Cyclometalation of the Platinum Metals with Nitrogen and Alkyl, Alkenyl, and Benzyl Carbon Donors

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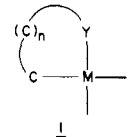
I. Introduction

Throughout the last decade, *intramolecular organometallic* reactions have experienced rapid growth in view of their diverse synthetic potential. Many such complexes are defined by an electron pair coordinate donor [Y], which is joined to either a σ- or π-bonded carbon donor. Cyclometalated complexes of the type **1**, in which Y is typically a Lewis base, have been the topic of several important reviews.[1-13] The chelate ring generally possesses three to seven members, with the five-membered ring being most prevalent. Precious metals are most common, although other transition metals can cyclometalate. In syntheses prior to 1980, the C-donor was sp^2-hybridized and primarily part of an aromatic ring.



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Interest in such organometallics has been generated in many areas, for example, the activation of a remote site in an organic molecule via formation of a new C–metal bond is indicative of tremendous synthetic importance of these compounds. Recent applications using the homogeneous and heterogeneous catalytic properties of some organometallics have also sparked many new challenging directions, motivated by industrial savings in these critical energy intensive times.

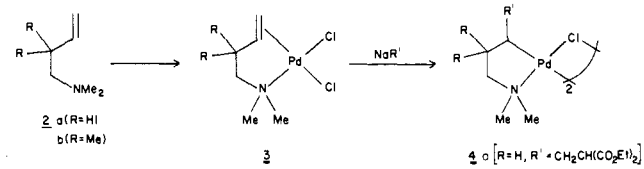
This review will be restricted to metallacyclic complexes, that have (a) C-donors that are *not* part of a benzene ring, (b) a N-donor (**1**, Y = N), and (c) a platinum metal (**1**, M = Ru, Os, Rh, Ir, Pd, or Pt). Since Omae reviewed[3] organometallic intramolecular coordination compounds containing a N-donor in 1979, this review will emphasize the recent work on organometallics which possess σ-C(sp^3)-donors; however, several sp^2 nonaromatic examples have been included for comparative purposes. In view of the emerging importance of these complexes, a limited review in this area was thought to be timely. Comprehensive tables of spectral and X-ray data are included so that the spectral characteristics and solid-state geometry of each class of complex can be correlated. Finally, a synopsis of reactions of these cyclometalated complexes has been incorporated.

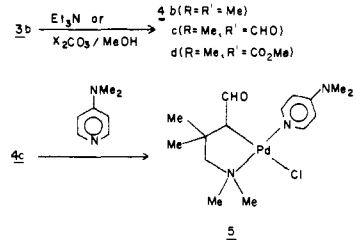
II. Syntheses and Reactions

A. σ-Bonded Complexes

1. C(sp^3)-Donors

Holton and Kjonaas[14] have synthesized five-membered palladacycles by nucleophilic attack directly on the coordinated olefin as envisioned in **3**. Typically, homoallylic amines **2** were treated with a Pd(II) salt to form the proposed π-bonded intermediate **3** which in the presence of a good nucleophile such as diethyl sodiomalonate can be converted (90%) to the dimeric metallacycle e.g., **4a**.[14] Related π-complexes have been transformed by this procedure to give the corresponding σ-bonded metallacycles; dichloro(2,2,*N*,*N*-tetramethyl-3-butene-1-amine)palladium (**3b**) when treated





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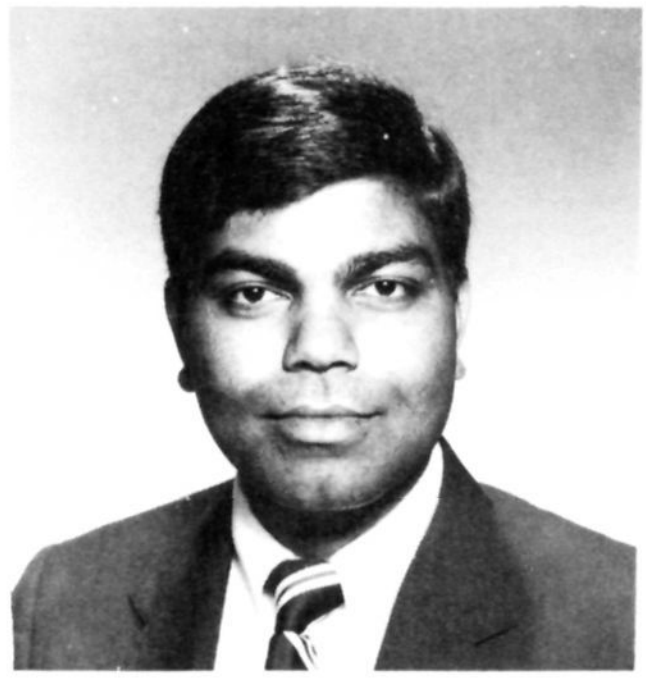
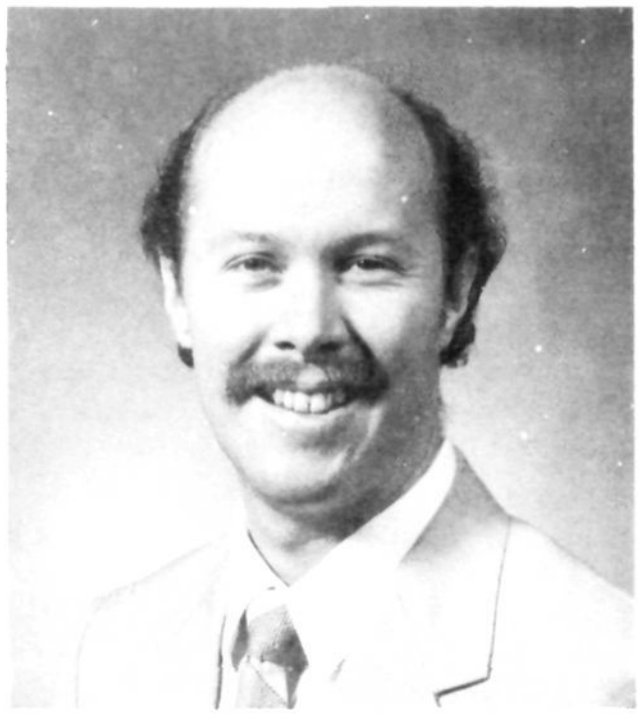
George R. Newkome received his Ph.D. from Kent State University in 1966 and after a two-year postdoctoral stint at Princeton University, he joined the chemistry faculty at Louisiana State University. He is currently Professor of Chemistry and the Executive Director for the LSU Center for Energy Studies. Effective July 1, 1986, he will become the vice-provost for research and graduate studies at the University of South Florida and continue his interests in synthetic chemistry. Professor Newkome is currently on the editorial board of the *Journal of Organic Chemistry* and editor of the *Chemistry of Heterocyclic Compounds*: *Pyridine and its Derivatives* (Volume 14) and was the recent recipient of the LSU Distinguished Research Master award.



Vinod K. Gupta received his B.Sc. (Honors), M.Sc., and Ph.D. degrees in Chemistry from University of Delhi, Delhi, India. He started teaching at University of Delhi in 1973, after completing his M.Sc. Presently, he is a senior postdoctoral research associate with Professor Newkome at Louisiana State University. His research interests are in the field of synthetic organic chemistry, organometallics, and inorganic complexation. In July 1986, he will be joining the Adhesives, Coatings and Sealers Division of 3M, St. Paul, MN, as a Senior Chemist.



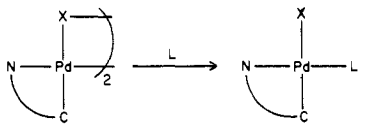
Wallace E. Puckett received his B.S. degree from the University of Central Florida in 1978 where he did undergraduate research with Professor J. P. Ikoux. His Ph.D. was completed in 1983 at Louisiana State University under the direction of Professor Newkome. Upon completing his graduate work, Dr. Puckett joined the Dow Chemical Co. and is currently a senior research chemist in the organic specialties laboratory of Dow Central Research in Midland, MI. Dr. Puckett's research interest include synthetic methodology in general organic, heterocyclic, and organometallic chemistry.

Garry Kiefer was born in Baltimore Maryland in 1954. He obtained his B.S. degree from the University of Central Florida in 1979 and his Ph.D. from Louisiana State University in 1984 under the direction of Professor Newkome. After postdoctoral studies with Professor Newkome, he joined the Central Research Division of Dow Chemical U.S.A., as a Senior Research Chemist. His research interests include synthetic organic methodology, design of macrocyclic host–guest inclusion compounds, mono- and dinuclear organometallics of biological importance, and the use of organometallics as synthetic intermediates.

with MeOH under basic conditions gave three μ-chloro-bridged dimers **4b–d**.[15] The mechanism is still speculative; however, the products were isolated in >70% combined yield with **4c** predominating (50%). The bridging chlorides in **4c** could be easily substituted by bromide, iodide, or thiocyanate upon treatment of an acetone solution of **4c** with LiBr, NaI, or NaSCN, respectively.[16] Treatment of aldehyde **4c** with 4-(dimethylamino)- or 4-cyanopyridine or $(C_6H_5)_3P$ resulted in bridge cleavage to give monomers of the type **5**.[16,17]

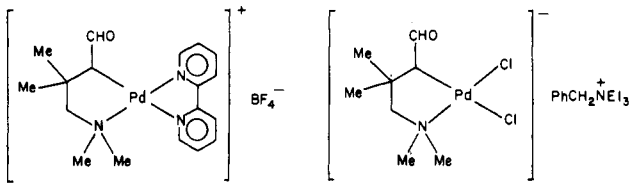
Nearly all μ-halo-bridged dimeric metallacycles, represented by **6**, react with good coordinating ligands, e.g., $(C_6H_5)_3P$ and pyridine, resulting in bridge cleavage and formation of the corresponding monomer **7**. In such cases, the entering ligand, L, is almost always trans to the N-donor. The bridging atoms can also be replaced with AcO^- or another halogen (usually Cl or Br). These

bridge cleavages are very common and normally do not result in metal expulsion from the metallacycle.[16,18]



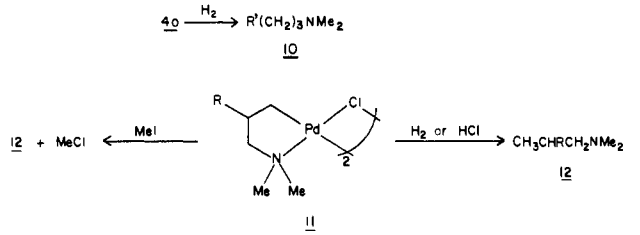
6 7

Bridge splitting of the **4c** occurs upon treatment with 2,2′-bipyridine in presence of $AgBF_4$ or with benzyltriethylammonium chloride to generate **8** and **9**, respectively. The low ν(C=O) are in agreement with the presence of a metal–carbonyl interaction as well as the influence of changes in the coordination sphere.[16]

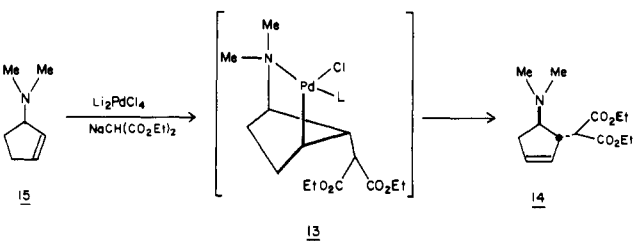


8 9

Complex **4a**, when treated with hydrogen gas at atmospheric pressure in THF, afforded (91%) the saturated diester **10**.[14] Isomer **11** reacted smoothly with H_2 and HCl, whereas with MeI, **11** afforded multiple products including substantial amounts of **12** and MeCl.[14,18] These results indicated that a Me–Pd(IV) species may have been formed, subsequent to reductive elimination of MeCl.[18] Complex **11** was found, however, to be *unreactive* toward CO or styrene under normal conditions.[18]

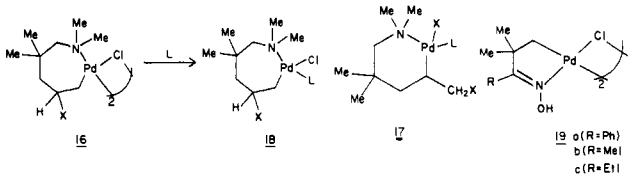


Holton has successfully employed cyclopalladated intermediates for a stereo- and regioselective prostaglandin synthesis.[19] Although palladacycle **13** was not isolated, its existence was inferred based upon isolation (92%) of pure olefin **14** from the reaction of cyclopentenylamine **15** with Li_2PdCl_4 and diethyl sodiomalonate, followed by diisopropylethylamine.[19]



15 13 14

An unusual seven-membered palldacycle has been prepared[20] by McCrindle et al. by the treatment of $PdX_2(C_6H_5CN)_2$ with $H_2C{=}CHCH_2C(CH_3)_2CH_2NMe_2$ to give initially dimer **16**. Dimer **16**, when treated with a good Lewis base, e.g., pyridine, $(C_6H_5)_3P$ or Me-$(C_6H_5)_2P$ gave the expected palladacycle **18**,[20] whose ^1H NMR spectrum showed a highly coupled signal at δ 3.99, which suggested **18** rather than isomer **17**. The ^{13}C NMR spectra of **18** would also have unambiguously confirmed the structure.

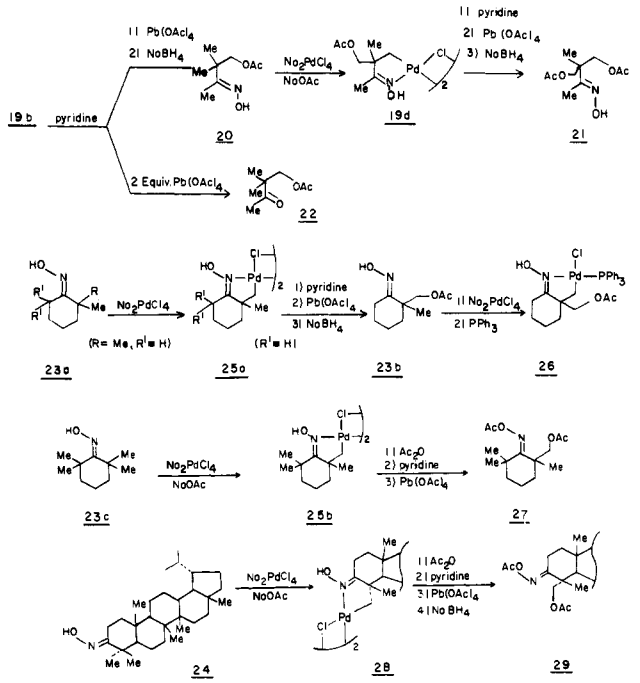


16 18 17 19 a(R=Ph) b(R=Me) c(R=Et)

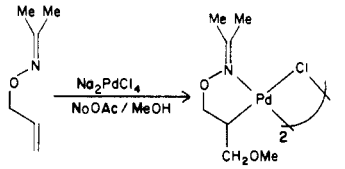
Oxime (*Z* isomer) of *tert*-butyl phenyl ketone, when treated with Na_2PdCl_4/NaOAc, cyclometalated on a *tert*-butyl (methyl) group to give **19a**.[22,23] Pinacolone and ethyl *tert*-butyl ketone oximes were similarly cyclometalated in high yield to form **19b** and **19c**, respectively. Baldwin et al.[21] conducted successive palladation–oxidation reactions on a series of oximes, which generated the corresponding β-acetoxy derivatives. Thus, palladacycle **19b** gave **20**, which subsequently underwent cyclometalation at another methyl group to generate **19d**, that was further transformed to the diacetoxy derivative **21**. When **19b** was treated with 2 equiv of $Pb(OAc)_4$, ketone **22** was isolated (64%). In a similar fashion oximes **23a**, **23c**, and **24** yielded the acetoxy derivatives **23b**, **27**, and **29**, respectively. On the basis of limited examples (e.g., **24**) the cyclic oximes underwent cyclometalation on the equatorial methyl group (Scheme I).[21]

Oxime *O*-allyl ethers were observed to undergo palladation on the central carbon of an allyl group with facile nucleophilic addition to the terminus of the double bond.[22] Thus oxime **30** smoothly reacted with Na_2PdCl_4–NaOAc in protic solvent (MeOH) to afford **31**; however, in stark contrast, pinacolone *N*,*N*-dimethylhydrazone (**32**) palladates regiospecifically at the α-methyl group via terminal N-coordination to generate

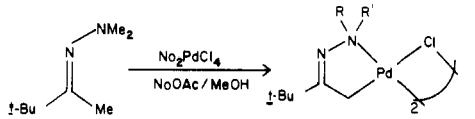
SCHEME I



33a.[22,23] This regiospecificity in palladation between oximes and *N,N*-dimethylhydrazones offers great synthetic directivity.

