and benzylideneamine complexes is a substitution reaction of the metal with the hydrogen at the ortho position. However, iridium complexes are probably formed by an insertion reaction instead of a substitution reaction. It might be considered that these reactions are caused by the affinity of the iridium metal to the hydrogen atom such as that shown when iridium complexes are used as hydrogenation catalysts.¹²⁶ Van Baar and co-workers¹²⁰ speculated on this insertion mechanism as follows: the first step should be $\sigma(\text{N})$ -coordination of the imine ligand, which would bring an ortho or olefinic CH group close to the metal atom; this property and the extra charge density on the metal atom brought about by the N-donor ligand should promote the second step in the reaction sequence, namely, the oxidative addition of the ortho or olefinic CH group to the metal atom (Scheme V).

SCHEME V. Reaction for Metalation of the Aromatic and Olefinic Azo or Imine Ligands

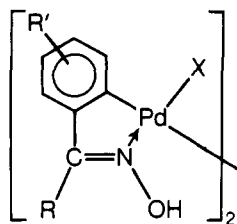


The reaction¹²⁷ of benzylideneamines with $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ in the presence of PPh_3 yields the same Rh complex as **166**. Van Baar and co-workers¹²⁷ considered that, for cyclometalation to occur, the metal atom must be electron rich; this is aided by basic phosphines as coligands. This nucleophilic behavior of the metal atom contrasts with the apparent electrophilic behavior of a transition metal in the orthometalation with benzylamine^{2,50} and azobenzene.^{2,128} (Both nucleophilic and electrophilic mechanisms are shown as in Table VI).

Treatment¹²⁹ of iridium complexes **166** with AgClO_4 and then with $\text{C}_6\text{H}_{11}\text{NC}$ or CO ($=\text{L}$) leads to the formation of the complexes **167**, the metallocyclic ring remaining intact.

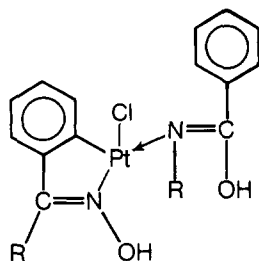


Orthometalation¹³⁰ by palladium(II) was observed in the reaction of lithium tetrachloropalladate(II) with various kinds of oximes. The obtained chloro-bridged complexes **168** have the five-membered ring structure of a benzylideneamine skeleton. These complexes react with triphenylphosphine resulting in cleavage of the metal-metal bridge. In the case of potassium tetrachloroplatinate(II), an orthometalation reaction was observed giving the complexes **169**, which have the intermolecular coordination bond of the nitrogen atom to the metal, but

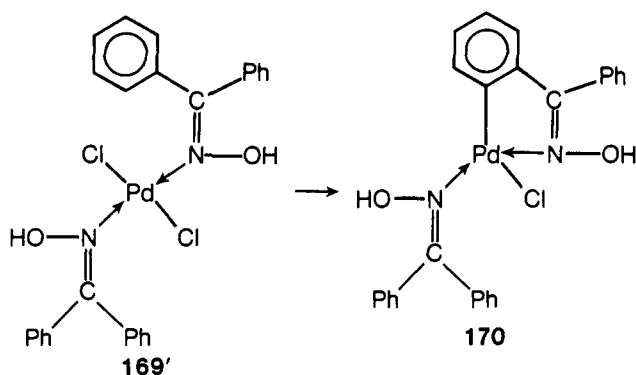


168

R' = H, MeO, NO, 3,4-benzo, 4,5-benzo
R = H, Me, Pr, *i*-Pr, Ph
X = Cl, Br

169, R = Me, *i*-Pr

chloro-bridged complexes could not be isolated. Onoue and co-workers¹³⁰ considered that the differences between palladium(II) and platinum(II) are partly attributed to the poor reactivity of platinum(II) compared to palladium(II), and that the reaction of the platinum salt with aromatic oximes would also proceed through an initial coordination of nitrogen to the metal followed by an electrophilic substitution by the metal at an ortho position on the benzene ring. In fact, they observed the following metalation in boiling tetrahydrofuran yielding complex **170** similar to **169**. If nitrogen coordinates strongly to the metal, dichlorobis-(oxime)-metal type complexes **169'** are formed and no orthometalation takes place. For example the *O*-methyl oxime of

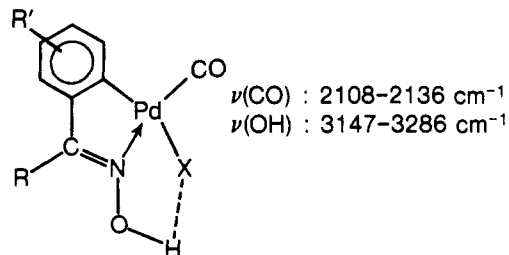


benzophenone and of acetophenone yield predominantly dichlorobis(*O*-methyloxime)palladium(II) similar to **169'**. They¹³⁰ concluded that the strong coordination of palladium with nitrogen, which was due to the presence of the electron-donating methyl group, reduced the formal charge of palladium, preventing its electrophilic attack on the benzene ring. On the other hand, both *O*-acetyl and *O*-benzylacetophenone oxime, in which the coordination power of nitrogen is reduced by the presence of the electron-withdrawing acyl groups, gave **168**.

The bridge-splitting reaction¹³¹ of **168** with CO yields the carbonyl complexes **171**. These complexes are very stable in a dry atmosphere, and the stability was considered to be due to the intramolecular hydrogen bond between the hydroxy group and the carbonyl group.

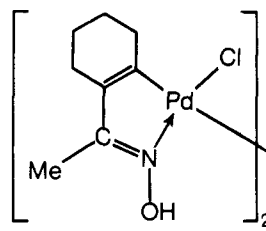
The cyclopalladation¹³² of vinylic oximes occurs for the sterically rigid oximes of 1-benzalicyclohexanone and 1-acetylcyclohexene, which are the alicyclic derivatives in this group, to afford **172** and **173**, respectively.

Rhodium salts¹³³ also afford the complexes **174** having the

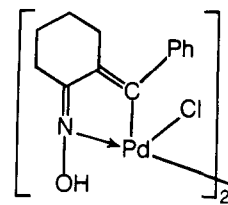


171, R' = H, OMe, 4,5-benzo
R = H, Me, Ph
X = Cl, Br, I

$\nu(\text{CO})$: 2108–2136 cm^{-1}
 $\nu(\text{OH})$: 3147–3286 cm^{-1}

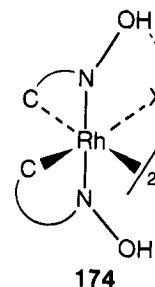


172



173

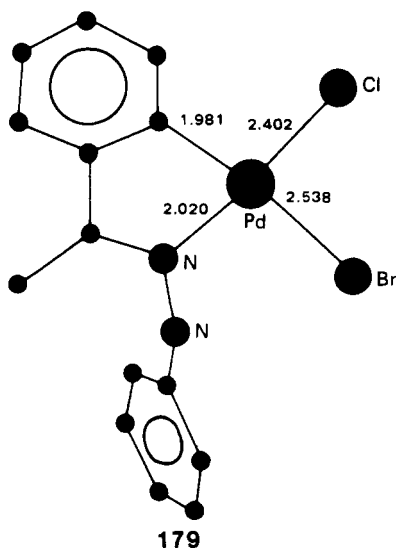
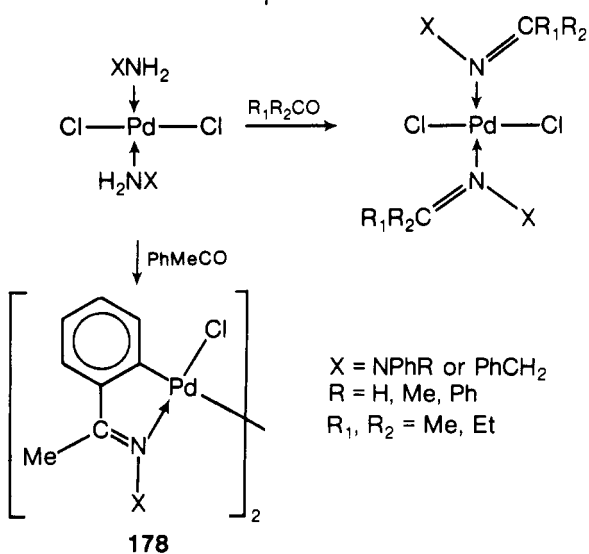
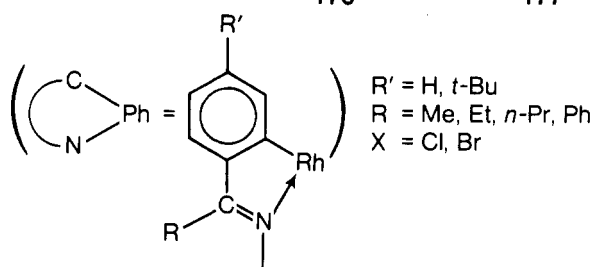
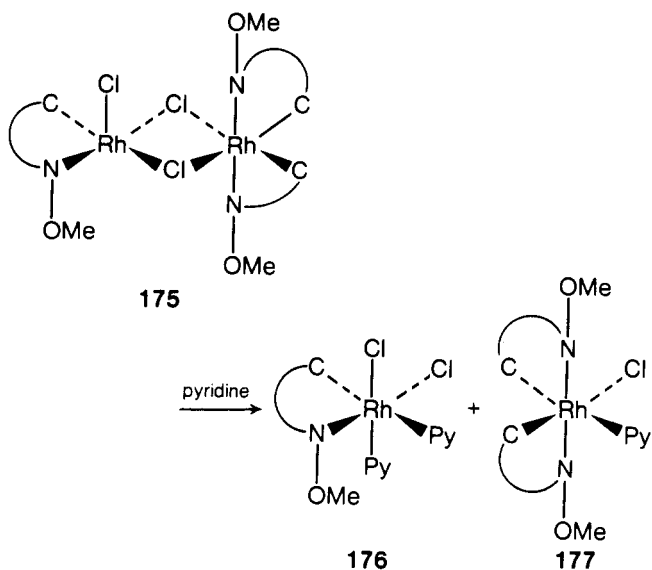
benzylideneimine skeleton by reaction with aromatic ketoximes. The structure of **174** is presumed to have an intramolecular hydrogen bond similar to **171** by the low-field shift of $\nu(\text{OH})$ absorption. Further, from the far-IR data of **174**, in which only one



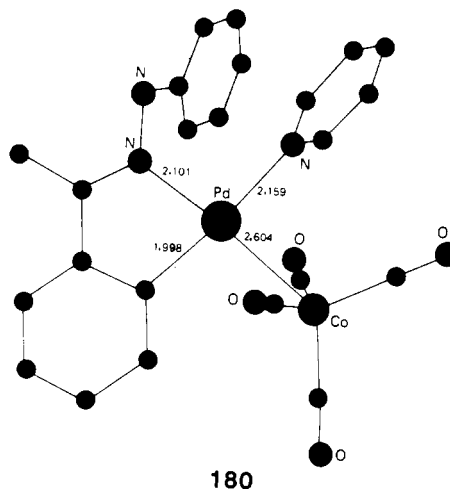
174

$\nu(\text{Rh}-\text{Cl})$ band is observed for each chloro complex in the range of 208–220 cm^{-1} , **174** is considered to be the symmetrical structure with chlorine trans to the Rh-C σ bonds because the terminal $\nu(\text{RhCl})$ vibration^{134,135} trans to alkyl appears at ca. 240 cm^{-1} and the bridging one¹³⁶ is about 20–40 cm^{-1} lower than the former. Reaction between *O*-methyloximes and lithium tetrachloropalladate(II) yielded predominantly dichloro(*O*-methyl oxime)palladium(II)¹³⁰ described above. On the other hand, orthometalated complexes **175** are isolated from the reaction of *O*-methyl derivatives of benzophenone and *p*-*tert*-butylacetophenone oxime with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$.¹³³ The terminal $\nu(\text{Rh}-\text{Cl})$ absorption and the C-H out-of-plane bending mode of the ortho-substituted benzene ring of **175** are found at 344–337 and 728 cm^{-1} , respectively. No definite bridging $\nu(\text{Rh}-\text{Cl})$ absorptions were identified, but, by the bridge-splitting reaction of **175** with pyridine, equimolar quantities of the complexes **176** and **177** were obtained.