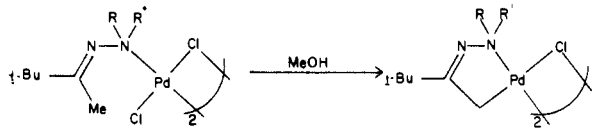


30 31

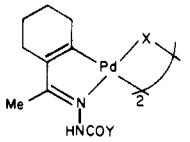


32 33 o(R=R'=Me)

Treatment of *trans*-$PdCl_2(MeCN)_2$ with a stoichiometric quantity of pinacolone *N,N*-disubstituted hydrazones in benzene generated the expected 1:1 adduct **34**, which subsequently underwent C–Pd bond formation in methanol to give the cyclopalladated hydrazone complexes **33**.[24,166] Further, the cyclopalladation was accelerated by addition of a weak base, e.g., NaOAc. Nonoyama[25] conducted a similar cyclopalladation of 1-acetylcyclohexene hydrazones with Li_2PdCl_4 in MeOH using NaOAc, as the base, to afford (33–85%) **35**. Like other cyclopalladated halogen-bridged dimers, **35** reacted smoothly with pyridine, $(C_6H_5)_3P$, and acetylacetone to give the expected bridge-cleavage products.

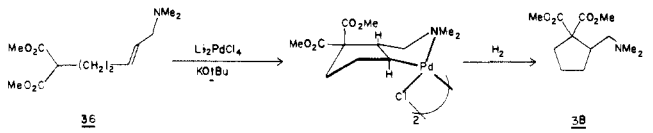


34 33 o(R=R'=Me) b(R=Me,R'=Ph)



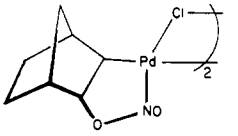
35 o(Y=Me) b(Y=OMe) c(Y=NH2) X=Cl or Br

The amino diester **36** was cyclized in the presence of Li_2PdCl_4 and KO-*t*-Bu to provide the regio- and stereospecifically fused bicyclic palladacycle **37**, which, upon hydrogenation, was converted to cyclopentane **38**. This cyclization has been extended by Holton and Zoeller to the preparation of six- and seven-membered rings as well as cyclic ketones in high yield.[26]



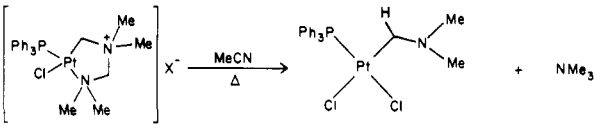
36 37 38

The reactivity of bis(μ-chloro)bis[3-(nitrosooxy)bicyclo[2.2.1]hept-2-yl-*C,N*]dipalladium (**39**), generated by treatment of norbornene with $PdCl(NO_2)(CH_3CN)_2$ during oxidative conditions, has been modified by adding $CuCl_2$.[27] Thus, with $CuCl_2$, the thermal decomposition of **39** leading to the formation of epoxynorbornane was completely suppressed, and the norbornene framework was observed to undergo skeletal rearrangement.[27,28]



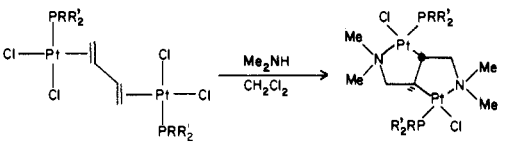
39

Reaction of $[(C_6H_5)_3P]_3Pt^0$ with $[(CH_3)_2N{=}CH_2]^+Cl^-$ gave complex **40a** which is a complex derived from the bidentate ylide ligand $[^-CH_2N^+(CH_3)_2CH_2N(CH_3)_2]$. On heating in CH_3CN, **40a** was quantitatively converted to carbene complex **41**, whereas the corresponding tetrafluoroborate salt **40b** did decompose in hot CH_3CN but at a slower rate.[29] Since **40b** did not generate the carbene complex, it was proposed that the chloride ion was important for this conversion rather than solvent effects.



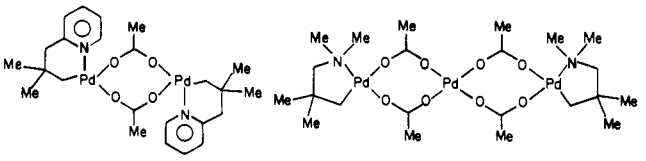
40 o(X=Cl) b(X=BF4) 41 (only when X=Cl)

The π-bonded *cis,cis*-$[Pt_2Cl_4(PMe_2C_6H_5)_2(\mu\text{-}C_4H_6)]$ complex (**42**), generated from $[Pt_2Cl_4(PRR'_2)_2]$ with butadiene in acetone over several days, on treatment with Me_2NH in CH_2Cl_2 gave (87%) complex **43**, which contains two trans-fused five-membered rings.[30] The molecular structures of both **42** and **43** were proven by X-ray diffraction studies.[30]



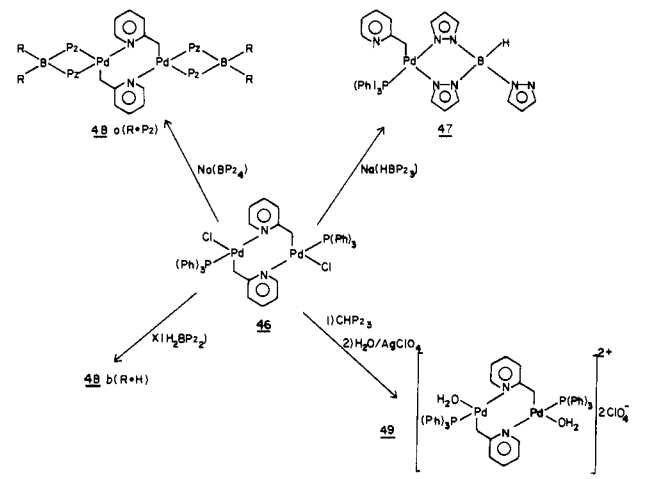
42 o(R=Ph, R'=Me) b(R=R'=Et) 43

Metalation of the 2-neopentylpyridine methyl group with $Pd(OAc)_2$ has been reported[31] to afford the novel six-membered cyclopalladated complex **44**, which was readily converted into the chloro-bridged analogue by treatment with LiCl. Bridge-splitting reactions also occurred when **44** was treated with 3,5-lutidine and thallium(I) acetylacetone to give the corresponding mononuclear palladacycle.[31] *N,N*-Dimethylneopentylamine gave an analogous five-membered trinuclear cyclopalladated complex **45** upon treatment with $Pd(OAc)_2$.[32] The standard bridge-cleavage reactions were observed with $(C_6H_5)_3P$ to give *trans*-$\{Pd(AcO)_2[P(C_6H_5)_3]_2\}$ in 56% yield.[32]

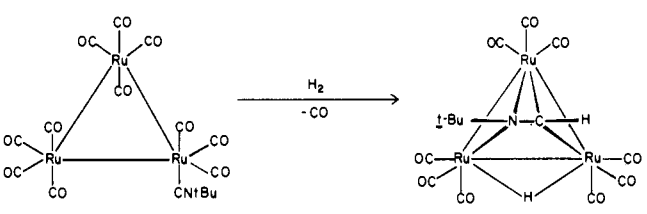


44 45

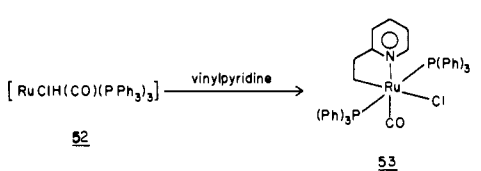
Oxidative addition of 2-chloromethylpyridine to $[(C_6H_5)_3P]_4Pd$ generated a 2-picolyl-bridged complex, **46**, in which each palladium atom is both N- and C-coordinated. Bridge cleavage occurred when **46** was treated with $Na(HBPz_3)$ (Pz = 1-pyrazolyl) to give **47**, whereas reaction of **46** with $Na(BPz_4)$ or $K(H_2BPz_2)$ resulted in the substitution of the terminal ligands to form **48a** or **48b**, respectively. The treatment of **46** with hydrated silver perchlorate, in the presence of tri-1-pyrazolylmethane, selectively replaces the chloride ligands, rather than $(C_6H_5)_3P$, by aquo ligands to afford **49**.[33]



The monosubstituted cluster complex $Ru_3(CO)_{11}$(CN-*t*-Bu) (**50**) reacted readily with hydrogen in refluxing cyclohexane to give five complexes, which upon chromatographic separation afforded the μ_3-formimidoyl complex **51**, as the major product. The structure of **51** was characterized by ^1H NMR and mass spectra.[34] The mechanistic aspects are purported to be the addition of hydrogen to the cluster with loss of CO, followed by insertion of the isocyanide into a Ru–H bond.



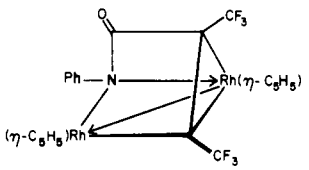
50 51



52 53

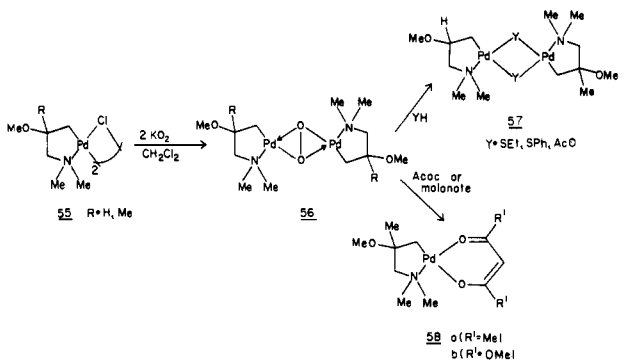
2-Vinylpyridine readily inserted into a H–Ru bond of $\{RuClH(CO)[(C_6H_5)_3P]_3\}$ (**52**) to yield a new substituted alkylruthenium complex **53**.[35,36] In addition, complex **53** underwent halogen exchange with $LiBr{\cdot}H_2O$ in acetone to generate the analogous bromo complex.[36] It was spectroscopically (NMR) determined that the P ligands were trans disposed.

Intramolecular interactions between organic isocyanates on a dirhodium center of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ or $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)$ in THF resulted in the formation of a novel complex **54**, which was the first example of the coordination of organic isocyanates to a dimetal center. Formation of the air-stable, orangish red complex **54** established that the RN=C=O group is highly reactive toward unsaturated carbon atoms of the type $=CCF_3$. Although even with vast spectral data, considerable uncertainty about the ligand–dirhodium bonding remained; the X-ray crystal structure of **54** was reported[37] and confirmed the mode of coordination.



54

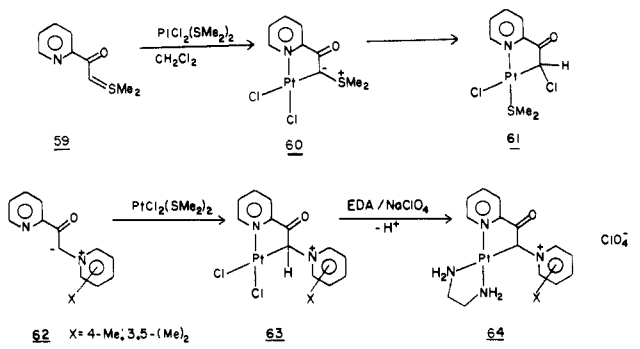
μ-Chloro-bridged complexes have been converted to novel dioxygen-bridged complexes via anion exchange; thus, the dinuclear palladacycle **55** with potassium superoxide in anhydrous CH_2Cl_2 under an inert atmosphere at 20 °C quantitatively gave complex **56**, which is stable for months under a dry environment. Upon treatment of **56** with diverse reagents, new bridged complexes **57** and **58** were formed and H_2O_2 was liberated; complex **56** did not, however, react with olefins, suggesting the bridging dioxygen is coordinated as O_2^{2-} and is a strong base.[38,39]



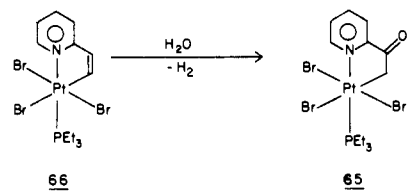
55 R=H, Me 56 57 Y=SEt, SPh, AcO 58 a(R'=Me) b(R'=OMe)

S,S-Dimethylsulfonium 2-picolinylmethylide (**59**) has been shown[40] to cyclometalate with $PtCl_2[S(CH_3)_2]_2$ in CH_2Cl_2 to give (17%) the yellow ylide complex **60**, which upon standing (25 °C; 96 h) underwent ligand exchange to generate the orange platinacycle **61** via C–S bond fission and chloride migration to the ylide carbon. Similarly, *N*-ylide **62** reacted with $PtCl_2[S(CH_3)_2]_2$ to form **63**, which underwent deprotonation and ligand exchange upon addition of ethylenediamine. Crystallization (the perchlorate) gave the cationic complex **64**,

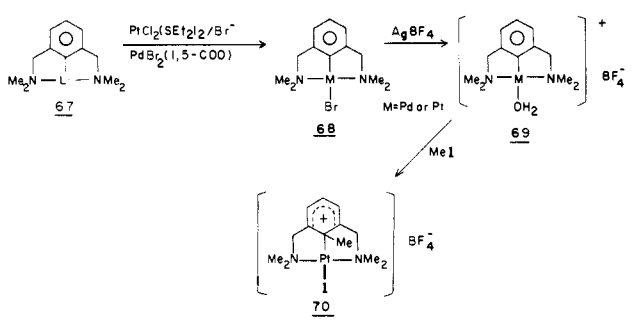
which possesses an unusual tricoordinate ylide carbon stabilized by contribution from the carbonyl group in an "enolate-like" structure. The C–C (*C*-carbonyl–C_{sp^3}) bond length is short [1.39 (2) Å] while the C=O bond distance is long [1.30 (1) Å], indicative of electron delocalization from the ylide C atom to the carbonyl group.[41] The preparation of Pd(II) and Pt(II) complexes with chelate ylides having carbonyl stabilization and a pyridinium ylide has been reported.[42]



Treatment of $Pt_2Br_2[P(CH_2CH_3)_3]_2$ with 2-vinylpyridine under anhydrous conditions gave predominantly *trans*-{$PtBr_4$[2-$CH_2CH(C_5H_5N)$][$P(CH_2CH_3)_3$]}, which upon recrystallization from damp solvents gave a high yield of **65**.[43] This Pt(IV) complex **65** has been proposed to be formed via initial cyclometalation, followed by the unusual oxidation of the cycloplatinated intermediate **66**. *trans*-{$PtBr_2$[2-($CH_2BrCHBr$)py](PEt_3)}, {$PtBr_3$[2-(CH_2CHBr)py](PEt_3)}, or *trans*-{$PtBr_4$[2-(CH_3CO)py](PEt_3)} failed to give **65**.[43]