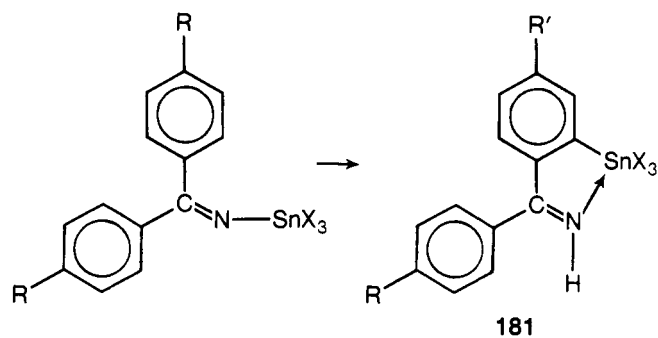
Dehand and co-workers^{137–141} have reported that orthometalations of ketones afford a number of the complexes having the benzylideneimine ligand, and the structure¹³⁸ has been determined by single-crystal X-ray diffraction method. Reaction^{137,139} of hydrazine-Pd complexes with carbonyl compounds of formula $\text{R}_1\text{R}_2\text{C}=\text{O} = \text{PhMeCO}$, cyclopalladate complexes, **178**. The chloro-bridged product¹⁴⁰ **178** is cleaved by $\text{R}'_4\text{NX}$ ($\text{R}' = \text{Et}$ or Bu ; $\text{X} = \text{Cl}$, Br , or I) to afford $\text{R}'_4\text{N}[\text{Pd}[\text{C}_6\text{H}_4\text{C}(\text{Me})=\text{NNHPh}]\text{X}_2]$, and the pyridium adduct $[\text{Pd}[\text{C}_6\text{H}_4\text{C}(\text{Me})=\text{NNHPh}]\text{ClPy}]$ ^{141,142} forms the bimetallic species, for $\text{X} = \text{Co}(\text{CO})_3$, $\text{Mn}(\text{CO})_5$, $\text{CpFe}(\text{CO})_2$, with NaX . The



crystal structure of $[(n\text{-Bu})_4\text{N}]^+ [\text{Pd}[(\text{C}_6\text{H}_4\text{C}(\text{Me})=\text{NNHPh})-\text{Cl}, \text{Br}]^-$ (**179**)¹³⁸ and $[\text{Pd}[(\text{C}_6\text{H}_4\text{C}(\text{Me})=\text{NNHPh}) \text{PyCo}(\text{CO})_4]$ (**180**)¹⁴³ have been determined by X-ray diffraction study.

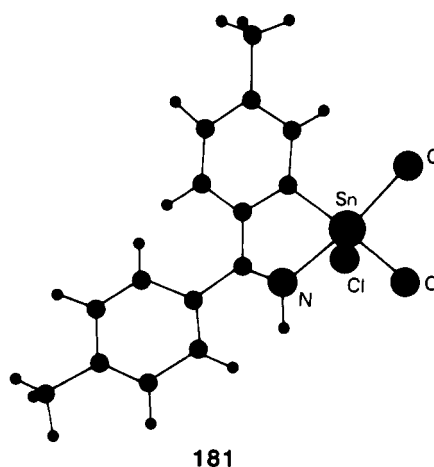


The benzylideneaminotin(IV) halides¹⁴⁴ spontaneously rearrange to form the *o*-trihalogenostannylbenzylideneamines **181**. The NMR signals due to aryl protons in the ¹H spectra show the changes appropriate for orthometalation, while the five-coordinated state of the tin atoms of **181** is indicated by the quadrupole splittings, ΔE , of their Mössbauer spectra. The structure of **181** has been determined from X-ray data. The coordination about tin is distorted trigonal bipyramidal, with the nitrogen atom and one chlorine atom in the axial position.

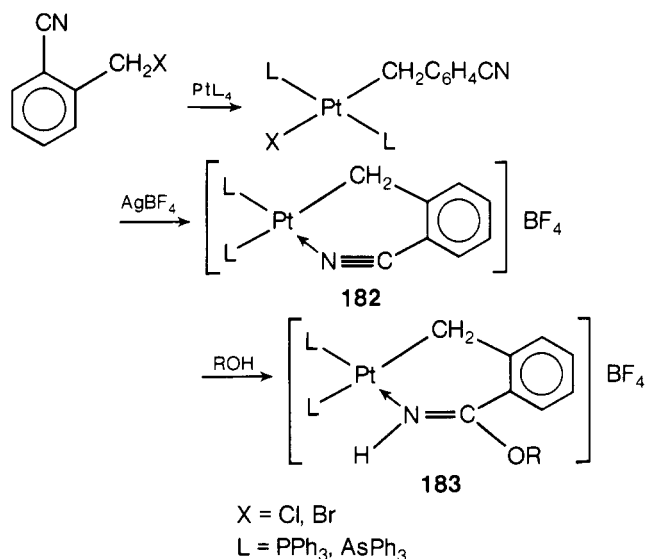


quadrupole splitting

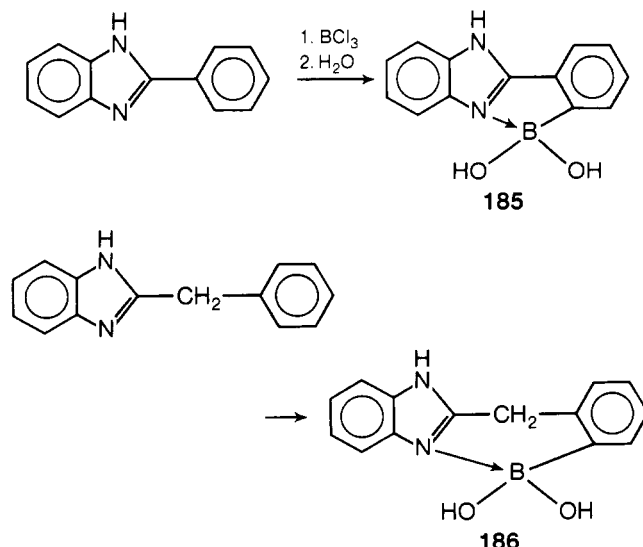
R	X	$\Delta E/\text{mm s}^{-1}$
Me	Cl	1.588
H	Cl	1.730
Cl	Cl	1.440
H	Br	1.486



The complexes¹⁴⁵ having the six-membered ring structure in the benzylideneamine group also have been obtained. Abstraction of X in *trans*-PtX(CH₂C₆H₄CN)₂ (X = Cl, Br; L = PPh₃, AsPh₃) gives a cis cationic complex in which the CN group is coordinated and is prone to nucleophilic attack by alcohols to give stable cis imino ether complexes **183** having the six-membered ring structure. The nucleophilic addition of amines¹⁴⁶ (ArNH₂, ArRNH, RR'NH), in place of the alcohol to the σ -coordinated CN group of **182**, yield stable amide complexes **184** quantitatively similar to **183**. The formation of an amidine complex is clearly seen in the infrared spectrum by its $\nu(\text{NH})$ band around 3300 cm⁻¹ and two new bands in the $\nu(\text{C}=\text{N})$ region around 1600 cm⁻¹ while the $\nu(\text{C}\equiv\text{N})$ around 2260 cm⁻¹ disappears.



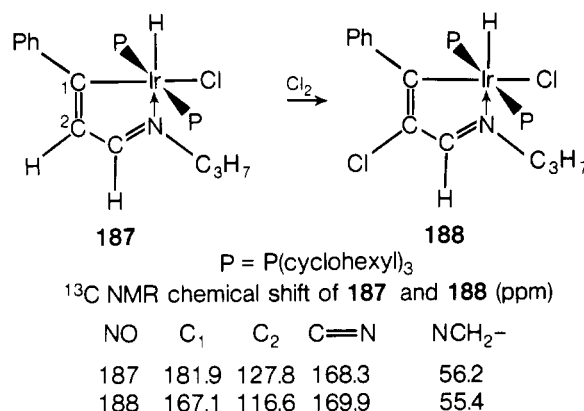
2-(2-Boronophenyl)benzimidazole (**185**)¹⁴⁷ and 2-(2-boronobenzyl)benzimidazole (**186**) are prepared by passing boron trichloride into melts of 2-phenylbenzimidazole and 2-benzylbenzimidazole and subsequently hydrolyzing the products. These compounds serve as catalysts in the formation of ethers from chloroethanol containing collidine. They are much more effective



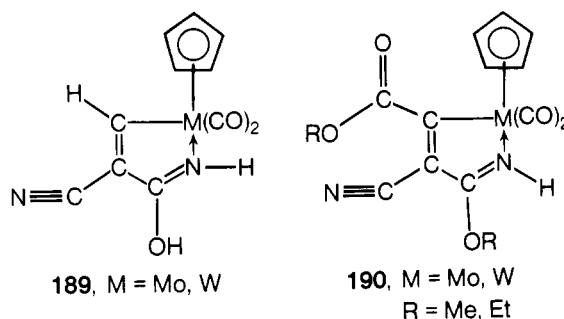
in this regard than benzenboronic acid, 2-phenylbenzimidazole, or a mixture of these two substances. Letsinger and MacLean¹⁴⁷ proposed that the borono group in **185** and **186** binds the alcoholic substrates and holds them in a position favorable for reaction, while the nitrogen participates by increasing the nucleophilicity of oxygen joined to boron.

F. Imines

The olefinic imines can easily afford the complexes having the five-membered ring structure. The reaction¹²⁷ of olefinic imines with [IrCl(C₆H₁₄)₂]₂ in the presence of cyclohexylphosphine gives cyclometalated complexes **187** similar to **166**. Treatment¹²⁹ of **187** with Cl₂ yields substitution product **188** without rupture of the Ir-C bond. Their ¹³C NMR data are also similar to the benzylideneamine complexes **166**.

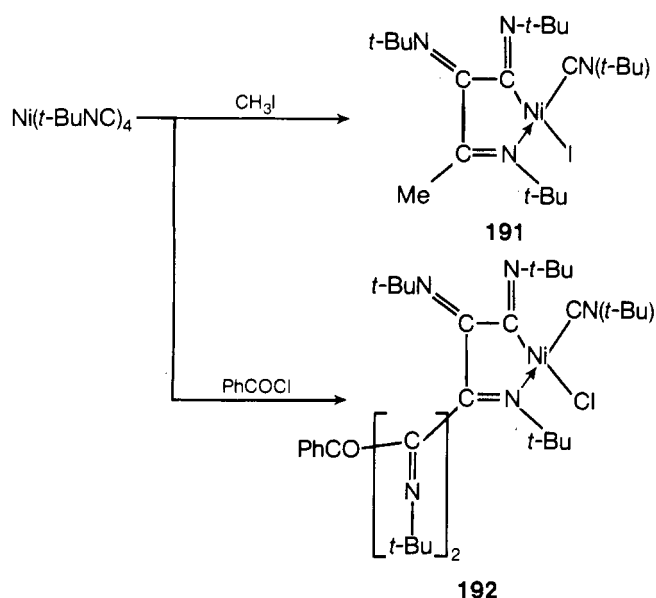


The hydrolysis¹⁴⁸ of (NC)₂C=C(CN)M(CO)₃(η -C₅H₅) (M = Mo, W) and the alcoholysis of (NC)₂C=C(CI)M(CO)₃(η -C₅H₅) (M = Mo, W) afford **189** and **190** having a cyclopentadiene.



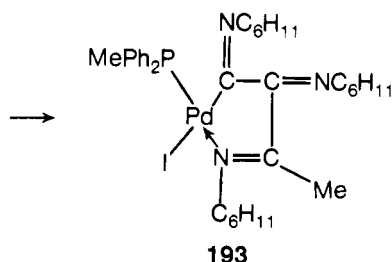
Ni,¹⁴⁹ Pd,^{150,151} and Fe^{152,153} complexes having the five- or four-membered ring structure have been prepared by the isocyanate insertion reaction. When Ni(*t*-BuNC)₄^{149,154} is treated with CH₃I, successive insertion of three isocyanide molecules takes place, affording a new σ -aminoacyl complex **191** in high yield. Chelate coordination through the lone pair electrons of the terminal imino nitrogen atom was deduced from the monomeric nature and enhanced stability of **191**.¹⁴⁹ In the same reaction of PhCOCl with Ni(*t*-BuNC)₄, a red crystalline complex **192** was also found in low yield. When an excess of *t*-butyl or other isocyanide was heated at 30–60 °C in the presence of **191**, the isocyanate was converted into polyisocyanide with a repeating unit. The above successive insertion reactions are considered to suggest a mechanism for the catalytic polymerization of isocyanides.

Yamamoto and Yamazaki^{150–153} have also reported the similar insertion reaction of other transition metal complexes. Reaction^{150,151} of *trans*-Pd[PPh₂Me]₂Me with cyclohexyl isocyanide gives the complex **193** which is postulated to possess the five-membered ring chelate structure coordinated through



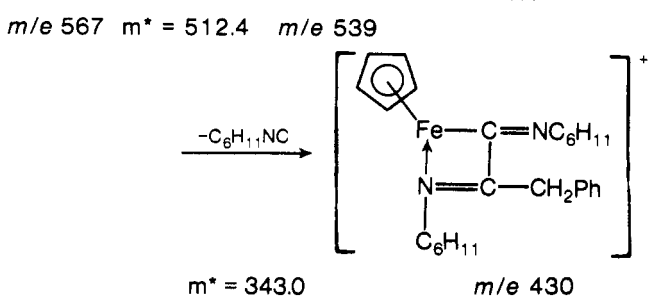
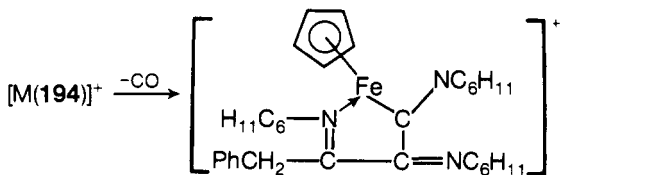
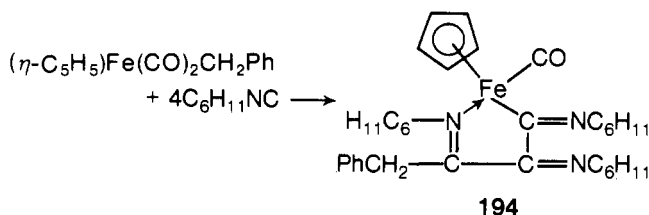
the lone-pair electron of the terminal imino nitrogen atom.

$\text{trans-Pd}[\text{PPh}_2\text{Me}]_2\text{I} + 3\text{C}_6\text{H}_{11}\text{NC}$

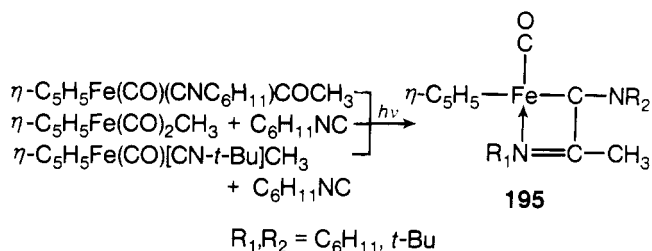


The reaction¹⁵² of benzyliron complexes with *tert*-butyl isocyanide also gives the complexes **194** having the chelate ring analogous to **193** by triple insertion reaction of isocyanide. The mass spectrum of **194** exhibits metastable ions to permit elucidation of part of the fragmentation scheme. It might be depicted as in Scheme VI. However, the photochemical reaction¹⁵³ of

SCHEME VI. Fragmentation of **194**

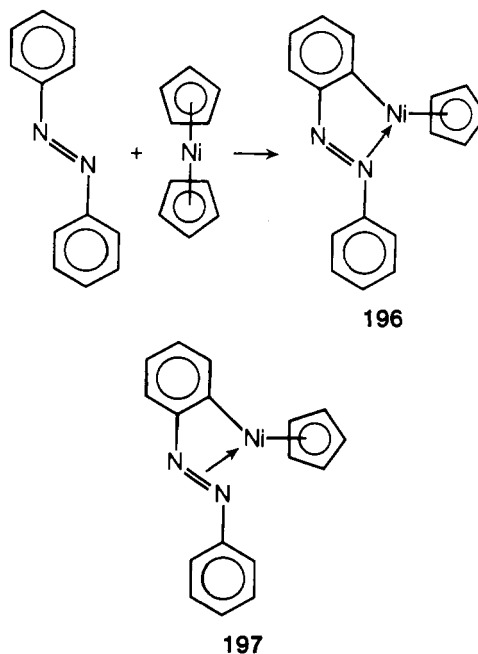


$\pi\text{-C}_6\text{H}_5\text{Fe}(\text{CO})(\text{CNC}_6\text{H}_{11})\text{COCH}_3$ gives the heterocyclic complexes **195** having the four-membered ring. The complex is also obtained by the photo-induced reaction of $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ with $\text{C}_6\text{H}_{11}\text{NC}$ or $\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})[\text{CN-}t\text{-Bu}]\text{CH}_3$ with $\text{C}_6\text{H}_{11}\text{NC}$.

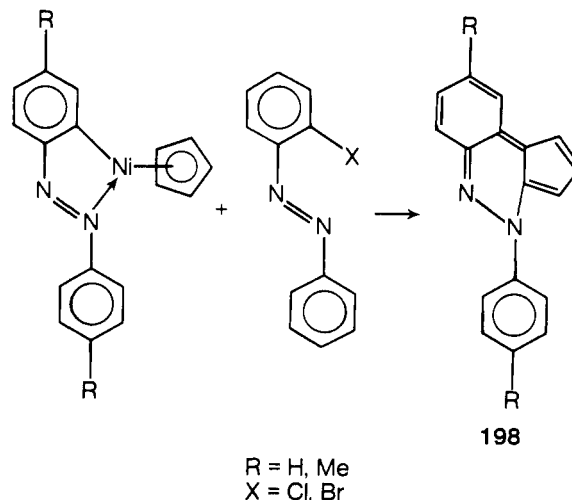


G. Azobenzenes

In 1963, Kleiman and Dubeck¹⁵⁵ reported that bis(cyclopentadienyl)nickel reacted with azobenzene to produce $\eta\text{-cyclopentadienyl-2-(phenylazo-}C^2, N')$ nickel (**196**). They originally assumed a structure of **197** in which the nickel atom was coordinated by the N,N π -electron such as $\text{Ni}(\pi\text{-PhN}=\text{NPh})(\text{CN-}t\text{-Bu})_2$,¹⁵⁶ not by the nitrogen lone pair. However, the

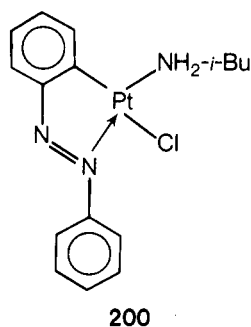
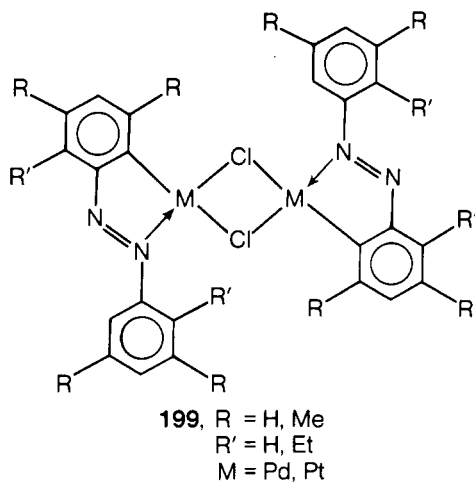


structures of the similar azobenzene complexes have been shown by X-ray diffraction studies¹⁵⁷⁻¹⁶² to have the coordination of the nitrogen lone pair. The complex **196** or its dimethyl derivative¹⁶³ reacts with the ortho-halogenated azobenzene to give

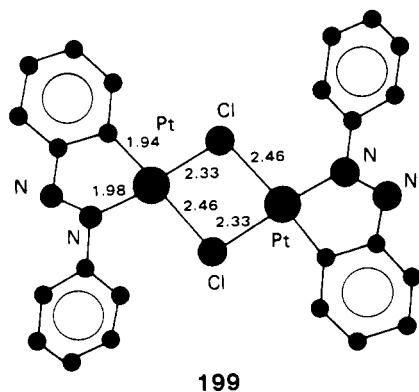


the pseudoazulene, i.e., 4-phenyl-4*H*-cyclopenta[*c*]cinnoline (**198**). 2-[(Arylazo)aryl]mercury derivatives,¹⁶⁴ obtained from the reaction of azobenzene-2-sulfonates and mercuric chloride, also afford a diazonickel complex **196** in high yield by the reaction with nickelocene.

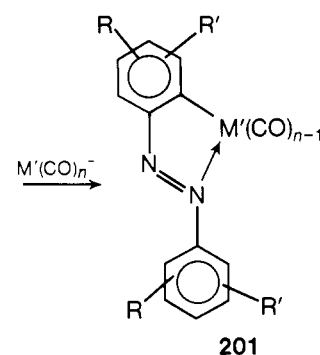
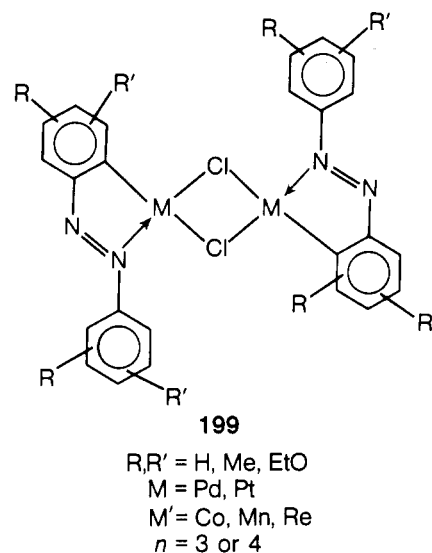
In 1965, Cope and Siekman¹⁶⁵ reported that chloro-bridged complexes of this group can be prepared by the reaction of aromatic azo compounds with potassium tetrachloroplatinate(II) or palladium(II) dichloride **199**. These complexes did not liberate azobenzene upon treatment with an excess of potassium cyanide, triphenylphosphine, or amines. Rather, new complexes, which are the cleavage products of the chloro-bridged compound **199**, e.g., **200**, were formed. The reaction of palladium(II) dichloride with azobenzene and its derivatives was found to be faster than that of the platinum salts.



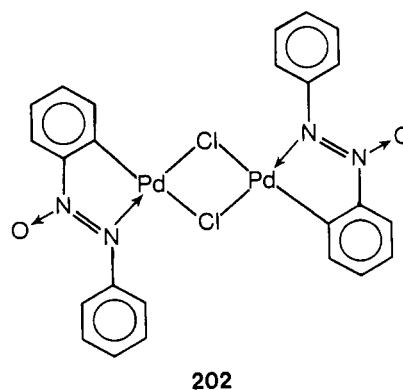
The crystal structure of the *trans*- μ -dichloro-bis(phenylazophenyl-*C*²,*N*)diplatinum(II), **199** (M = Pt) has been determined by X-ray diffraction techniques.¹⁵⁹ Each platinum atom is coordinated to the two bridging chloride ions, an ortho carbon atom of a phenyl ring, and the distant azo nitrogen atom such that the azobenzene ligand forms the five-membered chelate. The entire molecule is planar with the exception of the free phenyl rings which are twisted 39° about the C–N bond away from the bridging chloride ions.



In 1970, Fahey¹⁶⁶ reported the first example of a homogeneous coordination-catalyzed chlorination reaction, namely, that of azobenzene in the presence of PdCl₂. Upon increasing the PdCl₂ concentration and with an extended reaction time, 2,6,2',6'-tetrachloroazobenzene was obtained as the major product. He assumed that the reaction proceeds via **199** as an intermediate from the characteristic color of the chloro-bridged dimer¹⁶⁴; indeed, he isolated **199** from the reaction mixture during early stages of the reaction. At a later stage of the reaction, the chlorinated compounds of **199** at the ortho position or the palladium metal were isolated. These azobenzene complexes also show the cleavage of their chloro-bridged bond with ligand groups such as phosphine compounds,^{164–169} acetylacetonone,^{51,170} amine,¹⁶⁵ and pyrazole.⁵⁴ The ligand-exchange reaction¹⁶⁵ of the metal carbonyl anions with the chloro-bridged palladium dimers **199** yielded derivatives **201** of cobalt, manganese, and rhenium. The manganese complex **201** has also been obtained¹⁶⁴ in high yield by the reaction of [2-(phenylazo)phenyl]mercuric halide with Mn(CO)₅Cl.