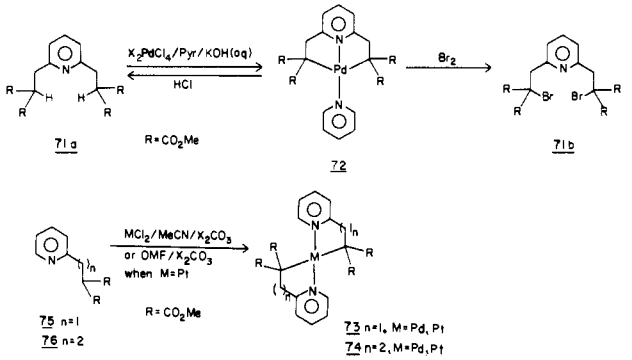


Ortho-metalated *trans*-2,6-bis[(dimethylamino)-methyl]phenyl-*N*,*N*′,*C* complexes of Pd(II) and Pt(II) have been prepared by the reaction of *cis*-[$PtCl_2(SEt_2)_2$] or [$PdBr_2$(*C*-1,5-C_8H_{12})], respectively, with the anion derived from 2,6-$(Me_2NCH_2)_2C_6H_3Li$. Upon treatment of Pt(II) complex **68** with $AgBF_4$, the aquo intermediate **69** was obtained, which in the presence of MeI formed a Pt–Me transient species, that underwent a Pt → C methyl shift to generate **70**. The structure of **70**, possessing a novel σ-aryl–platinum bond, has been established by single-crystal X-ray studies.[44,45]

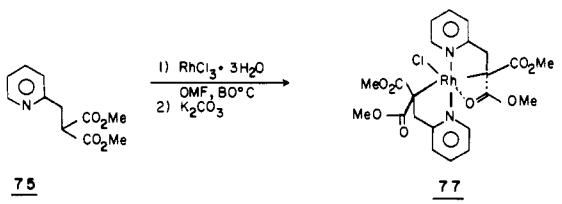


Palladium(II) complexes derived from ligands containing stabilized carbanions have recently been prepared. An ethanolic solution of pyridine derivative **71a** was stirred with K_2PdCl_4, aqueous KOH, and 1 equiv of an external ligand, e.g., pyridine, to afford **72** in good overall yield.[46,47] The external monodentate ligand was exchanged to form various mono- and dinuclear complexes.[48] Other Pd(II) and Pt(II) complexes possessing trans C–metal bonds in both five-[49,53] and six-membered[50,53] chelates (**73** and **74**, respectively) have been prepared and fully characterized; pyrazines have generated the related metal–C polymers.

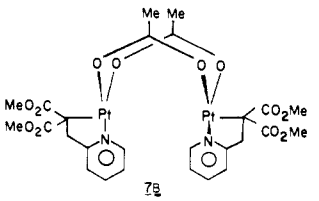
Complex **72** rapidly demetalated with Br_2 in CH_2Cl_2 to afford (100%) the novel dibromide **71b**. Reaction of **72** (R = CO_2Me) with HCl slowly regenerated **71a**, whereas under an atmosphere of hydrogen gas, the C–Pd bonds were very slowly broken to afford direct access to the formation of a palladium mirror and **71a**. Increased steric bulk of the ester alkyl groups in **72** resulted in the decreased rate of the cleavage processes; thus, **72** with carbethoxy or larger esters were generally stable to the hydrogenation conditions and could be used as homogenous catalysts. Complex **72** proved to be unreactive to CO, styrene, MeI, $MeCOCH{=}CH_2$, and Et_2S even under forcing conditions.[51]



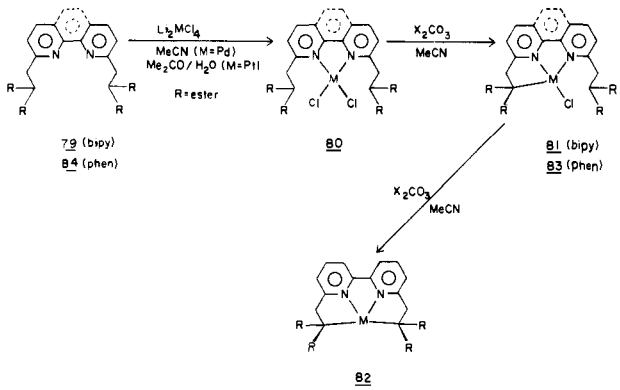
A novel bis-cyclometalated rhodium complex, **77**, has recently been synthesized by the reaction of **75** with $RhCl_3 \cdot 3H_2O$ in DMF and characterized by X-ray analysis. Interestingly, one of the ester carbonyl oxygens is coordinated to the metal (Rh–O = 2.26 Å). The ^1H and ^{13}C NMR spectra showed two different methoxy signals suggesting that an equilibrium exists in solution.[52]



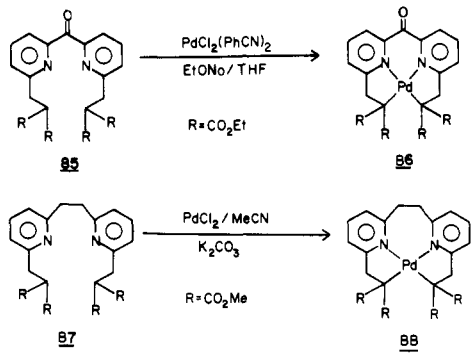
Also starting from **75**, the Pt(II) dimer **78** has been constructed and characterized by a single-crystal X-ray study.[53] The relative "trans" orientation of **78** in solution was postulated on the basis of the large upfield shift (^1H NMR) of one of the diastereotopic methylene protons (δ 2.97, 3.75).



These complexes are *not* μ-bridged dinuclear species, as is commonly the case. Analogous complexes having cis geometry have been prepared from dipyridine derivatives; thus **79**, when treated with Li_2PdCl_4 in anhydrous CH_3CN, gave the predicted intermediate **80**, which was isolated and fully characterized. Subsequent treatment of **80** with anhydrous K_2CO_3/CH_3CN gave initially **81**, which was structurally characterized confirming the formation of a single Pd–C bond. Ultimately, **81** was transformed quantitatively to **82** via addition of $AgNO_3/K_2CO_3$.[54,55] Although added $AgNO_3$ was found to promote C-metalation of Pd complex **81**, the corresponding Pt complex was observed to undergo predominantly reduction [(Pt(II) → Pt(0)], when subjected to the same conditions. If excess Pd salts were used in this procedure, the unexpected dichlorodioxazole palladium[56] was isolated, *even when the reagents and solvents were oxygen-free.* This oxazole complex was subsequently shown to be due to traces of oxazole in commercial CH_3CN; normal distillation procedures were shown not to remove this impurity from the CH_3CN. In fact this oxazole complex may be an excellent reagent, since the complex is readily soluble in organic solvents and the oxazole is easily removed in vacuo.

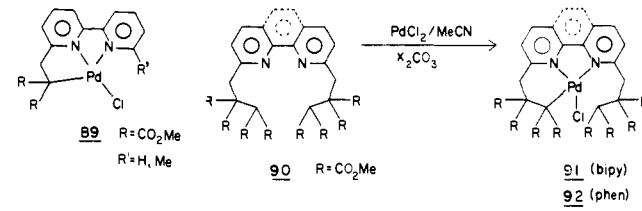


The introduction of a carbonyl moiety between the pyridines (e.g., **85**) increased the ligand "bite" to a more favorable disposition but simultaneously diminished the initial N-ligandophilicity via the increased electron withdrawal resulting from the carbonyl functionality. Despite this fact, the ketone **85** readily cyclometalated with $PdCl_2(C_6H_5CN)_2$ and NaOEt in anhydrous THF to give (15%) the 5.6.5 fused-ring complex **86**.[57] Ligand flexibility was further augmented via insertion of an ethano-bridging unit to generate **87**, which readily cyclometalated when treated with $PdCl_2$ in CH_3CN and K_2CO_3, as base. The resulting complex **88** was characterized by X-ray diffraction and displayed remarkable

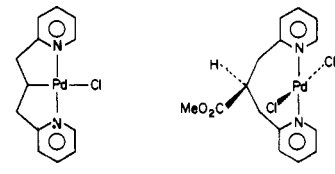


thermal stability.[57] Reaction of **87** with K_2PtCl_4 under diverse conditions resulted in the formation of only the mono-C-metalated complex. The cis-etheno-bridged ligand corresponding to **87** also formed only one palladium–carbon bond with $PdCl_2$.[58]

Unsymmetrical bipyridine derivatives gave the anticipated monometalated complexes, e.g., **89**, as did symmetrical 1,10-phenanthroline derivatives.[55] Even though these 1,10-phenanthrolines are potentially tetradentates; only *monometalated* complexes **83** have yet been isolated probably due to the rigid backbone of the heteroaromatic moiety precluding the ligand distortions necessary to accommodate tetracoordination to the core metal. The potential 6.5.6 ligand **90** has been prepared, but again only the monometalated **91** and **92** have been isolated;[57] **92** was characterized by X-ray diffraction. These complexes, which utilize a stabilized carbanion to C-coordinate, are among the most stable metallacycles yet reported. A combination of the steric bulk and the electronegativity of the β-dicarbonyl units help to stabilize the C–metal bond.



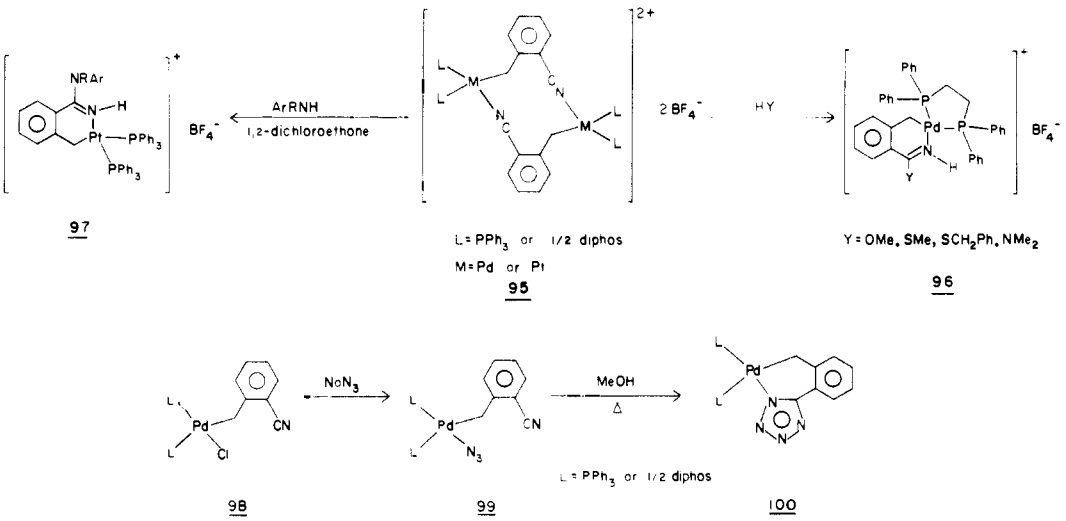
Hiraki et al. reported[59] the first example of an unactivated methylene carbon on an oligomethylene-α,ω-bis(*N*-heteroaryl) toward metalation by a transition metal. 1,3-Bis(2-pyridyl)propane upon treatment with $Pd(OAc)_2$ in CH_3CO_2H at 100 °C and subsequently LiCl gave the doubly chelated cyclopalladated complex **93**, which was characterized by ^1H and ^{13}C NMR and IR spectra.[59] Surprisingly, the reaction of 2-carbomethoxy-1,3-bis(2-pyridyl)propane with $PdCl_2$ gave only the dichloro adduct **94**,[51] rather than the expected cyclometalated product analogous to **93**.



2. Benzyl C(sp^3)-Donors

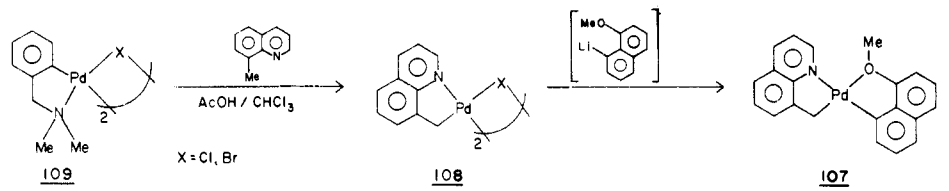
Bridged dinuclear *o*-methylenebenzonitrile palladium(II) complexes of type **95** underwent nucleophilic attack at the cyano carbon to give (90%) a six-membered metallacycle. Alcohols, thiols, and amines all added smoothly to **95** in acetone or neat at 35–50 °C to give **96**.[60] Uguagliati et al.[61] further exploited the lability of the N-coordinated metal in *o*-cyanobenzyl platinum(II) complex **95** toward nucleophilic attack. The cationic dimeric complex **95** was shown to form chelate amidino complexes of the type **97** upon reaction with both primary and secondary amines; kinetic studies were reported.[61] The mononuclear precursor **98** underwent azide–chloride displacement to give **99**,

SCHEME II



97 95 96 98 99 100

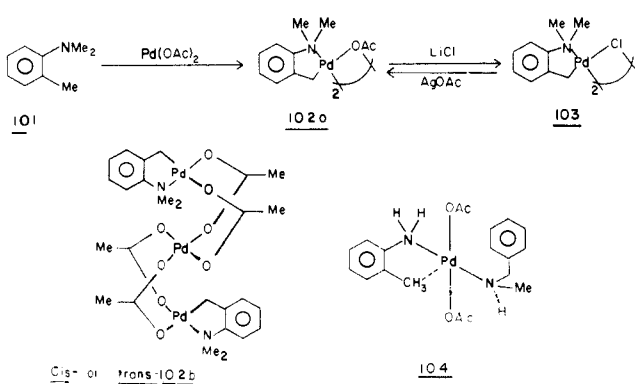
SCHEME III



109 108 107

which upon thermolysis gave **100** via 1,3-intramolecular cycloaddition of the azide moiety to the cyano group.[60,62] In general, palladium complexes, such as **95**, relative to platinum, show easier addition of nucleophiles to the coordinated nitrile carbon and cleavage of the M–C bond by acidic thiols (Scheme II).

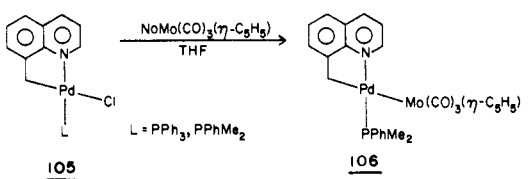
2-(Dimethylamino)toluene (**101**), upon treatment with $Pd(OAc)_2$ in AcOH at 50 °C, afforded (80%) of the cyclometalated complex **102a**.[63,64] A reinvestigation (using field desorbtion MS, NMR, and elemental analysis) of **102a** indicated it to be a trinuclear species with structure **102b**. The correct dimer **102a** could be synthesized by the reaction of *cis*- or *trans*-bis(μ-chloro)bis{[2-(dimethylamino)phenyl]methyl}dipalladium(II) (**103**) with silver acetate.[65] When **102** was treated with $(C_6H_5)_3P$ or pyridine, the bridge was cleaved, whereas metathesis with LiCl regenerated the μ-chloro-bridged derivative **103**.[63,64] Although complex **104** does not possess a formal C–Pd bond, the observed downfield shift ($\Delta\delta$ = 0.34) in the methyl resonance of *o*-toluidine has been interpreted in terms of a weak Pd···CH_3 interaction.[66]



101 102a 103

cis- or trans-102b 104

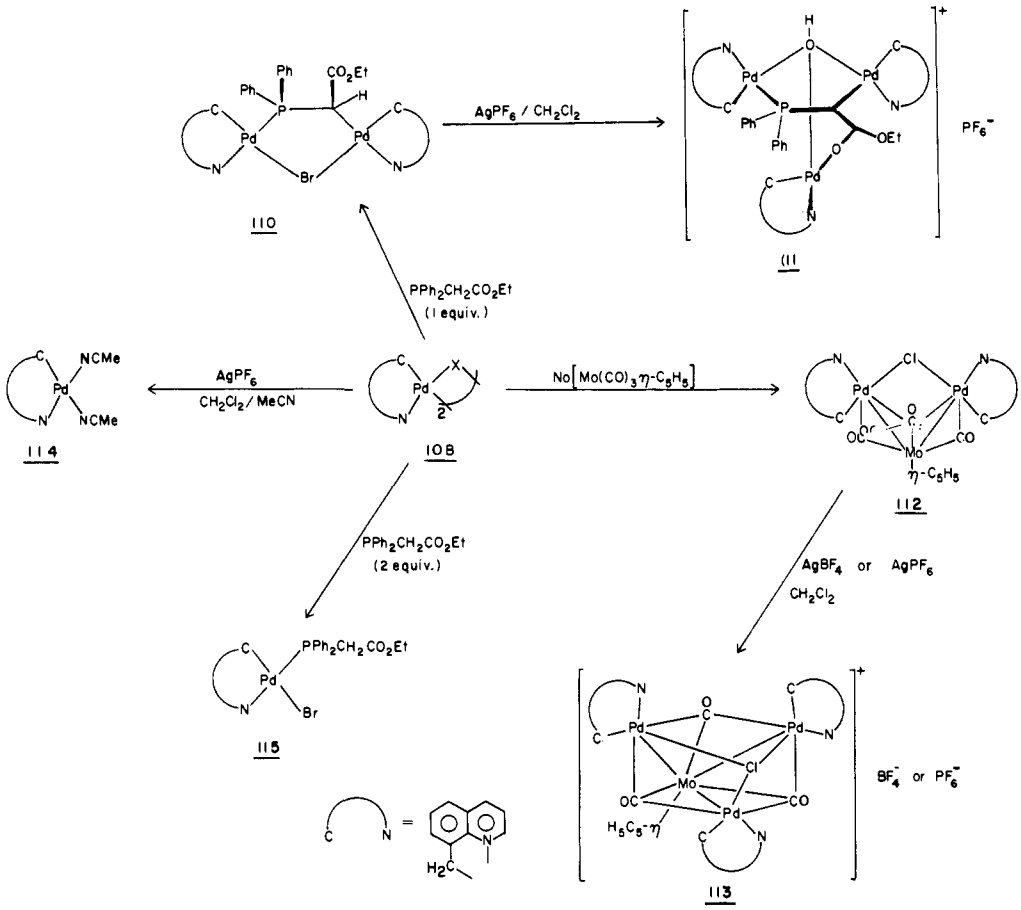
8-Methylquinoline has been cyclometalated and extensively studied by several groups, most notably those of Pfeffer[67] and Deeming.[68–70] Palladium complex **105** with carbonyl-metalated anions (metal–halogen exchange) gave a new dinuclear species, **106**, which was unstable in solution but stable in the solid state. X-ray analysis of **106** has shown that the Pd–Mo bond is very long (3.059 Å) and appears to be ionic, which may explain the rapid exchange with coordinating anions, such as Cl^- in THF.[67] Lithium chloride induced dissociation of the cyclometalated species when **105** [L = $P(C_6H_5)_3$] was subjected to CH_3CO_2H at 80 °C.[71]



105 106

An interesting palladacycle, **107**, has been obtained by treatment of cyclopalladated dimer **108** at 0 °C with 1-methoxy-8-lithionaphthalene, which was generated by directed metalation of 1-methoxynaphthalene upon treatment with BuLi in *n*-hexane/diethyl ether. An X-ray diffraction study of **107** revealed a "roughly" planar molecule with an overall cis configuration relative to the Pd–C bonds [$Pd–C_{alkyl}$ = 2.002 Å; $Pd–C_{aryl}$ = 1.986 Å]. In addition, the geometry of **107** was maintained in solution.[72] Complex **108** has been generated (64%) via $C_{aryl}–C_{alkyl}$ ligand exchange of the cyclopalladated chloro-bridged dimer **109** in $CH_3CO_2H/CHCl_3$ at 50 °C with 8-methylquinoline.[73] No such ligand exchange was observed without CH_3CO_2H, as cosolvent (Scheme III).[73]

SCHEME IV



Numerous polynuclear 8-methylquinoline cyclopalladated complexes **111–113** having novel μ_3-coordination modes for the anions $[(C_6H_5)_2PCHCO_2CH_2CH_3]^-$ and $Mo(CO)_3Cp^-$ have been synthesized by Pfeffer et al.[74] by the sequences shown below. The bridges in these molecules have been shown to be three- or five-electron donors. The complete structural analyses of these complexes have been reported.[74] Complex **113** is of particular interest since this is the first example of a palladium complex to be characterized via X-ray crystallography that possesses a triply bridged chloride ion [Pd–Cl = 2.522 Å] and a molybdenum atom that is bonded to each palladium [Pd–Mo = 2.781–2.800 Å], which forms a distorted tetrahedron (Scheme IV).

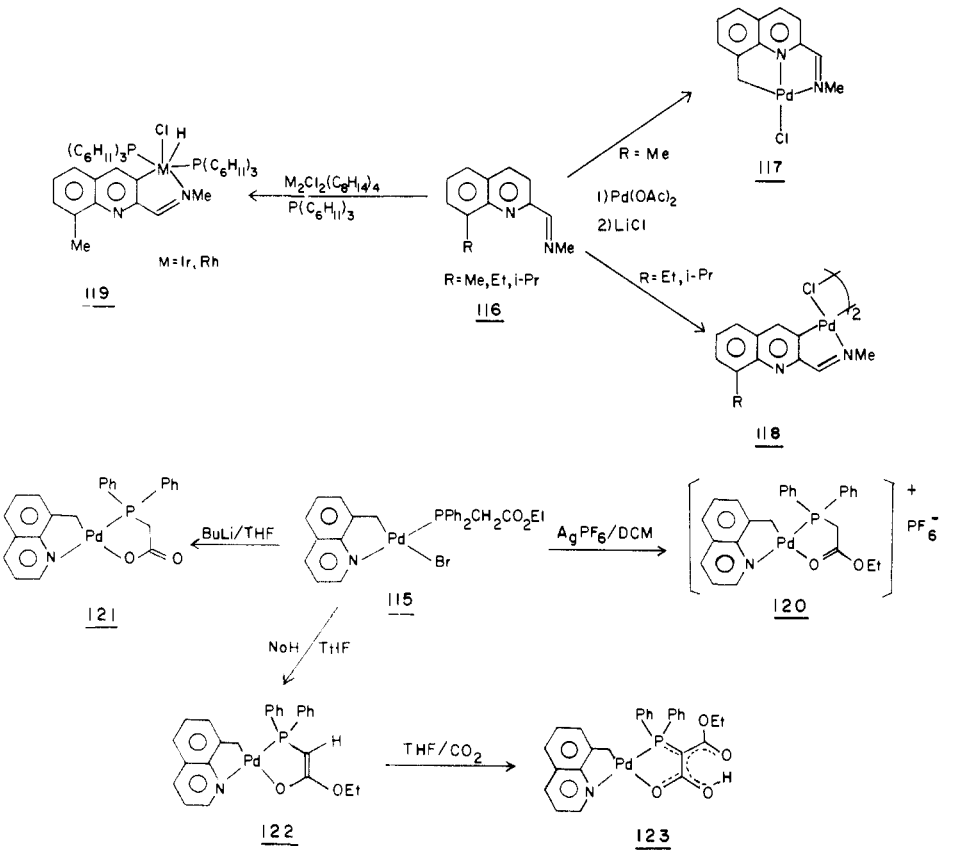
Deeming and Rothwell have conducted an excellent study of 2-substituted 8-alkylquinolines,[68] particularly the 2-carboxaldehyde *N*-methylimines **116**, which have been previosly cyclometalated with Pd, Rh, and Ir.[69] In general, **116** (R = Me) metalated smoothly with $Pd(OAc)_2$ at the 8-methyl position to give complex **117**, whereas the 8-ethyl and 8-isopropyl homologues cyclometalated exclusively at the C3-position affording **118**. With Ir and Rh salts, imine **116** (R = Me) metalated primarily at the 3-position of the electron-deficient ring to give **119**. Evidence was presented that 8-methyl cyclopalladation is electrophilic and must occur when this moiety is in the coordination plane of the Pd atom; thus it was hypothesized that the palladium is tricoordinate when the C–metal bond is formed (Scheme V).[70]

Braunstein et al.[75] have also explored the complexation properties of 8-methylquinoline with palladium(II) using $Ph_2PCH_2CO_2Et$, as the other bidentate ligand, coordinating through the phosphorus and the oxygen atoms. This polyfunctional phosphorus moiety in **115** was cyclized under the influence of $AgPF_6$, BuLi, and NaH to generate chelates **120**, **121**, and **122**, respectively. The nucleophilic character of the α-phosphino carbon was demonstrated by the reaction of **122** with CO_2 in THF under ambient conditions to generate the trapped carboxylate **123**, which was established by X-ray diffraction.[75] Bubbling of Ar through a THF solution liberates CO_2 and regenerated **122**. This is a unique, fully characterized example of reversible carbon dioxide fixation by a transition-metal complex occurring via C–C bond formation.

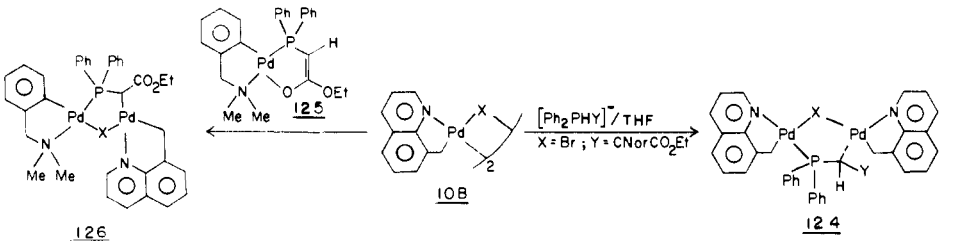
The bridging halogen in **108** has been substituted by the bidentate bridging ligand $Ph_2PCH_2CO_2Et$ either by direct substitution to generate **124** or by **125** to produce **126**. It has been deduced from their IR spectra that the ethoxycarbonyl moiety does *not* participate in the bonding to the palladium (Scheme VI).[75]

Sokolov et al. have synthesized an optically active palladacycle, **127**, via the chiral organomercurial **128**, which was prepared (68%) by treatment of the corresponding "benzylic" bromide with metallic mercury. The resultant (±)-**128** was resolved by recrystallization of the diastereomeric camphorsulfonate salts. Optically pure (–)-**128** reacted with Pd(0) reagents, e.g., $[(C_6H_5)_3P]_4Pd$ and $Pd_2(dba)_3$, in C_6H_6 to give optically active (+)-Pd complexes **127** and **129** in 79% and 81% yield, respectively; the configuration is the same. Whether the path to **127** and **129** occurred with retention or inversion of configuration was still under in-

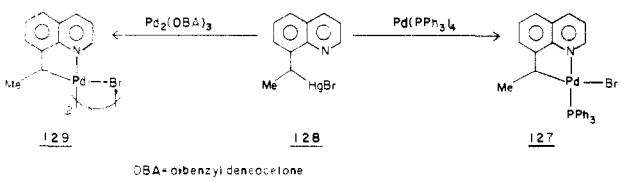
SCHEME V



SCHEME VI

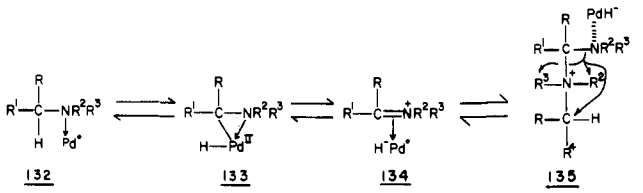


vestigation; however, any asymmetric induction in the *Pd* complexes was thought to occur via the C–Pd–Hg–Br intermediate rather than the C–Hg–Pd–Br species. Dinuclear **129** was converted readily to **127** upon addition of $(C_6H_5)_3P$.[76] Application of this procedure to synthesize organic palladium and platinum derivatives via mercury(II) intermediates has been reviewed.[77]



Suggs et al.[78] recently constructed a novel four-membered 1,3-dimetallacycle **130** by the deoxygenation of 8-quinolinyl phenyl ketone **131** in the presence of $[Rh(CO)_2Cl]_2$. X-ray single-crystal analysis of **130** indicated that the 1,3-dirhodacyclobutane ring is flat to within 0.1°, and there was no Rh–Rh metal bond as indicated by the interatomic distance of 3.164 Å.

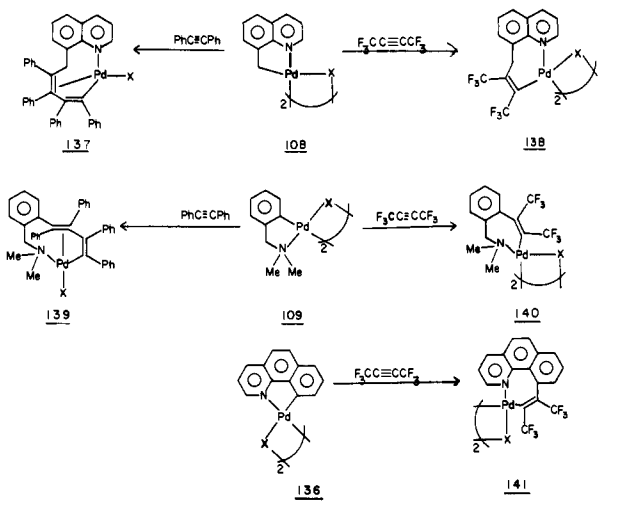
Laine et al.[79–82] and Murahashi et al.[83–87] have done considerable work involving palladium- and ruthenium-catalyzed transformation of primary, secondary, and tertiary amines, sulfides, and transalkylation reaction. The details of their work are outside the scope of this review but the proposed activation of the C–H bond by the formation of a cyclometalated intermediate must be noted. Thus, in a Pd-catalyzed reaction of tertiary amines, Pd(0) insertion into C–H bonds takes place by initial palladium N-coordination to generate **132** and then insertion into the adjacent C–H bond to afford **133**, which is in equilibrium with iminium ion complex **134**. A second tertiary amine can attack **134** to form **135**, from which the various exchanged amines can be obtained as shown by the arrows in **135**. Alternative mechanisms have also been suggested.[79–87]



132 133 134 135

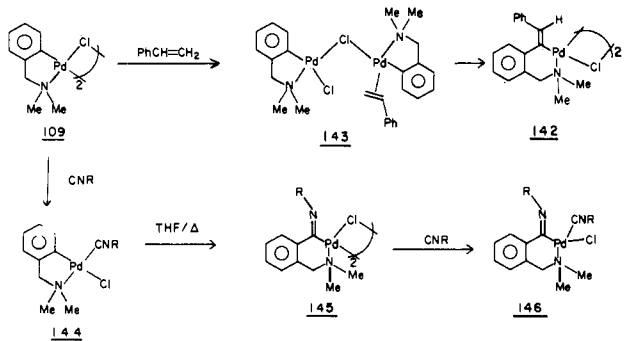
3. Alkenyl and Carbonyl C(sp²)-Donors

Alkenyl carbons can be metalated by insertion into an existing cyclometalated complex. Thus, representative complexes **108**, **109**, and **136** can react with activated alkynes to form new and unusual metallacycles **137–141**. The μ-bridges can be typically cleaved in



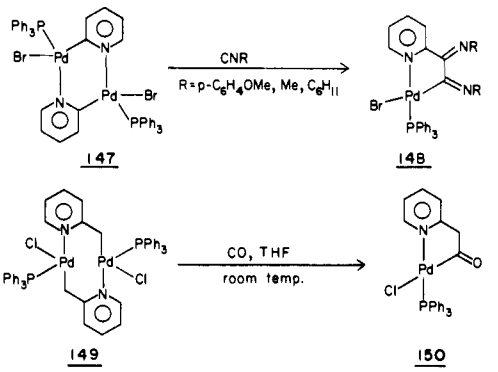
137 108 138 139 109 140 136 141

excellent yield by addition of pyridine or $(C_6H_5)_3P$ in a sealed tube with CH_2Cl_2, toluene, or benzene, as solvent.[88] For example, bis(μ-chloro)bis(*N*,*N*-dimethylbenzylamine-C^2,*N*)dipalladium(II) (**109**), upon treatment with styrene in benzene with catalytic AcOH at 50 °C, gave (18%) the unexpected alkenyl complex **142**;[89] **143** was suggested to be an intermediate based on a kinetic and mechanistic study. Addition of alkyl metal perchlorates and low concentrations of perchloric acid dramatically accelerated the transformation of **109** to **142** as evidenced by the short reaction time (1 h).[89,90] This procedure affords a novel entry into stilbene derivatives. Further, complex **109**, upon treatment with isocyanides, smoothly afforded (80+%) **144** in less than an hour. Heating **144** in THF caused a Pd–C rearrangement to generate **145**, which upon addition of a second equivalent of isocyanide gave monomer **146**.