The analogous chloro-bridged palladium compound¹⁷¹ **202** has been obtained by the reaction of azoxybenzene with

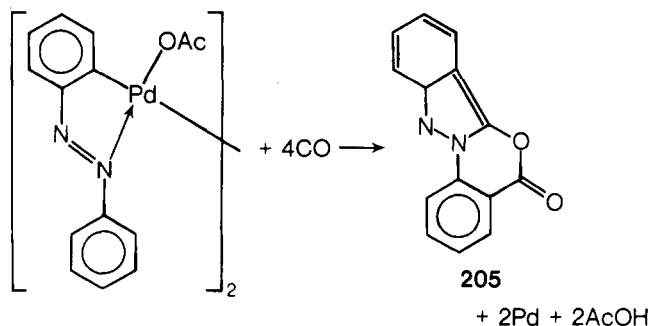
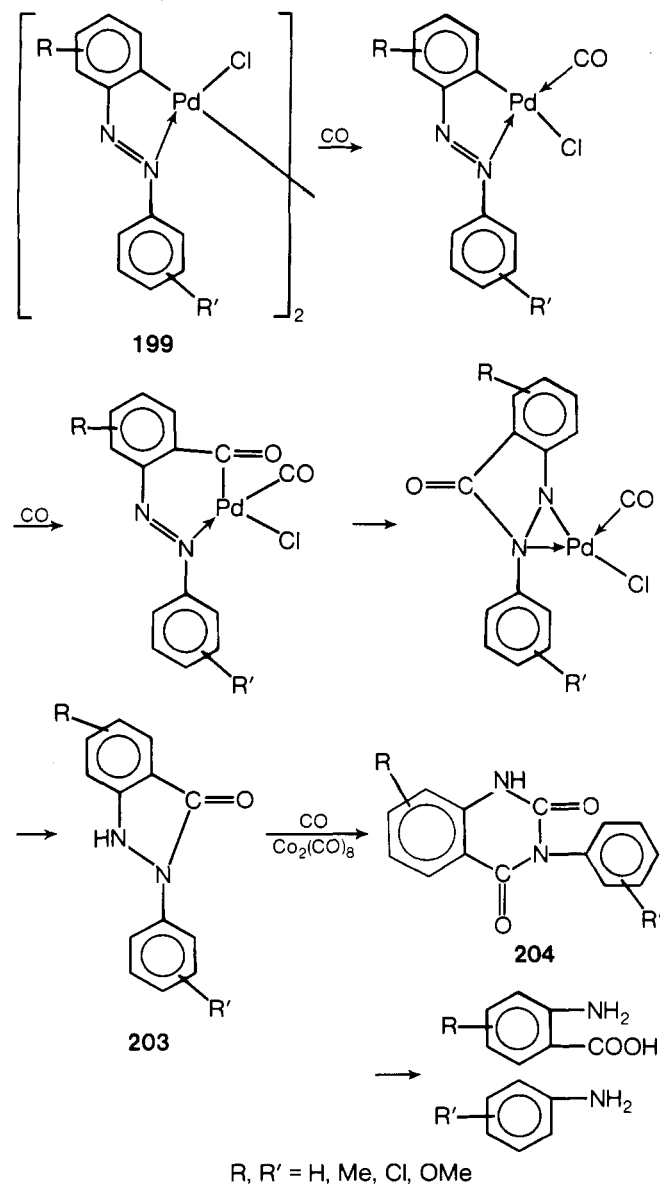


PdCl_4^{2-} , and this complex is cleaved without loss of the organic ligand by Lewis base such as triphenylphosphine and *n*-propylamines to give monopalladium complexes similar to **200**.

The azobenzene chloro-bridged complexes **199** were treated with carbon monoxide at a low pressure and room temperature, and 2-phenyl-1*H*-indazolone (**203**) was formed in a low yield.¹⁷⁰ However, a much better yield was obtained at a high temperature and pressure.¹⁷² It is known that **203** can be carbonylated further to give substituted quinazoline **204** by the catalytic action of cobalt carbonyl.^{173,174} The hydrolysis of the quinazolinone affords aniline and anthranilic acid derivatives. The 2-phenyl-1*H*-indazole also has been obtained directly by the reaction^{174,175} of azobenzene with carbon monoxide in the presence of $\text{Co}_2(\text{CO})_8$ (Scheme VII). The acetate-bridged complex,⁶⁸ which was obtained by the reaction of azobenzene with palladium acetate, was made to react with carbon monoxide to afford the lactone **205** in place of ketone **203**. On the other hand, the carbonylation of tricarbonyl-2-(phenylazo)phenylcobalt (**201**) in an alcohol solution produces 2-carbomethoxyhydrazonobenzene **206**, which is formed by the following mechanism presumed by Heck¹⁷⁰ (Scheme VIII).

The metal carbonyl complexes **201** also have been obtained by the direct reaction of azobenzene and manganese or rhenium carbonyls as first reported by Heck.¹⁷⁰ Analogous complexes

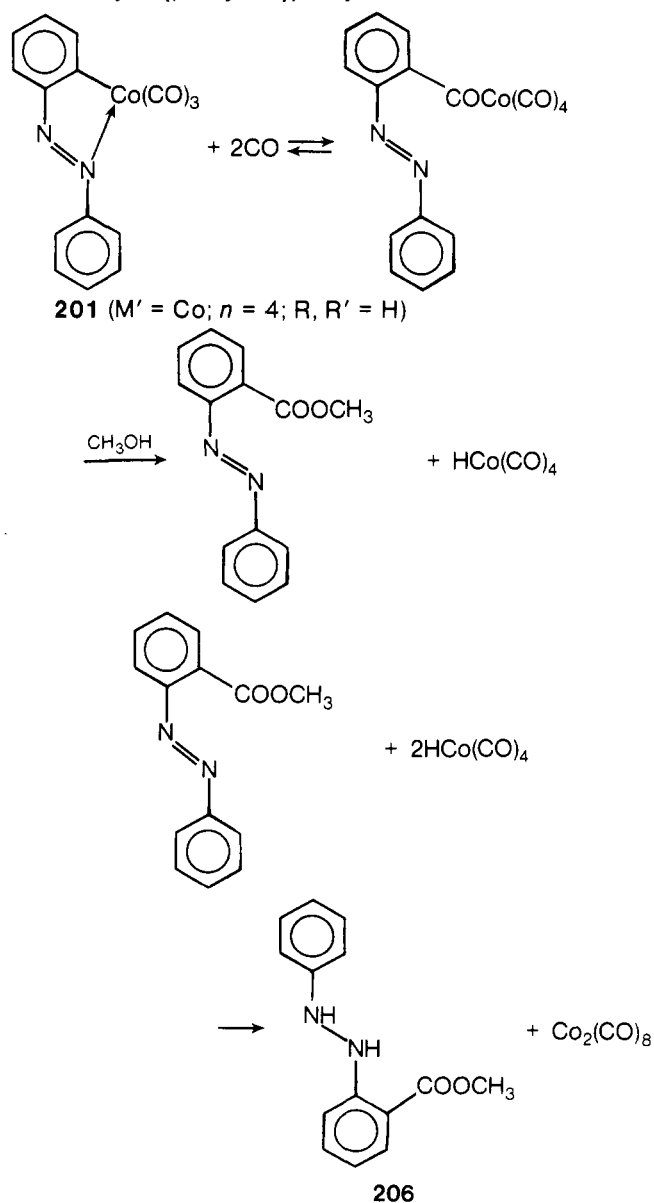
SCHEME VII. Carbonylation of Azobenzene-Palladium Chloride Complex **199**

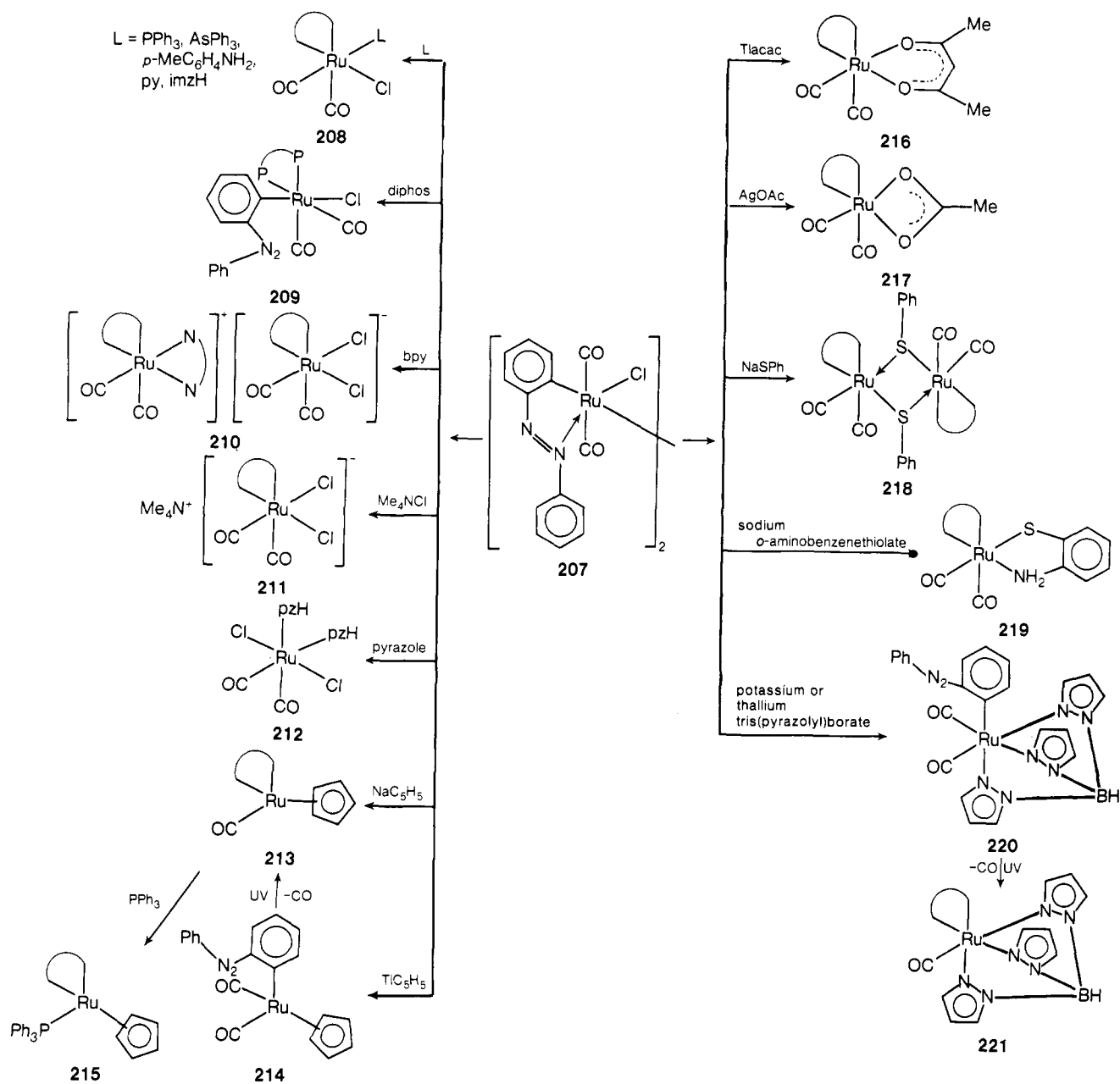


were obtained from $[\text{Mn}(\text{CO})_4\text{PPh}_3]_2$, $[(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Fe, Ru}$), and $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ by Bruce and co-workers.¹⁷⁶⁻¹⁷⁸ Much higher and nearly quantitatively yields of the manganese and rhenium complexes were obtained by the thermal reaction of the methyl compounds, $\text{MeM}(\text{CO})_5$ ($\text{M} = \text{Mn, Re}$) with azobenzene. The proton NMR spectra of these complexes are shown in Table V.^{176,178} The signal due to the proton on the carbon atom which is ortho to the carbon-metal σ bond occurs at the lowest field.