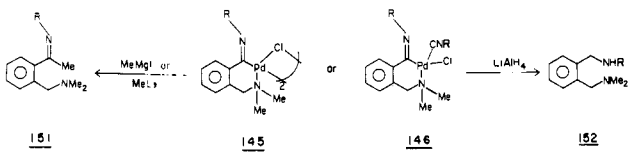
109 143 142 144 145 146

The yield of **145** was, however, diminished (<10%) as anticipated with increased steric bulk as with *tert*-butyl isocyanide.[91] Isocyanides were readily inserted at 25 °C into the 2-pyridyl-bridged dinuclear complex **147**,[93] prepared by reacting 2-bromopyridine with $[(C_6H_5)_3P]_4Pd^0$ at 90 °C;[94,95] to generate the mononuclear bis(imine) **148**.[92,165] This C–C bond formation was proposed to also occur via initial Pd–CNR coordination, followed by Pd–C migration of the pyridyl moiety to afford the monoimine; repetition gave rise to the bis(imine). Homologue **149** reacted with CO in THF at 25 °C to give (47%) the acyl complex **150**.[93,165] Acyl palladium complex **150**, upon treatment with NaOMe, afforded (47%) methyl 2-pyridylacetate.



147 148 149 150

The treatment of imine complexes **145** or **146**, with MeMgI or MeLi, gave (83%) the corresponding acyl imine **151**, which can be readily hydrolyzed to the respective ketone.[91] Complexes **145** or **146** were also reduced with $LiAlH_4$ to afford (70%) the expected *o*-[(dimethylamino)methyl][(*o*-tolylamino)methyl]-benzene (**152**, R = Me).

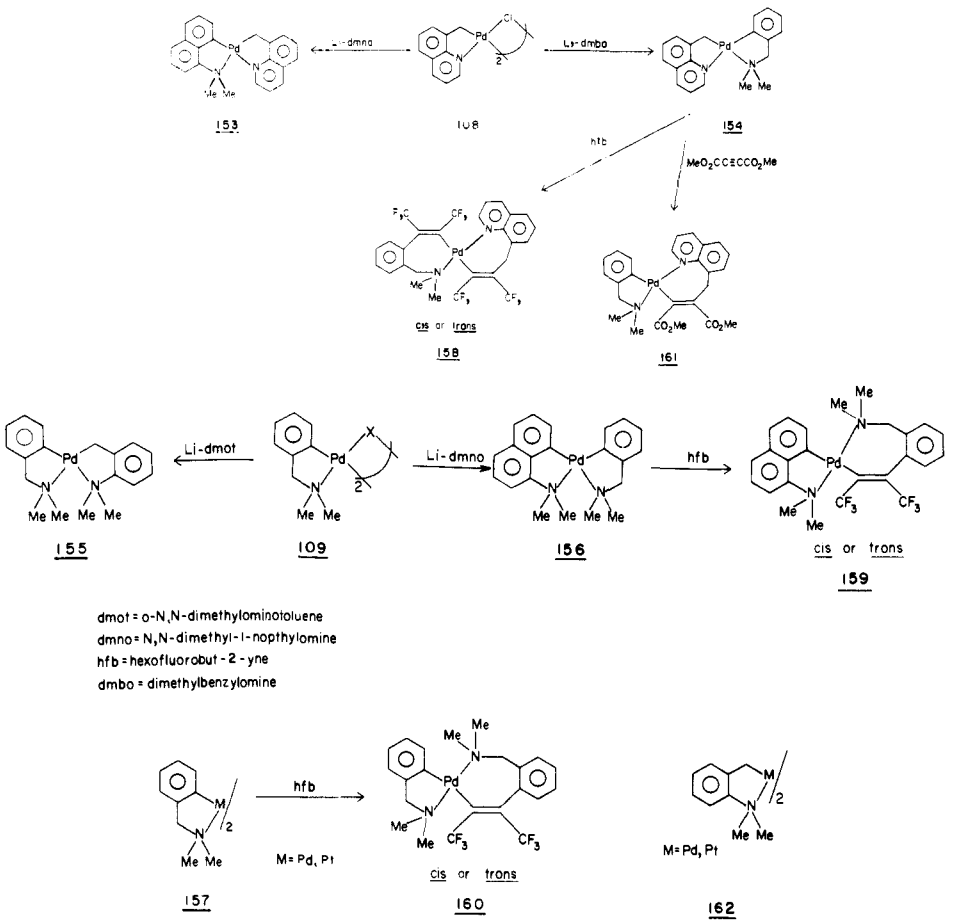


151 145 146 152

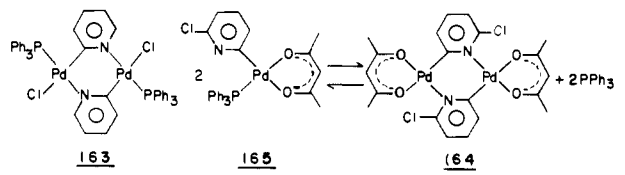
Bridging Pd(II) dimers **108** and **109** have been used for the generation of mononuclear metallabicycles **153–156** having the same size rings by the reaction with lithiated (dimethylamino)naphthalene (Li–dmna), (dimethylamion)toluene (Li–dmat), and *N*,*N*-dimethylbenzylamine (Li–dmba).[96] Metallacycles **154**, **156**, and **157** underwent ring expansion on reaction with hexafluorobut-2-yne (hfb) to afford **158–160**, respectively. The ester derivative **161** was also obtained by a similar ring expansion from **154**. Complexes **157** and **162** were prepared by treatment of $MCl_2(SEt_2)_2$ (M = Pd or Pt) with Li–dmba or Li–dmat. Detailed synthetic aspects and complete structural analyses were reported (Scheme VII).[96]

Crociani et al.[97] studied the protonation and methylation of 2-pyridyl Pd(II) complex **163** and investigated the nature of the resulting products mainly by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The electrophilic attack with alkyl or aryl phosphines involved *only* the 2-pyridyl nitrogen and *without* cleavage of the M–C σ-bond. In a related kinetic study[98] dealing with similar complexes, an equilibrium (**164** ⇄ **165**) has been pro-

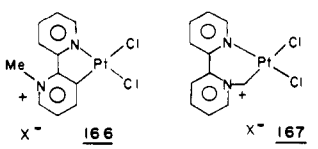
SCHEME VII



posed to generate the μ-pyridino complex **164** and $(C_6H_5)_3P$.

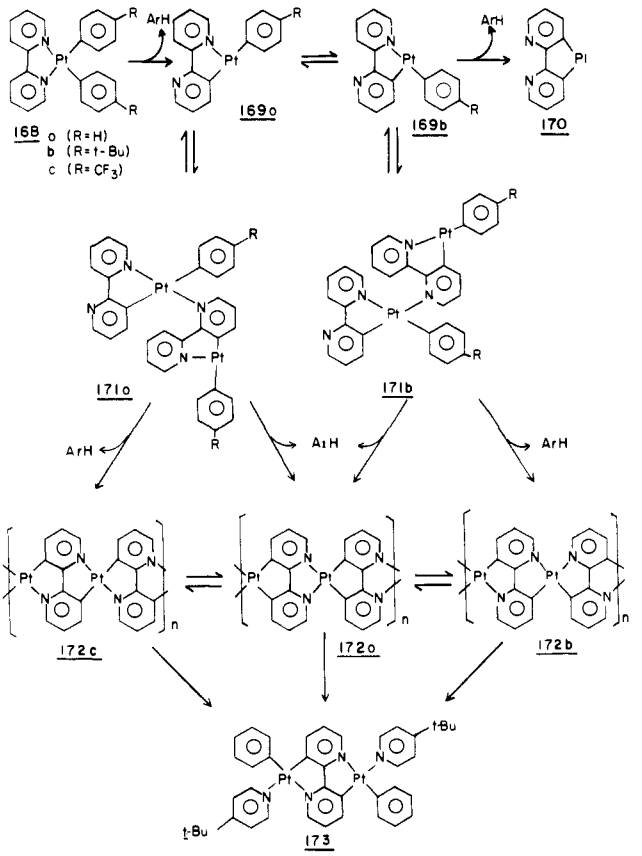


Wimmer et al.[99] have reported the isolation of the cyclometalated complexes **166** and **167** by heating for several hours a monodentate bipyridyl complex [Pt(bpyMe)X_3], obtained from K_2PtCl_4 and *N*-methyl-2,2′-bipyridylium ion [bpyMe]$^+$. Attempts to prepare the analogous palladium complexes from Pd(bpyMe)X_3 (X = Cl, Br) were unsuccessful; unreacted starting material was isolated.



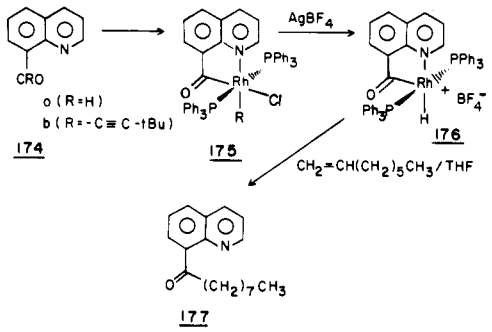
In a similar study, Skapski et al.[100] suggested that the thermal rearrangement of the diaryl(2,2′-bipyridyl)-platinum(II) **168** occurs in a stepwise manner where the bipyridyl undergoes metalation at the 3-position with hydrogen migration and elimination of 2 equiv of arene. In the presence of free pyridine, the formation of the polynuclear complex **172** was interrupted to form a

SCHEME VIII



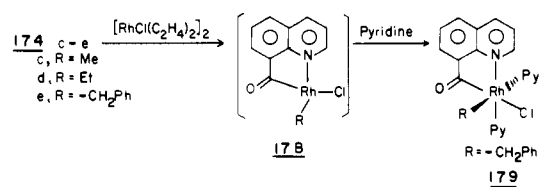
dinuclear complex, **173**, whose structure was confirmed by X-ray studies. A cis arrangement of ligating nitrogen atoms on each platinum was observed. Various steps of transformation from **168** to **172**, which have been suggested[100] on the basis of kinetic measurements, are shown (Scheme VIII).

8-Formylquinoline **174a**, upon treatment with $[(C_6H_5)_3P]_3RhCl$ in CH_2Cl_2, afforded (95%) the acyl Rh(III) hydride complex **175**, which quantitatively gave **176**, when subjected to $AgBF_4$ in toluene–CH_2Cl_2 at 0 °C. Complex **176** is a remarkably stable, coordinatively unsaturated Rh(III) complex and is suggested as a model for Rh(III) intermediates that lead to hydroacylation of terminal alkenes.[101] Complex **175** reluctantly decarbonylated (refluxing xylene; 4 h) to give (100%) quinoline, whereas the related coordinatively unsaturated rhodium complex **176** underwent hydroacylation of 1-octene under mild conditions (50 °C, 30

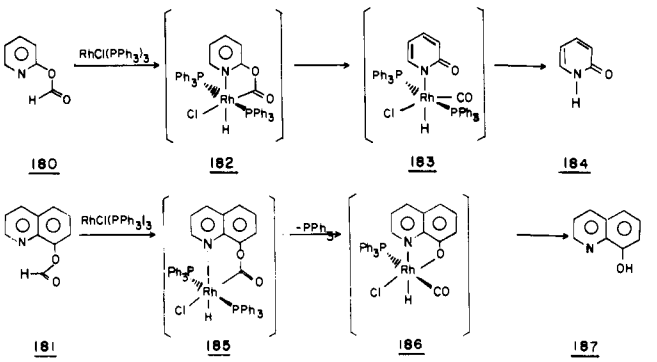


min) to generate (55%) **177**. Complex **175**, however, did *not* produce ketone **177** under similar conditions. This elegant conversion suggested that **176** can be used as a model for an intermediate in other hydroacylation processes. In addition to C–H bond insertion, facile C–C bond insertion occurred as well, whereby alkyne **174b** with $[(C_6H_5)_3P]_3RhCl$ in CH_2Cl_2 at 25 °C quantitatively gave acyl rhodium(III) complex **175b**. The analogous styryl ketone did not undergo aryl C–C insertion.[102]

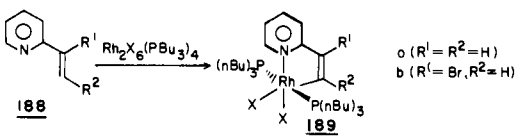
Similar Rh(III) complexes have been constructed[103] by the metal-directed cleavage of C–C bonds; thus **174c–e** react with $[(C_2H_4)_2RhCl]_2$ in benzene at 25 °C to give (100%) an ethylene-free chlorine-bridge polymer; subsequent treatment with pyridine gave **179** (R = $CH_2C_6H_5$). C–C bond cleavage occurred prior to solubilization by pyridine (generating the four-coordinate intermediate **178**), since treatment of **178** (R = $-CH_2Ph$) with a stoichiometric amount of Br_2 generated benzyl bromide. Single-crystal X-ray structural data for **179** (R = $CH_2C_6H_5$) established the presence of a very short Rh–CO bond (1.949 Å). Interestingly, all 8-quinolinyl ketones (i.e., **174**) and $[(C_2H_4)_2RhCl]_2$ investigated by Suggs et al.[103,161] have given C–C bond-cleavage products.



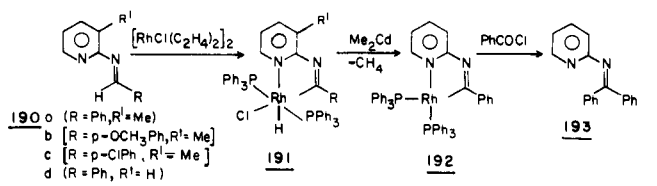
In order to study the transition-state geometry for intramolecular carbene insertions into a C–H bond,[104] 2-pyridyl formate (**180**) and 8-quinolinyl formate (**181**) were used as the coordinating ligands to evaluate the effects of metal geometries. Product studies showed that $RhCl[P(C_6H_5)_3]_3$ reacted cleanly with both of **180** and **181** to generate ultimately 2-pyridinone (**184**) and 8-hydroxyquinoline (**187**), respectively. The intermediate acyloxy rhodium hydrides **182**, **183**, **185**, and **186** could not be isolated.[104] With these ligands and reaction conditions, Suggs et al.[104] suggested that a triangular geometry was favored for metal insertion into a C–H bond.



2-Vinylpyridines (**188**) reacted with $\{Rh_2X_6[P(n\text{-}C_4H_9)_3]_4\}$ to afford (40–90%) the σ-bonded five-membered complex **189**.[105] The metalation was unselective for either the *E* or *Z* isomer of β-substituted 2-vinylpyridines suggestive of a carbocationic intermediate, followed by deprotonation. Only the halide (Br or Cl) trans to carbon could be readily exchanged. Bromine reacted with **189a** ($R^1 = R^2 = H$; X = Br) to give the unusual vinyl halide **189b** (R^1 = Br, R^2 = H), instead of the normal Br_2 addition product. Octahedral Rh(III) metallacycle **189** ($R^1 = R^2 = H$) failed to react with NaOMe, CO, or stoichiometric HBr but did ungergo a retrocyclometalation upon treatment with excess HBr in refluxing benzene.[105]

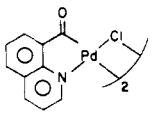


Activation of aldehydic C–H bonds to oxidative addition has also been conducted[106] via rhodium-catalyzed hydroacylation of the pyridylaldimines **190** to generate (>90%) of the yellow, air-stable complexes **191**. Subsequently, the rhodium(III) iminoacyl hydride (**191a**) was easily reduced with $(CH_3)_2Cd$ to give the Rh(I) iminoacyl complex **192**, which with benzoyl chloride afforded $RhCOCl[(C_6H_5)_3P]_2$ and imine **193** [hydrolysis yielded (72%) benzophenone].[107] Thus, changes in rhodium's oxidation state can drastically alter the chemical reactivity of the same functional group.



Anklin and Pregosin[108] prepared new Pd(II) chelates **194** and **195** in quantitative yields at 25 °C from quin-

oline-8-carbaldehyde and 2-(dimethylamino)benzaldehyde. These chloro-bridged dimers, which are related to **178**, were cleaved with neutral P and N ligands to give the corresponding monomeric complexes. It was proposed that the juxtaposed metal atom assists in making the aldehydic hydrogen more acidic through carbonyl–metal coordination.[108]



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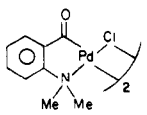

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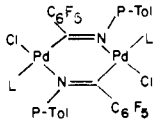
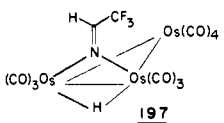


196

Uson et al.[109] described the synthesis of novel imidoyl-bridged Pd complexes **196**, which were generated from a dinuclear chloro-bridged polymer, prepared by insertion of isocyanides into Pd–C_6F_5 bonds as in the reaction of *trans*-$[Pd(C_6F_5)_2(CNR)_2]$ with $\{PdCl_2[NC(C_6H_5)]_2\}$. Complex **196** can be readily transformed back to the red polymeric imidoyl complex *cis*-$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6H_5)=N(p\text{-tol})]_2\}_n]$ and some (ca. 10%) of *N,N'*-di-*p*-tolylbis(pentafluorophenyl)-1,2-ethanediimine. The R group has been varied (R = *t*-Bu, *p*-tolyl, and C_6H_{11}) to examine substituent effects on the insertion process as well as product stability. The insertion of *p*-tolNC in benzene solvent was found to be faster than that of CH_3NC; *t*-BuNC and $C_6H_{11}NC$ did not insert under similar conditions.[109]

Trifluoroacetonitrile was reduced with a triosmium cluster, $[Os_3H_2(CO)_{10}]$, in a sealed tube with molecular hydrogen to generate **197** and **198** in 14 and 69% yields, respectively.[110,111] The X-ray data for **198** support the edge-bridged hydride, since one longer (2.918 Å) Os–Os bond and appropriate bond angles are found.[111] Each complex was further reduced with molecular hydrogen at 49 atm and 140 °C giving rise to a series of new triclinic osmium clusters. A mechanistic scheme was proposed for the stepwise reductive process.[110,111]



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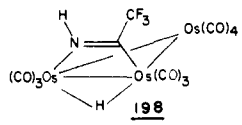
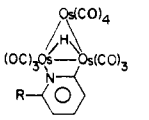
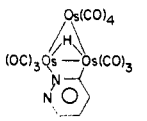


198

Mono-[112] and diazines[112,113] have been reacted with $[Os_3(CO)_{10}(Q)_2]$ (Q = cyclooctene or $NCCH_3$) to give clusters of the type $[Os_3H(CO)_{10}(\mu\text{-L})]$ (**199–203**), where L was a 2-metalated N-bonded electron-deficient heterocycle. Lewis et al.[112] constructed these triosmium clusters containing the ortho-metalated N-heterocycle by treatment of substituted pyridines with $[Os_3(CO)_{10}(NCCH_3)_2]$ in benzene, as solvent. The ^1H NMR spectrum of **199b** showed the bridging ligand to be in a locked configuration (NMR time scale) with no flexional bonding between osmium centers.[113] 2,2'-Bipyridine on treatment with $[Os_3(CO)_{12}]$ gave the related red complex **204**, which contained both a chelated bridging N,C^6-metalated bipyridine moiety as well as N,N'-chelation.[113] A related pentanuclear osmium carbido species, $[Os_5C(CO)_{14}H(NC_5H_4)]$, obtained by the pyrolysis of $[Os_3(CO)_{11}(NC_5H_5)]$, has been elucidated by X-ray analysis.[114] Even though several other known clusters were also isolated, the mechanism by which these compounds were formed is conjecture.[114]



199 a (R = Me)
b (R = Cl)
c (R = CN)
d (R = CH_2Ph)



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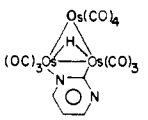

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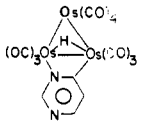

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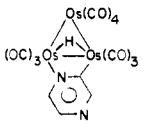

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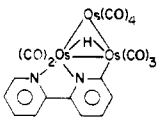
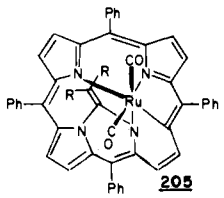


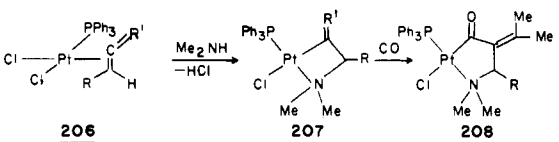
204

Balch et al.[115] recently reported the insertion of ruthenium into a pyrrole C–N bond of an *N,N'*-vinyl-bridged porphyrin to create **205**, which is best formulated as a complex of Ru(II) with the macrocyclic ligand present as a C,N-dianion possessing both carbanionic and amide characteristics. The structure and composition of **205** have been fully elucidated by X-ray diffraction studies.[115] The rupturing of a pyrrole ring in a N,N-bridged porphyrin is novel and offers new avenues to the chemistry of macrocycles.



205

The olefinic Pt(II) complexes **206** have been aminated with loss of HCl to form the unusual four-membered platinacycles **207**.[116] Subsequent treatment of **207a** or **207b** with CO in benzene under very mild conditions generated (100%) the ring-expanded acyl complex **208**.[116] It was observed that the **207a,b** were more reactive than the analogous saturated platinum(II) complexes **207c,d**; also open-chained complexes were unreactive under the mild reaction conditions. X-ray structural analyses of **207a** and **207d** have recently been reported.[117]

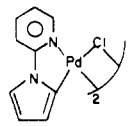


206 (R = H, Me) (R' = H, H; CMe_2)

207 a [R = H, R' = $C(CH_3)_2$]
b [R = Me, R' = $C(CH_3)_2$]
c (R = H, R' = 2H)
d (R = Me, R' = 2H)

208 a (R = H)
b (R = Me)

2-(1-Pyrrolyl)pyridine with Li_2PdCl_4 and $\{Rh_2Cl_6[P(C_4H_9)_3]_4\}$, afforded five-membered metallacycles **209** and **210**, respectively, in which the diheterocyclic moiety is coordinated by the *N*-pyridine and C^2-pyrrole atoms. The chloro bridges in **209** readily undergo cleavage with pyridine, $(C_4H_9)_3P$, and acetylacetone.[118] Metathesis of **210** (X = Cl) with excess LiI gave the mixed-halogen complex **211**. From the IR and NMR data,[118] the Cl donor is situated trans to the carbon as rationalized by the aryl trans effect; the phosphorus donors are mutually trans juxtaposed.



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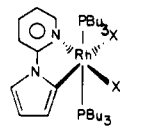
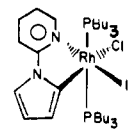


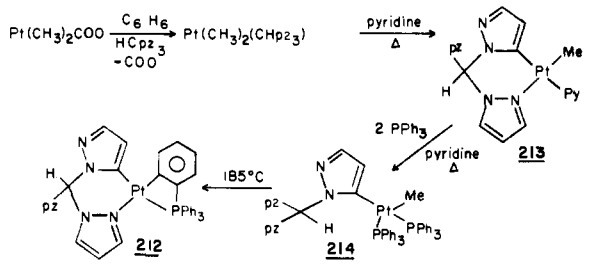
(X = Cl, Br)

210

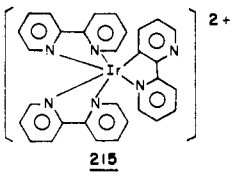


211

Complex **212**, possessing P-, N-, and C^2-donors as well as nonfused six- and four-membered rings, has been prepared by treatment of tri-1-pyrazolylmethane ($HCpz_3$) with $Pt(CH_3)_2(COD)$ to form $Pt(CH_3)_2(HCpz_3)$, which on heating in pyridine, cyclometalated (presumably with the loss of methane) the pyrazole ring at C5 to afford the crystalline complex **213**. Subsequently **213** with $(C_6H_5)_3P$ cleaved the Pt–N bond to produce **214**, which on slow heating gave complex **212** without visible decomposition to platinum(0). Complexes **212–214** were the first examples of metalated tri-1-pyrazolylmethane;[119,120] a single-crystal X-ray structure of **213** has also been reported.[120]



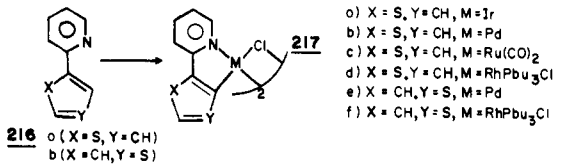
A C-bonded crystalline, red diamagnetic tris(2,2′-bipyridine)iridium(III) complex, **215**, has been synthesized and shown by X-ray analysis that the iridium was coordinated to five nitrogens and one carbon of the three bipyridine ligands.[121] Serpone et al.[122] reported earlier in 1981 the unexpected C3 metalation to one of the bipyridine moieties. Such examples offer a novel extension to the classical picture researchers have of bipyridine as exclusively a N,N′-donor.



215

4. Thienyl and Ferrocenyl $C(sp^2)$-Donors

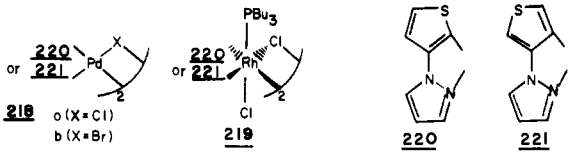
2-(2-Thienyl)- and 2-(3-thienyl)pyridines (**216**) have been cyclometalated with Ir(III),[123] Pd(II), Rh(III), and Ru(II) salts.[124] The dinuclear complexes **217a–f** were formed under mild to moderate conditions, ranging from refluxing MeOH, glyme, or xylene. The corresponding mononuclear species were readily formed when **217** were subjected to either pyridine or $(C_4H_9)_3P$; the halide donor is trans to the thiophene C ligand at least for the square-planar complexes. Ligand **216** underwent cyclometalation in a manner analogous to that of 2-phenylpyridine, except that **216b** did not metalate with Ru(II); complexation studies are yet to be conducted with Ir(III).



216 a (X = S, Y = CH)
b (X = CH, Y = S)

217
a) X = S, Y = CH, M = Ir
b) X = S, Y = CH, M = Pd
c) X = S, Y = CH, M = $Ru(CO)_2$
d) X = S, Y = CH, M = $RhPbu_3Cl$
e) X = CH, Y = S, M = Pd
f) X = CH, Y = S, M = $RhPbu_3Cl$

N-(3-thienyl)pyrazole similarly formed the cyclopalladated complex **218**, in which palladation occurred primarily at the thiophene 2-position (**220**); detectable amounts of corresponding 4-substitution (**221**) were also observed (ratio 3:1). These data are contrary to lithiation results which have been reported to give exclusively 2-metalation. Cyclometalated complex **219** was also prepared by using $\{Rh_2Cl_6[P(C_4H_9)_3]_4\}$; as usual, the bridge was cleaved with pyridine or $(C_4H_9)_3P$.[125]



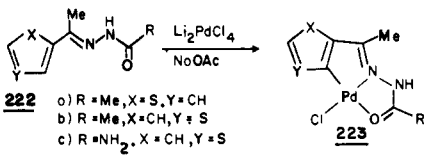
218 a (X = Cl)
b (X = Br)

219

220

221

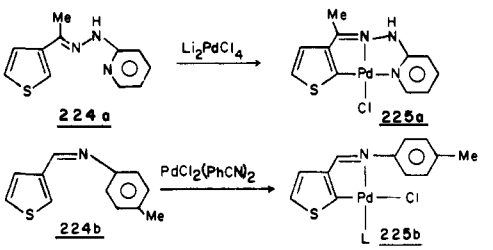
2-Acetylthiophene acetylhydrazone **222a** has been smoothly cyclopalladated with Li_2PdCl_4 under mild conditions (25 °C) to afford (70%) **223a**.[126] Though C^2-metalation on thiophene has been preferred over 4-metalation for 3-directing substituents, facile C^3-metalation occurred when the directing functionality occupies the 2-position. Activation of the C^3-position was rationalized on the basis of initial N,O-chelation to generate the stabilized intermediate for favorable metalation. In addition, the IR studies suggested that the amide was O-coordinated without deprotonation. Hydrazone derivatives of 3-acetylthiophene (**222b,c**) formed stable C,N chelates **223b** and **223c**, similar to **223a**; however, exclusive C^2-metalation occurred upon treatment of **222b,c** with Li_2PdCl_4 in protic solvent and no C^4-metalation was observed.[127]



222 a) R = Me, X = S, Y = CH
b) R = Me, X = CH, Y = S
c) $R = NH_2$, X = CH, Y = S

223

2-Pyridylhydrazone **224a** cyclopalladated in an analogous fashion to **222a** to give complex **225a**, in which pyridine acted as the N-donor.[128] In contrast, imine **224b**, upon treatment with $PdCl_2(C_6H_5CN)_2$ in dry benzene, afforded (91%) **225b**.[129] Originally C^4-metalation was proposed;[129] however, the lack of concrete spectroscopic evidence (low solubility prevented ^1H NMR analysis) and the X-ray crystal data leave this assignment tenuous at best. C^2-Metalation of thiophene appears to be more reasonable based on the results obtained for structurally related **223** and **225a**.[129]