Bruce and co-workers^{177,178} have reported many ruthenium complexes, **208-221**, containing phenylazophenyl group from

SCHEME VIII. The Carbonylation Mechanism of Tricarbonyl-2-(phenylazo)phenylcobalt in Methanol





the chlorobridged dimer **207**. Monodentate ligands, L, cleave the halogen bridge to give monomeric complexes, $(\text{azb})\text{LRu}(\text{CO})_2\text{Cl}$ (**208**). The bidentate ligand, 2,2'-bipyridyl (bpy), gives the ionic complex, $[(\text{azb})\text{Ru}(\text{CO})_2(\text{bpy})][(\text{azb})\text{Ru}(\text{CO})_2\text{Cl}_2]$ (**210**). Cyclopentadienide and tris(pyrazolyl)borate anions react initially to give complexes containing phenylazophenyl- C^2 group (**214**, **220**); strong heating or irradiation converts them into chelating phenylazophenyl- C^2, N' complexes, **213**, **221** with loss of carbon monoxide. Other anionic chelates, e.g., acetylacetonate or *o*-aminobenzenethiolate, give monomeric $(\text{azb})\text{Ru}(\text{CO})_2$ (chelate)

TABLE V. ^1H NMR Chemical Shift (ppm) in CS_2 ¹⁷⁸

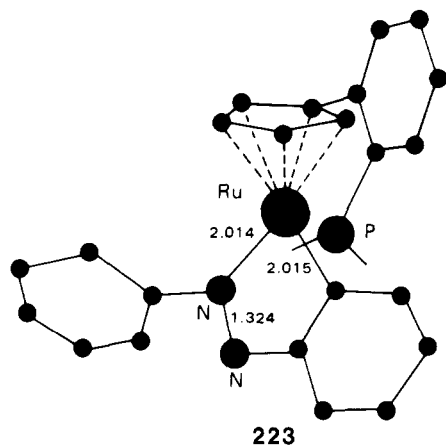
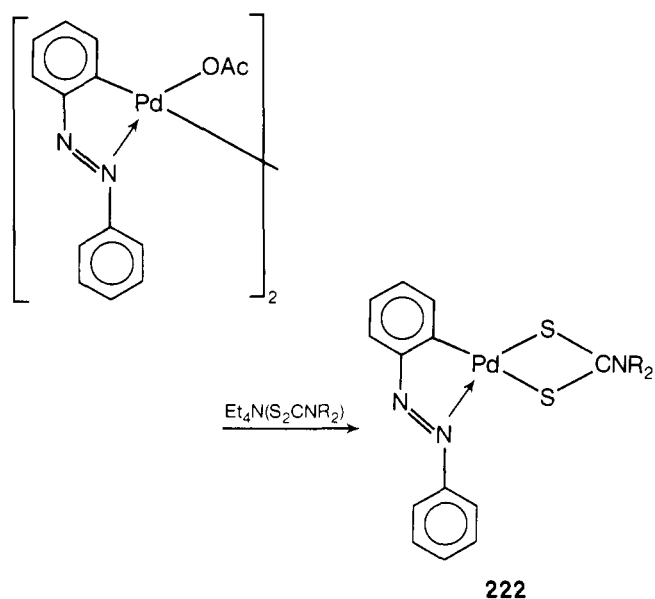
M	$\eta\text{-C}_5\text{H}_5$	^1H
		8.18
		8.15
		7.83
	4.40	8.08
	5.27	8.01
	5.15	8.35
	4.12	
	4.85	8.08

complexes, **216** and **219**, whereas, benzenethiolate gives a dimeric compound $[(\text{azb})\text{Ru}(\text{CO})_2(\text{SPh})]_2$, **218**, containing an SPh bridging group.

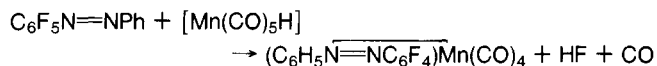
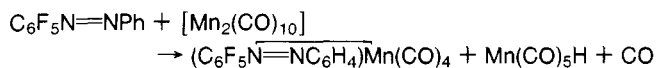
The sulfur bridged compound,¹⁷⁹ **222**, has been obtained by the reaction of acetyl-bridged azobenzene with $\text{Et}_4\text{N}(\text{S}_2\text{SNR}_2)$. Treatment of **222** with bromine gave 2-bromoazobenzene by removal of the metal.

The η -cyclopentadienylphenylazophenyl- C^2, N' -(triphenylphosphine)ruthenium **215** also has been prepared by the reaction¹⁸⁰ of azobenzene and $(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Me}$ with loss of methane. The ruthenium compound of $\text{RuMe}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$, which is very prone to form metalated complexes,¹⁸⁰ reacts with decafluoroazobenzene¹⁶¹ to afford $\text{RuC}_6\text{F}_4\text{N}=\text{NC}_6\text{F}_5\text{-}(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}\eta\text{-C}_5\text{H}_5)$ (**223**). The ^1H NMR spectrum contains four multiplets at 5.78, 5.56, 5.42, and 4.91 ppm, all of equal intensity, but not so sharp a singlet as expected for the $\eta\text{-C}_5\text{H}_5$ group. The structure, established by a single-crystal X-ray diffraction study, shows that the substitution of both a C_6F_5 and an $\eta\text{-C}_5\text{H}_5$ ring has occurred.

The reaction¹⁸¹ between $\text{Mn}(\text{CO})_5\text{Me}$ with 2,3,4,5,6-pentafluoroazobenzene proceeded readily to give the expected complex $\text{C}_6\text{F}_5\text{N}=\text{NC}_6\text{H}_4\text{Mn}(\text{CO})_4$; however, $[\text{Mn}_2(\text{CO})_{10}]$ af-



formed two complexes,¹⁸² albeit in low yields, one of which was above product. In the latter reaction, metalation by abstraction of fluorine occurs, in addition to the usual metalation reaction found with azobenzene. The fluorine atom is presumed to be eliminated as HF, or as some manganese fluorine species, a possible reaction course is as follows:



The usual orthometalation of azobenzene with decacarbonyldimanganese proceeds with the elimination of $[\text{Mn}(\text{CO})_5\text{H}]$ as shown in the first reaction, which takes no further part in the reaction. This may also provide an explanation for the consistently low yields of metalated product obtained in this reaction.¹⁷⁶

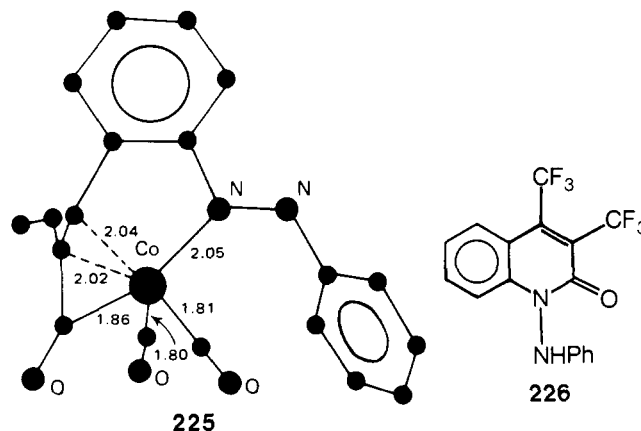
It is generally accepted that palladation^{2,172} of azobenzene and related ligands occurs by electrophilic attack on the aromatic ring at the ortho position by the metal to form chelate complexes containing metal-carbon σ -bonds. Bruce and co-workers¹²⁸ first reported the electrophilic and nucleophilic reaction mechanism concerning the orthometalation of azobenzene by the reaction of meta-substituted azobenzene (A, B, C) and metal complexes (see Table VI). The results are consistent with the accepted electrophilic mechanism for palladation, in that 80% of the resulting mixture was metalated in the nonfluorinated ring (A). Further, where palladation has occurred in the substituted ring (B), reaction occurs para to fluorine, i.e., the position most fa-

TABLE VI. Isomers Formed in Metalation Reaction of $\text{FC}_6\text{H}_5\text{N}=\text{NPh}$

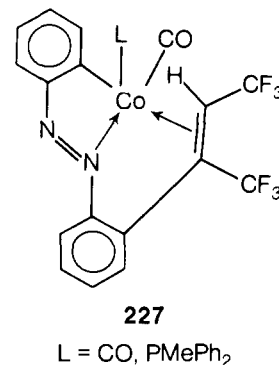
	NO	R ¹	R ²	R ³	M	yield, %
A		F	H	H	Pd(η -C ₅ H ₅)	80
		F	H	H	Mn(CO) ₄	20
B		H	F	H	Pd(η -C ₅ H ₅)	20
		H	F	H	Mn(CO) ₄	—
C		H	H	F	Pd(η -C ₅ H ₅)	<1
		H	H	F	Mn(CO) ₄	80

vored for electrophilic attack. Using $\text{MeMn}(\text{CO})_5$, the major isomer obtained (C) is that which is substituted ortho to fluorine, a result consistent with nucleophilic attack on a carbon atom powerfully activated by the inductive effect of fluorine. It should be presumed that this nucleophilic attack of the manganese atom to the benzene ring is also activated by the electron-donating methyl group.

The reaction^{160,183} between the azobenzene-cobalt carbonyl complex with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ affords a mixture of an organocobalt derivatives **225** (60%) and an quinoline compound **226** (30%). The crystal structure of the cobalt compound **225** shows that the molecule is formed by insertion of one acetylene and CO molecule into the cobalt-carbon bond of the azobenzene-cobalt

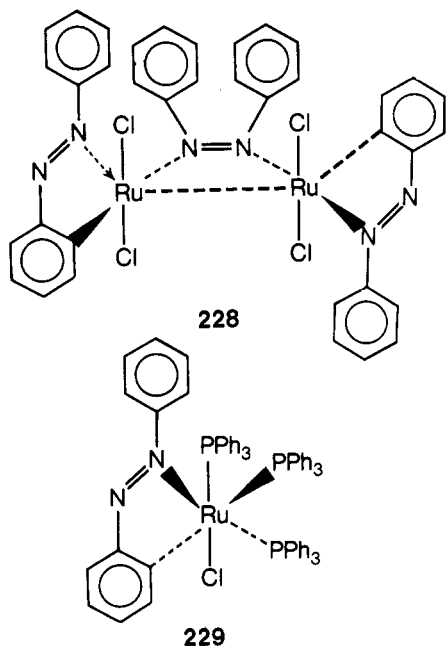


carbonyl complexes. Thermolysis¹⁸³ of **225** affords **227** (L = CO), corresponding to loss of CO from **225**, presumably by cleavage of the strained bond between the phenyl carbon and the olefin carbon. A similar product, **227** (L = PMePh_2), was obtained by addition of PMePh_2 to **225**, the complexes showing only one $\nu(\text{CO})$ band and no acyl $\nu(\text{CO})$ absorption.



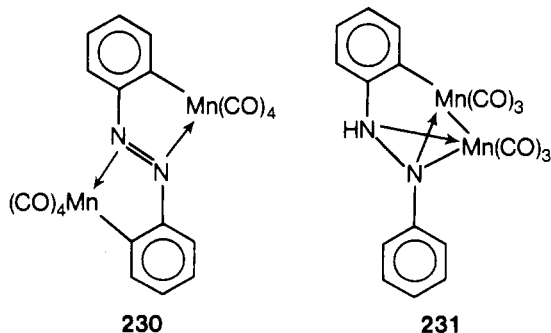
The reaction¹⁸⁴ of azobenzene with $[\text{Ru}_5\text{Cl}_{12}]_2^-$ affords complexes **228** having an unusually low magnetic moment per ruthenium atom, suggesting metal-metal interaction. On heating the complex **228** under reflux with triphenylphosphine in

methanol, bridge cleavage and reduction occur to give the complexes **229**.



Bruce and co-workers¹⁸⁵ have reported some reactions of η -cyclopentadienylruthenium phosphine complexes with azobenzene derivatives: with azobenzene, m - $\text{RC}_6\text{H}_4\text{N}=\text{NPh}$ ($\text{R} = \text{H}, \text{Me}, \text{OMe}, \text{COEt}, \text{or } \text{CF}_3$), the complex $[\text{Ru}(\text{C}_6\text{H}_5)(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ yielded a mixture of isomers $[\text{Ru}(\text{C}_6\text{H}_3\text{YN}=\text{NC}_6\text{H}_4)\text{Z}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ ($\text{Y} = \text{H}, \text{Z} = \text{R}; \text{or } \text{Y} = \text{R}, \text{Z} = \text{H}$). Using m - $\text{RC}_6\text{H}_4\text{N}=\text{NC}_6\text{F}_5$ ($\text{R} = \text{H}, \text{Me}, \text{or } \text{CF}_3$), the complexes $[\text{Ru}(\text{C}_6\text{H}_3\text{N}=\text{NC}_6\text{F}_5)(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ ($\text{R} = \text{H}, 19\%$), $[\text{Ru}(\text{C}_6\text{F}_4\text{N}=\text{NC}_6\text{H}_4\text{R})(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ ($\text{R} = \text{H}, 15.5\%$), and $[\text{Ru}(\text{C}_6\text{F}_4\text{N}=\text{NC}_6\text{H}_3\text{-R-C}_6\text{H}_4\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{H}, 9\%$) were formed, while from $\text{C}_6\text{F}_5\text{N}=\text{NC}_6\text{F}_5$ only $[\text{Ru}(\text{C}_6\text{F}_4\text{N}=\text{NC}_6\text{F}_5)(\eta\text{-C}_5\text{H}_5\text{C}_6\text{H}_4\text{PPh}_3)]$ was isolated.

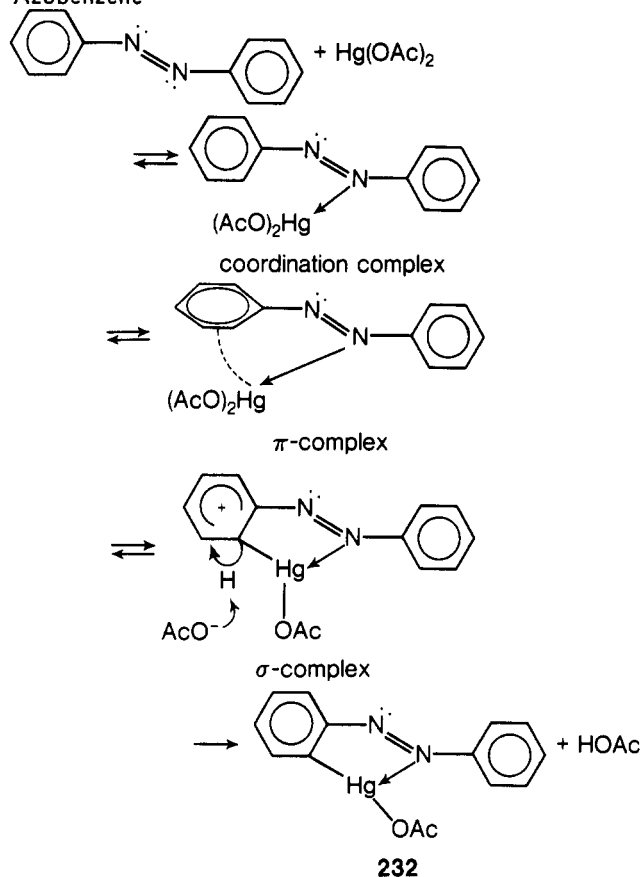
The reaction¹⁸⁶ of azobenzene and $\text{MnF}(\text{CO})_5$ ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{Ph}, \text{CH}_2\text{C}_6\text{Me}_5, \text{COCF}_3, \text{COCH}_2\text{C}_6\text{F}_5, \text{COCH}_2\text{OPh}, \text{Ph}, \text{or } \text{C}_6\text{F}_6$) affords $\text{Mn}(\text{C}_6\text{H}_4\text{N}=\text{NPh})(\text{CO})_4$ (**201**), while internal metalation¹⁸⁷ of **201** with $\text{Mn}(\text{CO})_5\text{Me}$ affords **230**. Interestingly, the analogous reaction of $\text{Mn}(\text{CO})_5\text{Ph}$ gives a different product, **231**.



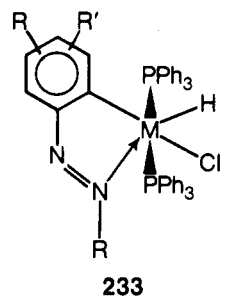
The mercuration¹⁸⁸⁻¹⁹⁰ of azobenzene has occurred exclusively in the ortho position to yield 2-chloromercuriazobenzene (**232**) and a mixture which, on iodination, gave 2,2'- and 2,6-diiodoazobenzenes. The usual orthometalation mechanism presumed from the regioselectivity¹⁸⁸ of these reactions that the mercury is directed into an ortho position by coordination of the mercury to an azo nitrogen and then subsequent electrophilic substitution as shown in the Scheme IX.

The iridium and rhodium complexes^{120,127,191} **233** similar to ruthenium **229** have been prepared by the reaction of azobenzene or its derivatives with $[\text{MCl}(\text{C}_6\text{H}_{14})_2]$ ($\text{M} = \text{Ir}, \text{Rh}$) in the

SCHEME IX Regiospecific Mercuration Reaction of Azobenzene

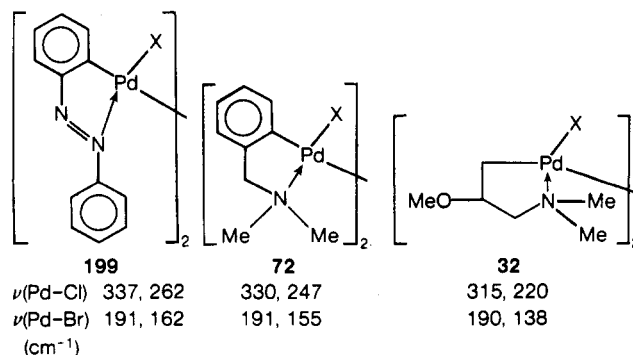


presence of PR_3 ($\text{R} = \text{Ph}$ or cyclohexyl) according to Scheme V.

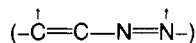


233
 $\text{R}' = \text{H}, \text{Me}$
 $\text{R} = \text{Ph}, \text{Me}, \text{tolyl}, \text{xylyl}$
 $\text{M} = \text{Ir}, \text{Rh}$

Crociani and co-workers⁸⁸ reported the trans influence of halo-bridged complexes of the azobenzene (**199**), benzylamine (**72**), and alkylamine complex (**32**). On the basis of the greater trans influence of a σ -bonded carbon compared with that of a nitrogen atom, the higher frequency band was attributed to the



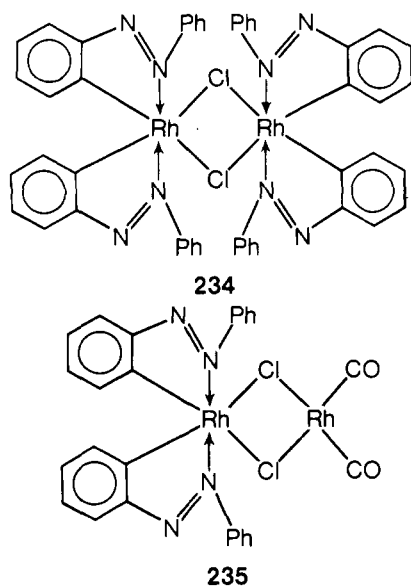
stretching vibration $\nu(\text{Pd-X})$ trans to the nitrogen atom, and the lower frequency one to the $\nu(\text{Pd-X})$ trans to the σ -bonded carbon. The $\nu(\text{Pd-X})$ bridging bands are shifted toward lower wavenumbers in the order **199** > **72** > **32** with the exception of the higher frequency $\nu(\text{Pd-Br})$ which remains almost constant. This is accounted for in the azobenzene derivatives in terms of the formation of the five-membered aromatic ring involving the two conjugated double bond of the system



and the filled palladium d orbitals of appropriate symmetry.^{192,193} For the other complexes, such a possibility is ruled out. As a consequence, the trans influence of either of the σ -bonded carbon or the coordinated nitrogen (which becomes more basic) increases. Moreover, it should be noted that an aliphatic carbon has generally a higher trans influence than the aromatic carbon.

Rhodium chloro-bridged dimer $[(\text{Azb})_2\text{RhCl}]_2$ (**234**) has been prepared by the reaction of hydrated rhodium(III) chloride with azobenzene.^{51,194,195} This rhodium complex reacts with donor ligands to give $(\text{Azb})_2\text{RhCl(L)}$ ($\text{L} = \text{PPh}_3, \text{THF}$). With $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, azobenzene affords the $\text{Rh}^{\text{I}}\text{-Rh}^{\text{III}}$ complexes $[(\text{Azb})_2(\text{RhCl}_2\text{Rh}(\text{CO})_2)]$ (**235**), which also can be obtained from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $[(\text{Azb})_2\text{RhCl}]_2$.

Bruce and co-workers¹⁹⁵ also presumed for the formation of **234** and **235** by the following conventional electrophilic sub-

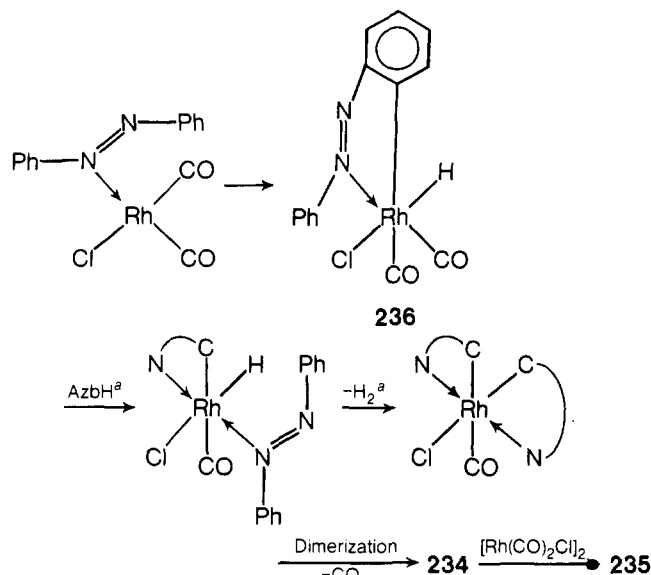


stitution mechanism: the formation probably occurs via an electrophilic attack by a coordinated rhodium atom on an ortho carbon atom, with elimination of HCl , following an initial reaction in which the nitrogen is attached to the metal. The reaction is analogous to the well-known orthometalation of azobenzene and related ligands by palladium chloride.^{51,165} In the case of the complex **235**, it is likely that the first step is coordination of azobenzene to the rhodium atom, followed by an oxidative-addition reaction, which results in the formation of intermediate **236**. Subsequent reaction with a second molecule of azobenzene, via an orthometalation reaction with elimination of hydrogen, and coordination, giving **234**, can then be followed by combination with excess $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to afford complex **235** (Scheme X).

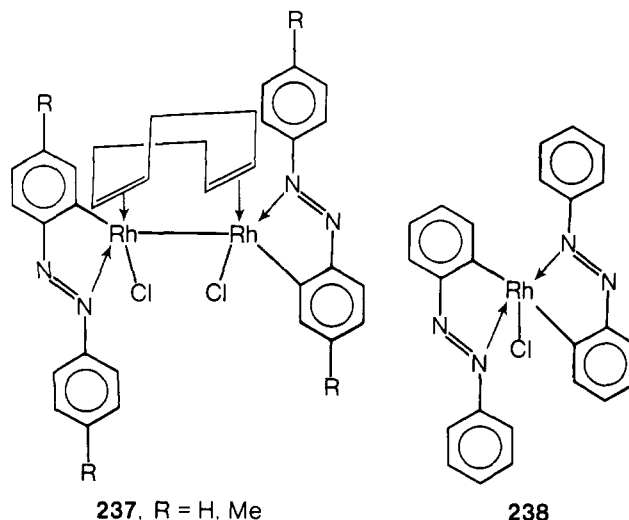
The reaction¹⁹⁶ of azobenzene with $[\text{RhCl}(1,5\text{-cyclooctadiene})_2]$ affords not a bridging complex but one having the Rh-Rh bond, **237**. However, the reaction of the azobenzene with $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ in EtOH affords rhodium bisazobenzene complex **238**.

The treatment¹⁵⁷ of the chloro-bridged dimeric compound

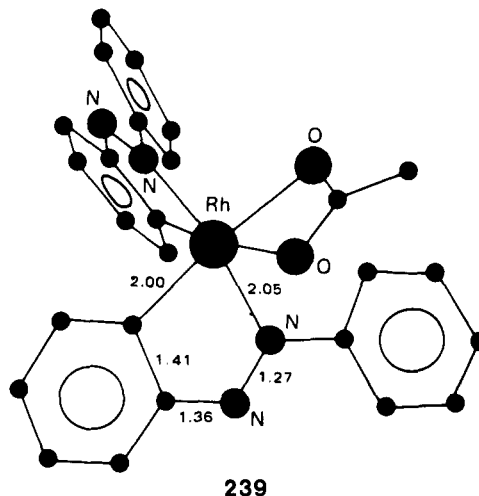
SCHEME X. Formation of Chloro-Bridged Rhodium Complexes **234** and **235**



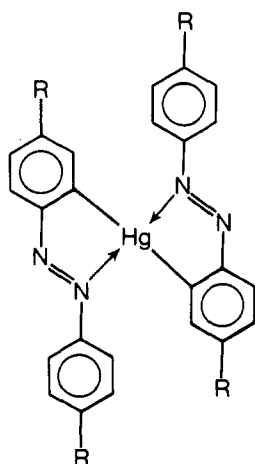
^a These two steps may occur in reverse order.