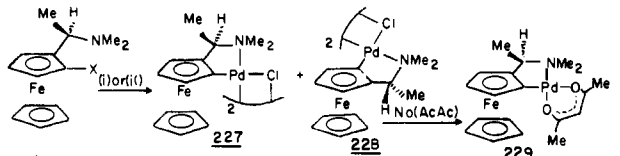
224a

225a

224b

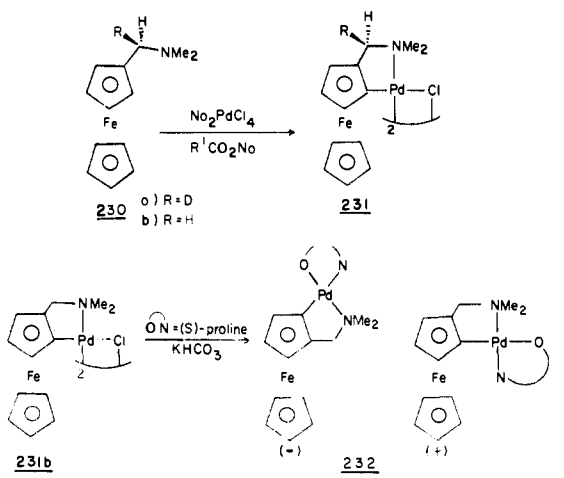
225b

Chiral (+)-[(dimethylamino)ethyl]ferrocene **226a** was cyclopalladated with Na_2PdCl_4 in MeOH to give (84%) a mixture of diastereomers predominantly (−)-**227**[130] as well as (+)-**228**. Dimers of (−)-**227** and (+)-**228** having the same absolute configuration at the chiral center and opposite absolute configuration of the chiral plane were initially separated by hand-picking single crystals and then further purified via recrystallization from C_6H_6/C_6H_{14}. Thus, optically pure samples (−)-**227** ($[\alpha]^{20}_D$ −427.7°) and (+)-**228** ($[\alpha]^{20}_D$ +475.4°) were obtained and characterized by NMR and elemental analysis. Organomercury reagents, e.g., (+)-**226b**, prepared from (+)-**226a** via metalation with *N*-BuLi and subsequent Hg–Li exchange, had been utilized to prepare pure diastereomers of the [(dimethylamino)ethyl]ferrocene Pd derivatives **227** and **228**.[131,159] Stereoselectivity for direct palladation of **226a** was found to be 70%, whereas ortho lithiation gave 92%.[131] In addition, the tetranuclear species **227** or **228** gave the dinuclear complex **229** upon treatment with sodium acetylacetonate [Na(acac)].[130,131] Under similar conditions, the enantiomeric deuterated derivative **230a** was cyclopalladated to afford **231a**; however, only 1% asymmetric induction was observed.[132]



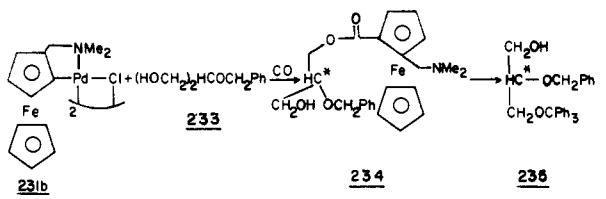
226 a [X = H; (i) = Na_2PdCl_4, NoOAc]
b [X = HgCl; (ii) = $Pd_2(DBA)_3$]
DBA = dibenzylideneacetone

The difference in stereoselectivity with respect to palladation was attributed to the steric preference of the methyl group in **226a** to remain exo to the ferrocenyl moiety in the transition state.[132] Prochiral [(dimethylamino)methyl]ferrocene (**230b**) has been cyclopalladated with Na_2PdCl_4 in the presence of chiral carboxylate salts; planar chirality was successfully induced, suggesting that the carboxylate was intimately associated with the transition state during cyclometalation.[133,134] Thus, optically active dimer **231b** was induced in high yield when *N*-acyl-α-amino acids were employed as the carboxylate source. In addition, the extent of asymmetric induction was influenced by changes in pH, whereas no dependence was observed on the nature of the cation present.[133]

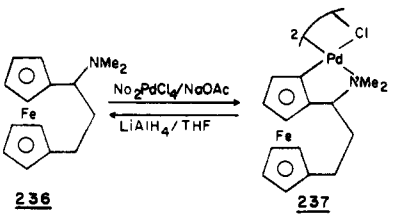


Chiral resolving agents have been successfully employed for the separation of diastereomers. Cleavage of the μ-chloro-bridged cyclopalladated ferrocene complex **231b** was conducted by using the potassium salt of (*S*)-proline. The resulting diastereomeric mixture **232** was subsequently resolved by selective crystallization to yield analytically pure samples of (−)-**232** and (+)-**232**.[135] It was believed that optically pure complexes so obtained may be useful intermediates for the synthesis of optically active ferrocenes.

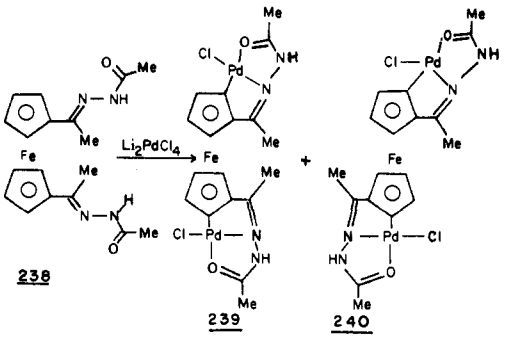
The high reactivity of the C–Pd bond in **231b** has been utilized[134,158] for the enantioselective synthesis of organic molecules. First, the asymmetric induction of a new chiral center by a chiral plane has been observed with the enantioselective synthesis of glycerides, e.g., in the presence of a prochiral diol **233**, carbonylation of **231b** generated a new chiral center in the resultant monoester **234**, which after tritylation and alkaline hydrolysis gave the chiral glycerine **235**. Second, with ferrocene being regarded as a latent form of cyclopentane, some analogous of prostaglandins based on the ferrocene framework have been synthesized.[134]



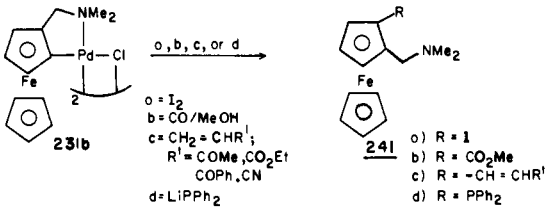
The [3]ferrocenophane **236** was cyclopalladated in the presence of the sodium salt of *N*-acetyl-D(or L)-leucine to afford metallacycle **237**, which has both a center and a plane of chirality.[136] When subjected to $LiAlH_4$ in THF, palladacyclic ferrocenophane **237** regenerated (73%) ligand **236**.



Double cyclopalladation has been achieved on each of the cyclopentadienyl rings of the ferrocene complex to yield a trinuclear species. Thus, treatment of **238** with Li_2PdCl_4/NaOAc in MeOH afforded (93% overall) both *dl*-**239** and *meso*-**240**.[137] O-Coordination of the amide functionality was indicated by the IR data; however, introduction of a good Lewis base [$(C_6H_5)_3P$] readily displaced oxygen from the coordination sphere in which the phosphorus is now trans to the N-donor.[137]

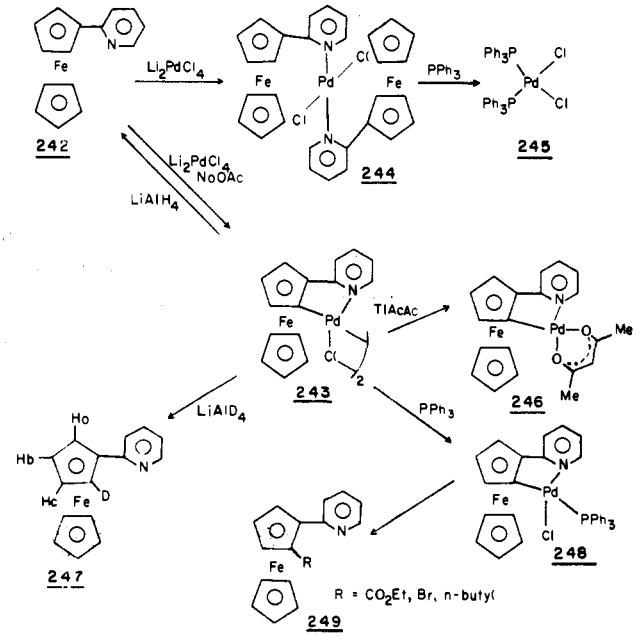


Cyclopalladated ferrocene **231b** reacted with I_2 to afford the iodoferrocene **241a**.[133] Complex **231b** also reacted with CO in MeOH to afford the ferrocenyl amino ester **241b**,[133,138] as well as underwent the Heck reaction with a variety of alkenyl reagents to give C–H insertion products (e.g., **241c**) in variable yields.[133,138–140,158] Replacement of the dimethylamino moiety with a 2-pyridyl group was accomplished, and the resultant complexes have been demonstrated to be less reactive with olefins.[140] Treatment of **231b** with $(C_6H_5)_2PLi$ occurred to generate (50%) ferrocenylphosphine **241d** via a proposed ferrocenyl palladium phosphide intermediate which undergoes decomposition without isolation.[141]

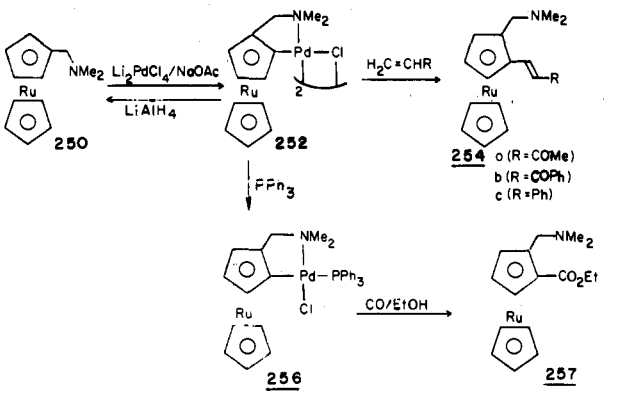


2-Pyridylferrocene **242** upon treatment with Li_2PdCl_4 in dioxane or MeOH gave the non-palladated dichlorobis(2-pyridylferrocene)palladium(II) complex (**244**). The reaction of **244** with $P(C_6H_5)_3$ gave quantitative conversion to **245** indicative of a simple ligand–ligand exchange. In contrast, when **242** was subjected to slightly different conditions (Li_2PdCl_4/NaOAc/MeOH), the bridged intramolecularly ortho-palladated dimer **243** was isolated;[142] thus, added acetate has been again shown to promote cyclometalation.[24] Treatment of **243** with thallium(I) acetylacetonate, $LiAlD_4$, and $P(C_6H_5)_3$ generated **246**, **247**, and **248**, respectively. Complex **248** was readily carbonylated in the presence of CO/EtOH to generate the noncyclized ethyl ester. Furthermore, **248** gave the brominated and butylated derivatives (**249**) when treated with Br_2 and butyllithium, respectively (Scheme IX).[142]

SCHEME IX

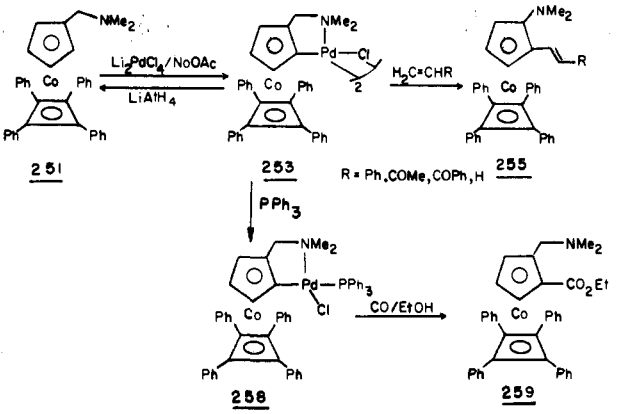


The related ruthenocene **250**[143] and [π-((dimethylamino)methyl)cyclopentadienyl](tetraphenylcyclobutadiene)cobalt(I) (**251**)[144] have been cyclopalladated, under conditions analogous to those described for **226**,[130] to afford **252** and **253**, respectively; treatment of cyclopalladated complexes with $LiAlH_4$ readily regenerated the starting materials. In both cases, acetate ion was essential to the formation of the cyclometalated species. In addition, both **252** and **253**, when treated with $(C_6H_5)_3P$ or Tl(acac), underwent typical μ-bridge



fragmentation. In contrast to other metallacycles, the ruthenocene **252** failed to react with Br_2 or BuLi under various conditions but when subjected to Heck reaction conditions gave an usually high yield (ca. 89–94%) of **254**. Further, even though dimer **252** failed to react with CO in EtOH, the monomeric palladacyclic ruthenocene **256** reacted slowly with CO to afford amino ester **257**.[143]

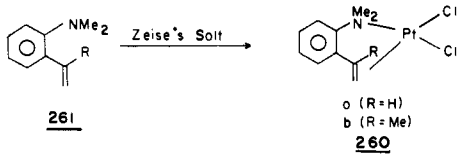
The cyclometalated cobalt sandwich **253** gave the vinyl-substituted derivatives **255** upon addition of activated olefins. The greatest yield (78%) for C–H insertion into **253** occurred when ethene was used as the olefin source; interestingly, traces (1.5%) of a disubstituted ethylene were isolated. Again dimer **253** did not react with CO in ethanol; whereas, under moderate (100 °C) conditions monomer **258** gave (42%) the noncyclic amino ester **259**.[144]



B. π-Bonded Complexes

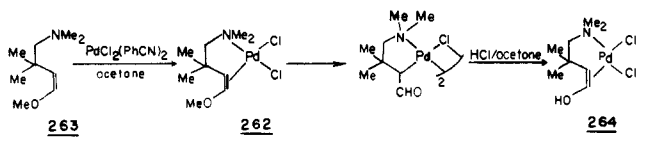
A series of Pt(II) complexes derived from monolefins was synthesized in order to investigate the bonding characteristics of the olefin–Pt π-bond. The π-complex dichloro(*o*-vinyl-*N*,*N*-dimethylaniline)platinum(II)

(**260a**), prepared from *o*-vinyl-*N*,*N*-dimethylaniline (**261**) and Zeise's salt, was recrystallized (44%) from $CHCl_3$/MeOH.[145] *o*-Vinyl-*N*,*N*-diphenyl-, *o*-(1-methylvinyl)-*N*,*N*-dibenzyl-, and *o*-(1-methylvinyl)-*N*,*N*-dimethylanilines formed similar monolefin π-complexes upon treatment with Zeise's salt. The use of Zeise's salt generally gave better yields over the use of $PtCl_2$. Dichloro[*o*-(1-methylvinyl)-*N*,*N*-dimethylaniline]platinum(II) (**260b**) was subjected to chloride ligand exchange (L = Br^-, I^-, NCO^-, SCN^-, and N_3^-) so that changes in allylic coupling, as a factor of the ligand (trans)–olefin relationships, could be evaluated. The ^{195}Pt–^1H NMR coupling constant data within this series were determined.[145]

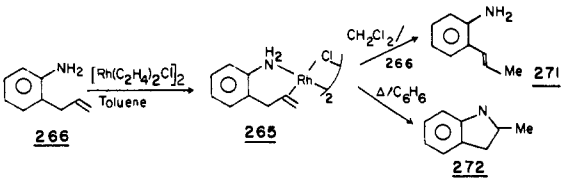


Aliphatic polydentates, such as dimethyl(2,2-dimethylbut-3-enyl)amine (**2b**), have received considerable attention because of their enhanced tendency to chelate as well as the increased solubility of the resultant complex in organic solvents. In addition, this type of ligand is potentially useful as sensitive NMR probes for delving into the nature of metal–olefin coordination, since restricted confirmation mobility should result in magnetic nonequivalent of the methyl groups. Accordingly, the π-complex **3b** was easily obtained via treatment of **2b** with $PdCl_2(C_6H_5CN)_2$ in CH_2Cl_2. The related dibromo and diiodo complexes were subsequently prepared via metathesis of **3b** with LiBr or NaI in acetone.[146]

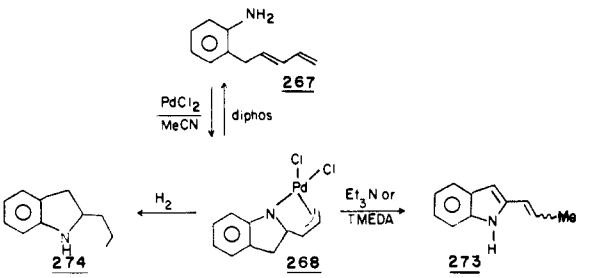
It has been suggested that dichloro[dimethyl(4-methoxy-2,2-dimethylbut-3-enyl)amine]palladium(II) (**262**) is a key intermediate in the pathway leading to **4c**, when **3b** is treated with K_2CO_3 or Et_3N in MeOH. To test this hypothesis, McCrindle[147] et al. conducted a study in which authentic samples of **3b** were subjected to the standard reaction conditions and the product evolution was monitored by NMR. Although vinyl ether chelate **262** was not detected, there was indirect evidence to support its existence as a transient precursor to **4c**. For NMR comparative purposes, **262** was prepared via an alternate synthetic route from **263** and fully characterized by X-ray crystallography.[147] A related η^2-vinyl alcohol complex **264**, also believed to be involved in the sequence leading to **4c**, has been synthesized via treatment of **4c** with HCl in acetone and subsequently characterized by X-ray crystallography.[148]



π-Bonded complexes can serve as useful intermediates in the syntheses of heterocycles via metal-catalyzed intramolecular functionalization. In order to investigate possible effects of the metal atom on ligand rearrangements, Aresta and De Fazio prepared (85%) the yellow dimer **265**[149] by treatment of 2-allylaniline (**266**) with $[Rh(C_2H_4)_2Cl]_2$ in C_6H_6 or C_6H_5Me; ethylene was evolved.