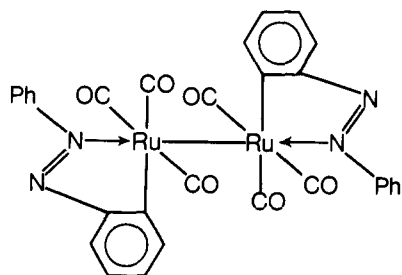
$(\text{Abz})_2\text{RhCl}_2\text{Rh}(\text{Abz})\text{Cl}$ with sodium acetate, affords the well-crystallized dark-red complex **239**. The structure of the mononuclear bis(azoarene)rhodium acetate has been established by X-ray crystallography. The two Rh-C bonds are cis and the two Rh-N bonds are trans to one another. The chelating acetato group completes the octahedral coordination polygon of the rhodium and lies on an idealized molecular twofold axis.



Bisazobenzene-metal complexes¹⁹⁷ **240**, with a "spirane" metal atom, have been prepared in high yield by treating bis(2-aryldiazo)arylmercury with the dibenzylideneacetone complex of zerovalent palladium, $\text{Pd}_2(\text{DBA})_3\text{-C}_6\text{H}_6$.¹⁸⁴ In refluxing petroleum ether the reaction¹⁹⁸ between $\text{Ru}_3(\text{CO})_{12}$ and azobenzene also affords a dimeric complex, **241**, having a metal-metal bond analogous to **237**.

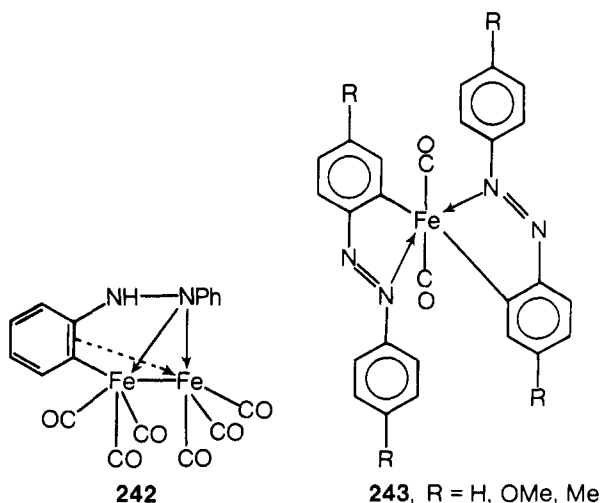


240, R = H, Me



241

The irradiation^{74,199} of azobenzene or its derivatives with iron pentacarbonyl affords dimetal monomer complexes, **242**, and a small amount of iron-bisazobenzene complex, **243**. The latter complex **243** is also obtained by the treatment of the chlorobridged palladium complex **199** with metal carbonylates.

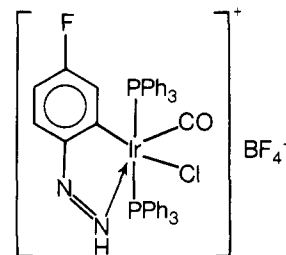


242

243, R = H, OMe, Me

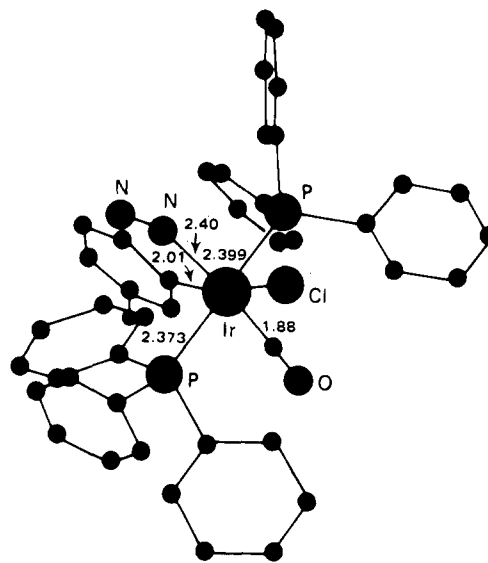
H. Phenyldiimides

It has been found that the reaction^{158,200} of *p*-fluorobenzenediazonium tetrafluoroborate with Vaska's complexes, *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, affords two products: the red, diamagnetic air-stable tetrazone complex^{201,202} and the yellow diamagnetic air-stable complex, **244**, obtained as the acetone



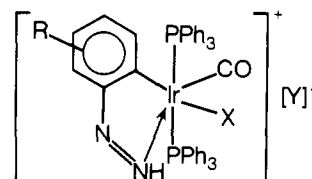
244

solvent. The latter complex has been studied by X-ray diffraction. The complex cation contains an orthometalated aryldiimide moiety, with the acetone of crystallization weakly hydrogen bonded to the hydrogen atom on the coordinated nitrogen atom of the azo function.



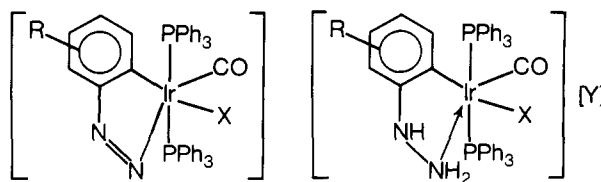
244

A wide range of various substituted aryldiazonium^{203,204} ions react with $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ and its analogs, and in the presence of lithium chloride, benzene-ethanol, or benzene-propanol-2 to yield orthometalated aryldiazene complexes **245**. These may be deprotonated to yield orthometalated aryldiazonato complexes (**246**) and hydrogenated in the presence of a palladium catalyst to give orthometalated arylhydrazine complexes (**247**).



245

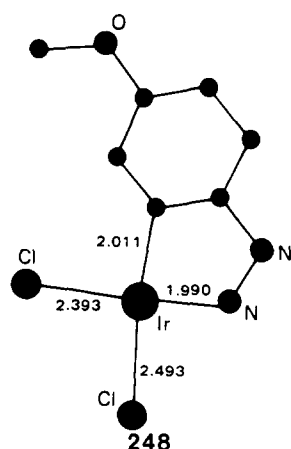
X = F, Cl, Br, I, OCIO_3
R = H, F, Br, Cl, Me, CF_3 , NH_2 , NO_2 , OMe
Y = BF_4 , ClO_4



246

247

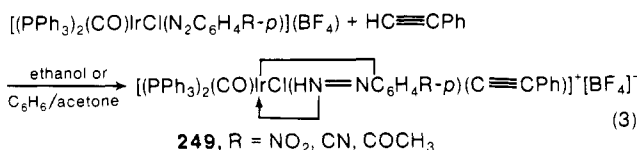
The structure¹⁶² of dichloro(4-methoxyphenyldiimide- C^2, N')-bis(triphenylphosphine)iridium-chloroform (1:1) (**248**), which is one derivative of **244** and **245**, has been determined



by X-ray diffraction study. The metal atom, which displays a distorted octahedral coordination, is bonded to the terminal nitrogen atom.

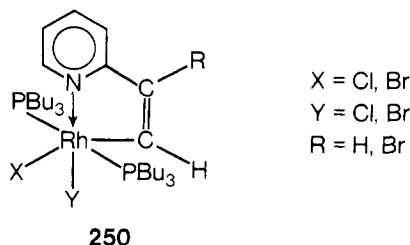
The reaction²⁰⁵ of $\text{IrH}_3(\text{PPh}_3)_3$ with *p*-anisyl diazonium tetrafluoroborate gives an insertion product which very easily undergoes orthometalation, yielding $[\text{IrH}(\text{PPh}_3)_3\text{NHNC}_6\text{H}_3\text{OMe}]^+\text{BF}_4^-$. By reaction with halides, X^- , the metalated fluoroborate gives the neutral $\text{IrHX}(\text{PPh}_3)_2\text{NHNC}_6\text{H}_3\text{OMe}$, which with halogens, X_2 , affords $\text{IrX}_2(\text{PPh}_3)_2\text{NHNC}_6\text{H}_3\text{OMe}$.

Toniolo and co-workers²⁰⁶⁻²⁰⁹ have also reported phenylidimide complexes; for example, the aryldiazene-iridium(III) complex reacts with phenylacetylene to give the aryldiazene-phenylacetylide complex **249**, according to eq. 3. The formation of **249** is considered to occur via the orthometalation reaction of the cationic iridium metal.

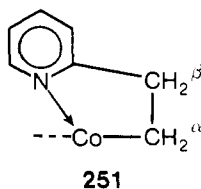


I. Heteroaromatic Compounds

Nitrogen-containing heteroaromatic compounds such as pyridine,^{22,54,210-213} quinoline,^{51,214,215} and benzo[*h*]quinoline^{51,54,215-218} afford complexes having the coordination of the nitrogen to the metal to form the five-membered ring structure. Metalation²¹⁹ of 2-vinylpyridine (vpy) occurs on reaction with $[\text{Rh}_2\text{X}_6(\text{PBu}_3)_4]$ ($\text{X} = \text{Cl}, \text{Br}$) to give $[\text{Rh}[2-(\text{CH}=\text{CH})\text{py}]-\text{X}_2(\text{PBu}_3)_2]$ (**250**), which undergoes an unusual substitution reaction with bromine to give $[\text{Rh}[2(\text{CH}=\text{CBr})\text{py}]\text{Br}_2(\text{PBu}_3)_2]$.

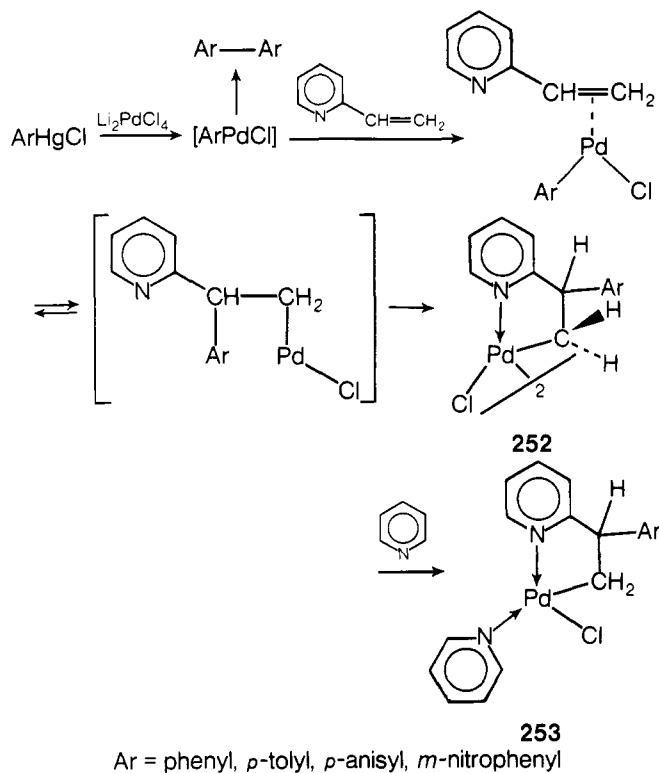


Cobalt carbonyl catalyzed hydroesterification of olefin with carbon monoxide and an alcohol generally proceeds under mild conditions in the presence of pyridine.²²⁰⁻²²⁵ The reaction²¹³ of the hydroesterification catalyst, $\text{H}_2\text{Co}_3\text{Py}_5(\text{CO})_9$,²²⁶ with 2-vinylpyridine yields an alkylcobalt complex **251**, which was considered²¹³ to be an intermediate complex in the hydroest-

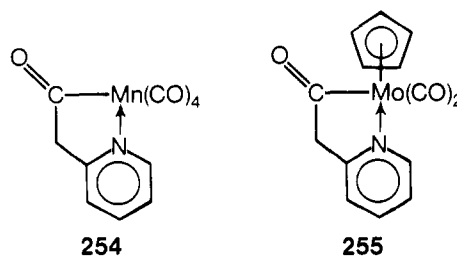


erification of 2-vinylpyridine. The ^{13}C NMR parameters of the α - and β -methylene groups are 60.0 ppm ($J_{\text{C-H}} = 147$ Hz) and 37.4 ppm (132 Hz), respectively.

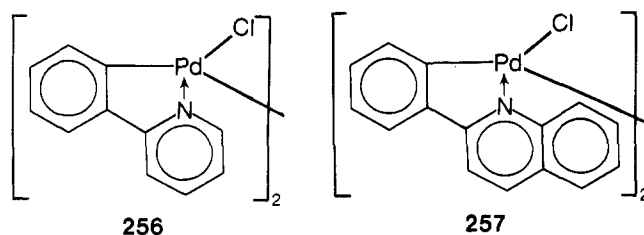
2-Vinylpyridine²¹² also reacts with arylmercuric chloride to afford di- μ -chloro-bis[2-phenyl-2-(α -pyridyl)ethyl- C^1, N]dipalladium (**252**). The chloro-bridge bond of **252** is cleaved by pyridine to afford the complexes **253**.



Reaction²² of 2-chloromethylpyridine with $\text{NaMn}(\text{CO})_5$ or $\text{NaMo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ gives $\text{NC}_5\text{H}_4\text{CH}_2\text{COMn}(\text{CO})_4$ (**254**) or $\text{NC}_5\text{H}_4\text{CH}_2\text{COMo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ (**255**), respectively, with a five-membered ring containing a part of pyridine ring.

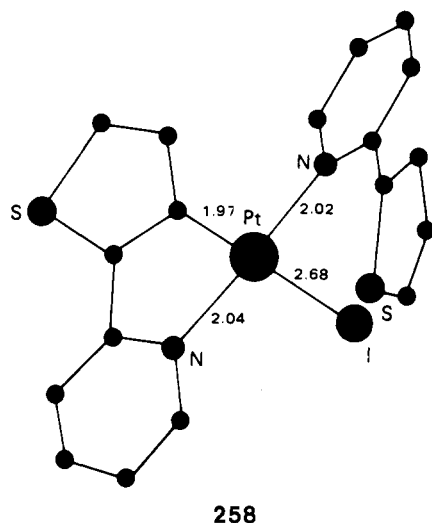


2-Phenylpyridine²¹⁰ or 2-phenylquinoline reacts with palladium dichloride to afford in high yield a chloro-bridged dimer, **256** or **257**, having a five-membered ring structure. This chloro-bridged palladium dimer, **256**, reacts with sodium tetrakis(1-pyrazolyl)-

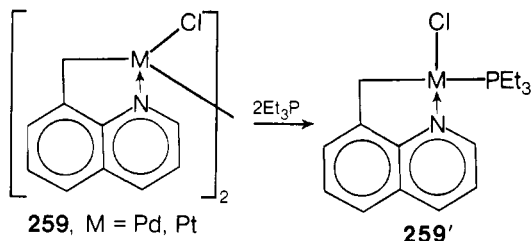


borate to afford pyrazolyl-coordinated palladium complex⁵⁴ similar to compound **77**. The chelate structure of 2-pyridium metal compounds has been determined by the X-ray diffraction study²¹¹ of iodo[2(2'-thienyl)pyridine- C^2, N][2-(2'-thienyl)pyridyl]platinum(II) (**258**). The platinum atom is coordinated by two pyridyl nitrogens trans to one another, a thienyl carbon, an iodine

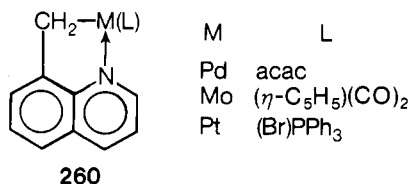
which lies slightly below the plane formed by the platinum, and the other three coordinating atoms. The complex is obtained by the reaction of 2-(2'-thienyl)pyridine with PtCl_4^- .



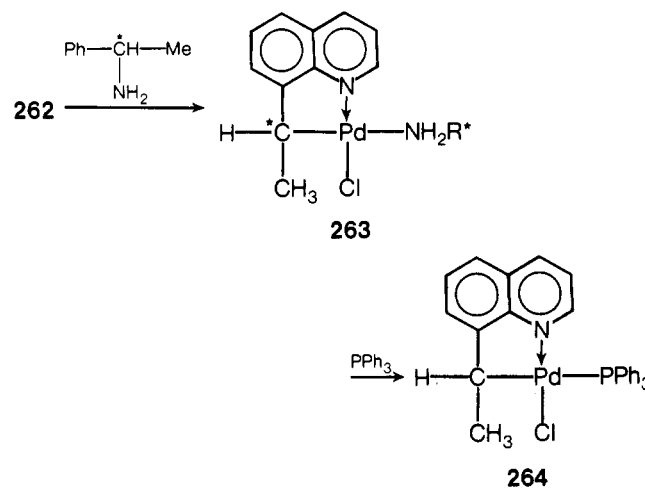
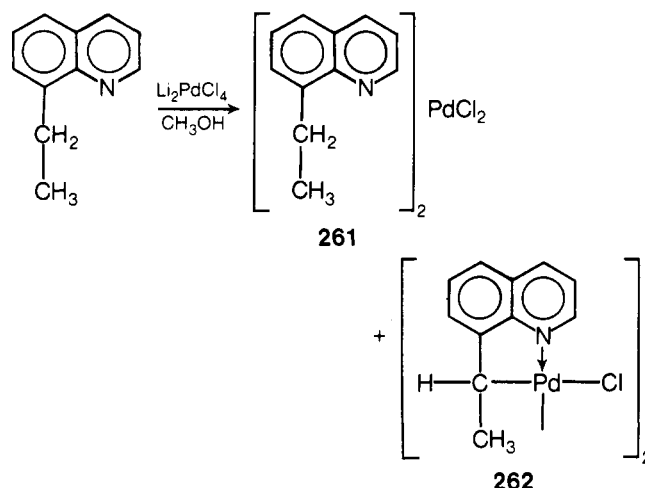
The reaction²¹⁵ of 8-methylquinoline with lithium tetrachloropalladate(II) affords the chloro-bridged dimer **259**, having a five-membered ring. The bridged dimer is easily cleaved by a stoichiometric amount of triethylphosphine in benzene. The NMR spectrum of the 8-methylquinoline complex **259** in CDCl_3 shows the methylene protons, 3.12 ppm, as a doublet, $J_{\text{PH}} = 4$ Hz, in agreement with *trans*-bromobenzylbis(triethylphosphine)palladium(II). However, the proton ortho to the ligand nitrogen is also coupled to phosphorus, $J_{\text{PH}} = 5$ Hz, 9.58 ppm.



The corresponding 8-methylquinoline complex of platinum is also prepared. The chloro-bridged dimer⁵¹ also easily affords its cleaved acetylacetonate derivatives **260** by the reaction of it with 2,4-pentanedione. 8-Methylquinolineplatinum phosphine bromide (**260**), is obtained by the reaction of 8-bromomethylquinoline with $\text{Pt}(\text{PPh}_3)_3$. Methylquinolinemolybdenum carbonyl complex (**260**) is prepared by 8-bromoquinoline with $\text{Mo}(\text{CO})_6$ and sodium cyclopentadienide.

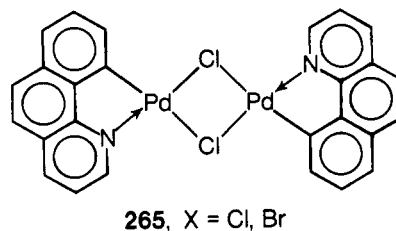


The reaction²¹⁴ between 8-ethylquinoline (L) and lithium tetrachloropalladate produces a mixture of two products, a complex of type L_2PdCl_2 (**261**) and a chloro-bridged dimer having a five-membered ring, **262**. The mixture is established through use of the well-resolved methyl bands in the NMR spectrum: 1.22 ppm (triplet) and 0.93 ppm (doublet) for **261** and **263**, respectively. The metal-chlorine bridge in the dimer **262** can be easily cleaved upon treatment with optically active (1-phenylethyl)amine, and crystallization of the resulting product **263** affording one of the diastereoisomers, $[\alpha]_D +29.2^\circ$ (*c* 4, CH_2Cl_2). If the optical active amine part in this complex is replaced by triphenylphosphine, compound **264** is obtained, $[\alpha]_D +41.5^\circ$ (*c* 4.5, CH_2Cl_2). The optical activity of the latter compound is solely



due to the presence of the chiral carbon atom.

Benzo[*h*]quinoline^{215,217} also affords the chloro-bridged palladium complexes $[\text{Pd}_2\text{X}_2(\text{bhq})_2]$ (**265**) by the reaction with palladium halide. The bridged dimers^{218,227} are cleaved by pyridine tributylphosphine, triphenylarsine, and dimethyl sulfoxide to afford a four-coordinate complex $\text{PdCl}(\text{bhq})\text{L}$ whose ligand is coordinated at the *trans* position to the nitrogen atom. The bridged dimers **265** also react with acetylacetonate to afford $[\text{Pd}(\text{acac})(\text{bhq})]$, or with sodium tetrakis(1-pyrazolyl)borate (NaBPz_4) to afford pyrazolyl-coordinated palladium complex.



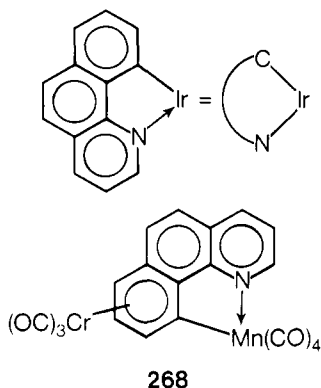
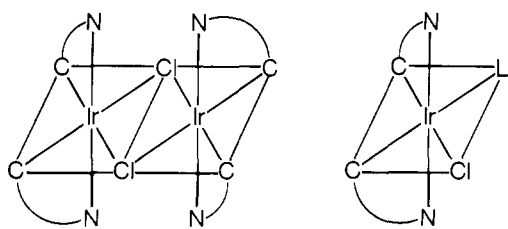
Benzo[*h*]quinoline is also metalated with $\text{Na}_3[\text{IrCl}_6]$ to give the chloro-bridged dimer $[\text{Ir}(\text{bhq})_2\text{Cl}]_2$ (**266**).²¹⁶ This complex reacts with a ligand (L) such as tri-*n*-butylphosphine and diethyl sulfide to yield $[\text{Ir}(\text{bhq})_2\text{ClL}]$ (**267**).

Reaction²¹⁷ between benzo[*h*]quinoline and $\text{M}(\text{CO})_5\text{Me}$ (M = Mn, Re), $\text{M}_3(\text{CO})_{12}$ (M = Ru, Os), and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gives the complexes $\text{M}(\text{CO})_4(\text{bhq})$ (M = Mn, Re), $\text{M}(\text{CO})_2(\text{bhq})_2$ (M = Ru, Os), and the chloro-bridged complex $(\text{bhq})_2\text{RhCl}_2\text{Rh}(\text{CO})_2$ similar to **165**, respectively; $\text{Cr}(\text{CO})_3(\pi\text{-bhq})$ is metalated on reaction with $\text{Mn}(\text{CO})_5\text{Me}$, affording $[(\pi\text{-bhq})\text{Mn}(\text{CO})_4]\text{Cr}(\text{CO})_3$ (**268**).

In closing this review, we summarize the relationship between the metal-nitrogen bond length and the electron-withdrawing groups bound to the metal in Table VII with some X-ray diffraction data described above. These show precisely that the compounds

TABLE VII. Metal-Nitrogen Bond Length of Organometallic Intramolecular-Coordination Compounds Having the Five-Membered Ring

compd no.	metal	bond length, Å	electron-withdrawing group
179	Pd	2.020	Cl, Br
37		2.076	Cl
80		2.090	<i>o</i> -oxybenzylamine
180		2.101	py
79		2.115	carbonyl oxygen
163	Mn	2.070	(CO) ₄
69		2.139	(CO) ₄
66		2.30	none
		2.40	
		2.42	
199	Pt	1.98	Cl
258		2.04	I



having a stronger or more electron-withdrawing group have much shorter bond lengths of the metal-nitrogen bond just as shown in the silicon compounds 20-24.

III. Concluding Remarks

Organometallic intramolecular-coordination compounds containing the nitrogen-donor ligand can be classified into the following nine groups according to the ligand groups in the organic residues bound to metals: alkylamines, benzylamines, benzoylamines, aminoferrocenes, benzylideneamines, imines, azobenzenes, phenyldiimides, and heteroaromatic compounds.

Almost all of the compounds formed from these groups have a five-membered ring structure which is considered to have the lowest strain among possible ring structures. Very few compounds have a six- or four-membered ring structure. However, the ferrocene compounds can form compounds having a six-membered ring in good yield. This fact is considered to show that the steric hindrance of the six-membered ring containing the ferrocene ring must be much less than in those rings containing a benzene, alkene, or alkane moiety.

The metal having more electron-withdrawing groups is prone to induce metalation, giving more stable compounds which are known from X-ray diffraction studies to have a tighter bond between the metal and nitrogen atom.

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