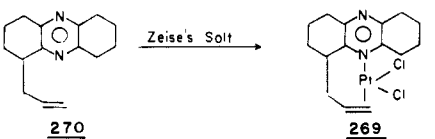


Similarly, Hegedus et al. have investigated the Pd(II)-assisted N-alkylation of indoles.[150] Thus, treatment of (2,4-pentadienyl)aniline (**267**) with $PdCl_2(MeCN)_2$ in THF afforded (95%) the stable allyl-2,3-dihydroindole palladium complex **268**; none of the desired tricyclic indole was detected due to the stability of the complex.[150]

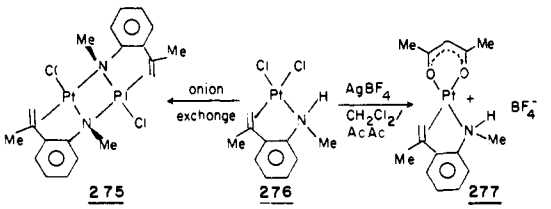


π-Bonded rhodium dimer **265**, on treatment with 2-allylaniline in CH_2Cl_2, isomerized the olefin and generated a $[Rh(L)_2Cl]_2$ in 4% yield as well as the isomeric *trans*-2-propenylaniline (**271**), whereas, when this dimer $[RhL_2Cl]_2$ was refluxed in C_6H_6, rhodium was lost to give 2-methylindoline **272**. Similarly, treatment of the π-allyl complex **268** with diphos, which normally promotes allylic amination in systems of this type, regenerated the starting ligand **267**.[150] In attempts to transform **268** to tricyclic amine, complex **268** when heated with Et_3N gave (51%) only the 2-(1-propenyl)-indole (**273**), whereas with TMEDA a mixture of **273** and 2-allylindole was produced. Complex **268**, when subjected to H_2, afforded (57%) the reduced derivative **274**.

Jullien et al. have characterized the square-planar, strain-free π-complex **269**, which was prepared by treatment of 1-allyloctahydrophenazine (**270**) with Zeise's salt.[151]

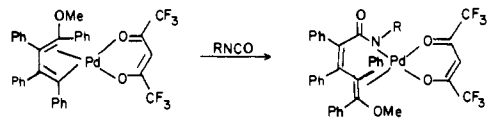


An amino-bridged dimer, **275**, was constructed by deprotonation of the yellow crystalline complex **276**, using an anion-exchange resin in the hydroxide form.[152] Complex **276** was prepared (80%) from *o*-isopropenyl-*N*-methylaniline and $PtCl_2$ in $CHCl_3$.[152] The chloro ligands in **276** could be exchanged with acetylacetone to generate (87%) **277** in the presence of $AgBF_4$. The X-ray structure of **275** offered interesting insight into the steric factors associated with a fused four-membered ring; one conclusion is that in square-planar Pt(II) complexes, the amido nitrogens exert a relatively strong trans effect as suggested by the Pt–Cl bond length [2.318 (9) Å].[152]



275 276 277

π-Complex **278**, which exists in solution as an equilibrium mixture of η^3- and η^1-butenyl forms, was transformed by isocyanate insertion into the C–metal bond to give imide **279**. π-Bonding to the γ,δ-olefin rather than the α,β-olefin is favored based on molecular models but not proven. A Hammett correlation for the reactions of 4-substituted aryl isocyanates exhibited a linear relationship ($\rho = +1.13$) in which electron-withdrawing substituents facilitated the insertion process. A four-centered transition state for the insertion process was proposed and is consistent with the kinetic data.[153]



278 279

III. Structural Analyses

During this last decade, NMR and X-ray spectral information have become the major experimental techniques to study organometallics. These studies provide necessary structural details of these complexes so that the intrinsic nature of the ligand–metal bond can be truly understood. IR was the most important tool during previous decades because it was readily accessible and could give results in both solution and solid state. Because of the increased availabiltiy of Fourier transform instrumentation, the often low solubility of these organometallics is no longer a serious problem, especially for NMR studies. Thus, NMR is rapidly becoming the method of choise for structural characterizations since it gives more specific connectivity information than IR and crystallization is not necessary. Even with FT NMR, X-ray crystal analysis is still the most unambiguous technique for structural characterization and the wealth of other information gained makes it the most desirable source of data.

A. Nuclear Magnetic Resonance Studies

The NMR discussion will be confined to data which deal directly with the chelate ring. Table I lists representative data for complexes, which possess a sp^3 σ-C-donor. Few alkenyl σ-C-donors are compiled since proton data are still very limited. ^{13}C NMR data would be most informative, but there seems to be a dearth of accurate assignments for chelate rings. In Table I only pertinent NMR data associated with the chelate ring was considered and compiled. In a N,C-chelate ring the α-position is the carbon *directly* attached to the metal followed by β and γ. Other key information concerning the chelate ring are given.

Chemical shift differences were most helpful in going from an *acyclic* ligand to the *cyclic* complex. These comparative data are easily applied when an unsaturated ligand was cyclometalated to form a saturated metallacycle, e.g., **16**. Upon cyclometalation, the loss or gain of spin–spin coupling interactions can be characteristic and most informative; e.g., in **75** the α-methylene doublet is transformed to a singlet, or in **63** the appearance of a new doublet due to the Pt–H coupling. The appearance of new signals (chemical shift) upon cyclometalation are helpful as in pinacolone oxime **19b**, where a new Pd–CH_2 signal arises. Although peak assignments of hydrogens bound directly to chelate ring are desired, these signals are often obscured, missing due to substitution or highly coupled making individual assignments difficult. Periodically useful data are gained from observation of characteristic shifts in hydrogen-containing groups not directly bonded to the metal. Thus, when a dialkylamino moiety is utilized as the N-donor, a shift in its signal to lower field can be indicative of N-coordination. Likewise, pyridine proton resonances, especially at H6, are often useful because of the characteristic downfield shifts caused by inductive electron density loss and nonbonded interactions.

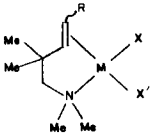
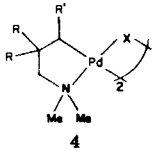
The magnitude of coupling constants has been used to study trans effects of O vs. S atom.[154] The Pt–olefinic proton coupling constant was shown to be sensitive to the π-bonding ability of the trans ligand; thus the coupling constant was used to assess the trans influence of diverse ligands (N_3^- to I^-).[143] Variable-temperature (VT) NMR studies have been conducted on **3b**, **63**, and **99**, as well as other complexes to assess various conformational characteristics of the chelate ring.

The NMR studies of other nuclei are becoming more popular but inherent problems must be overcome. ^{13}C NMR has great potential especially for exploring the nature of C–metal and C–C–metallacyclic interactions. Examination of Table I reveals that some researchers are now routinely including ^{13}C in their studies. As yet, there appears to be no cohesive theoretical or empirical rules to predict the effect(s) of C–metal coordination or chelate ring formation on the ^{13}C chemical shift. ^{13}C NMR may be most useful in this aspect of a study since the metallacycles usually contain at least three carbons of varying degrees of hybridization, while the accessible proton data are not very sensitive to minor structural changes. ^{103}Rh NMR was included[155] since the ^{103}Rh nucleus in a chelate ring was found to resonate at higher field as the σ-donor strength of the ligands increased. Other precious metals can be studied via NMR, platinum being one with sufficiently small line width but little or no comparative data have yet appeared.

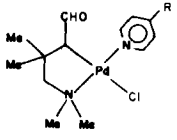
B. Infrared Spectrophotometric Studies

Infrared (IR) spectroscopy has become more useful for the confirmation of suspected functionality than for detailed structural characterization. Thus, standard signals in the regions from 3500 to 2900, 2000 to 1200, 1000 to 600, and 400 to 100 cm^{-1} are usually mentioned in support of a specific moiety. There are, however, several special new IR techniques, which enhance the usefulness of this tool.

Table I. Selected Comparative NMR, IR, and X-ray Data of the Cyclometalated Complexes

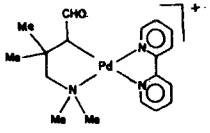
complex	NMR[a] nucleus (solv)[b]	α	β	γ	other	IR (M-halogen), cm^{-1}	X-ray[c] M-halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
 3													
M = Pd; X = X′ = Cl; R = H	^{1}H (A)	6.01	1.15, 1.86 (C*Me*)	2.35, 3.05	2.82, 2.93 (N*Me*)	304, 323, 331							146
						309, 330	2.296 (3)	2.124 (10) [84.1 (4)]	1.51 (1) [107.3 (7)]	1.52 (2) [109.3 (9)]	1.49 (2) [112.9 (9)]	2.072 (8) [110.0 (7)]	148
M = Pd; X = X′ = Br; R = H	^{1}H (D)	6.15	1.16, 1.79 (C*Me*)	2.42, 3.35	2.99, 3.15 (N*Me*)	1.91, 199							146
M = Pd; X = X′ = I; R = H	^{1}H (A)	6.05	1.11, 1.80 (C*Me*)	2.16, 3.12	2.87, 3.12 (N*Me*)	164							146
M = Pd; X = X′ = Cl; R = OMe	^{1}H (H)	4.49	1.18, 2.58 (C*Me*)	2.56, 3.47	2.52, 2.97 (N*Me*)		2.298 (1) 2.321 (1)	2.135 (3) [83.6 (1)]	1.507 (4) [108.3 (2)]	1.529 (4) [108.5 (3)]	1.497 (4) [112.9 (2)]	2.082 (2) [109.9 (2)]	147
M = Pd; X = X′ = Cl; R = OH	^{1}H (H)	4.59	1.20, 1.80 (C*Me*)	2.26, 3.68	2.72, 2.99 (N*Me*)	309, 330	2.296 (3) 2.342 (3)	2.268 (11) [92.9 (3)]	1.51 (1) [107.3 (7)]	1.52 (2) [109.3 (9)]	1.49 (2) [112.9 (9)]	2.076 (8) [110.0 (7)]	148
M = Rh; X = Cl; R = H; X′ = CH_2=CH_2	^{1}H (A)	3.13	0.98, 1.81 (C*Me*)	2.11, 2.58	2.57, 2.72 (N*Me*)								155
	^{13}C (A)	86.9	42.3	70.6	52.4, 52.4 (N*Me*)								
	^{103}Rh				652.4 (Rh)								
X′ = MeCN	^{1}H (A)	3.62	1.10, 1.74 (C*Me*)	1.74, 2.27	2.52, 2.62 (N*Me*)								155
	^{13}C (C)	73.0	42.1	72.6	53.5, 54.5 (N*Me*)								
	^{103}Rh				1696.3 (Rh)								
X′ = py	^{1}H (A)	3.14	0.99, 1.82 (C*Me*)	1.75, 2.26	2.51, 2.64 (N*Me*)								155
	^{13}C (E)	72.4	41.7	73.0	53.7, 54.6 (N*Me*)								
	^{103}Rh				2095.1(Rh)								
 4													
X = Cl; R = H; R = $CH_2CH(CO_2Et)_2$	^{1}H (A)	1.6-2.7 (m)	1.6–2.7 (m)	1.6–2.7 (m)	2.70, 2.72 (N*Me*)								14
X = Cl; R = R′ = Me	^{1}H (A)			2.22 (d), 2.68 (d)	2.77 (N*Me*)								15
X = Cl; R = Me; R′ = CHO	^{1}H (A)	3.56		2.12 (d), 3.66 (d)	2.55, 2.71 (N*Me*)		2.335 (1)	2.036 (4) [84.5(2)]	1.583 (7) [107.9(3)]	1.571 (7) [107.3(3)]	1.512 (6) [112.5(4)]	2.076 (4) [108.8(3)]	15, 16
X = Cl; R = Me; R′ = CO_2Me	^{1}H (A)			2.18 (d), 2.93 (d)	2.78 (N*Me*)								15
X = Br; R = Me; R′ = CHO	^{1}H (H)	3.64	1.01, 1.62 (C*Me*)	2.33, 3.65	2.62, 2.85 (N*Me*) 9.40 (C*HO*)	1642 (C=O)							16
X = I; R = Me; R′ = CHO	^{1}H (E)	3.66	1.01, 1.56 (C*Me*)	2.18, 3.72	2.68, 2.98 (N*Me*) 9.31 (C*HO*)	1640 (C=O)							16

X = SCN; R = Me; R' = CHO	^{1}H (E)	2.75	0.97, 1.46 (C*Me*)	2.19, 3.62	2.61, 2.78 (N*Me*) 9.20 (*CHO*)	1651 (C=O)						16
X = Cl; R = Me; R' = CH_2OMe	^{1}H (H)		0.94, 1.50 (C*Me*)	2.28, 3.18	2.78, 2.84 (N*Me*)							147



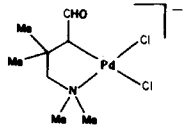
5

R = H	^{1}H (A)	3.08	1.03, 1.63 (C*Me*)	2.28 (d), 3.66 (d)	2.70, 2.87 (N*Me*) 9.12 (*CHO*)	1625						16
R = NMe_2	^{1}H (A)	3.02	1.04, 1.60 (C*Me*)	2.17 (d), 3.61 (d)	2.63, 2.80 (N*Me*) 9.03 (*CHO*)	1621, 1630 (C=O)	2.413 (1)	2.052 (4)	1.528 (5)	1.532 (6)	1.515 (5)	2.086 (3)	16, 17
R = CN	^{1}H (A)	3.05	1.07, 1.65 (C*Me*)	2.37 (d), 3.62 (d)	2.80, 2.94 (N*Me*) 9.38 (*CHO*)	1627, 1636 (C=O)							16



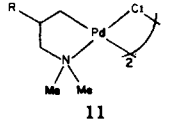
8

BF_4^-	^{1}H (B)	3.55	1.11, 1.61 (C*Me*)	2.65 (d), 3.85 (d)	2.92, 3.09 (N*Me*) 9.80 (*CHO*)	1640 (C=O)							16



9

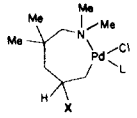
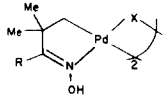
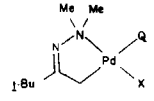
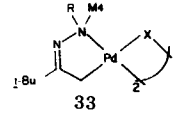
$PhCH_2N^+Et_3$	^{1}H (A)	3.57	1.00, 1.53 (C*Me*)	2.03 (d), 3.57 (d)	2.49, 2.72 (N*Me*) 9.19 (*CHO*)	1621 (C=O)							16

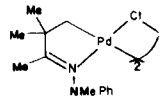


11

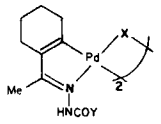
R = $CH(CO_2Et)_2$	^{1}H (A)	1.8, 2.1	2.6 (m)	2.4–2.6 (m)	2.67, 2.80 (N*Me*)							18
	^{13}C(A)	24.0, 25.0			49.7, 53.8 (N*Me*)							
monomers:	^{1}H (A)	0.93, 1.2	2.8 (m)	2.4–2.7 (m)	2.86 (N*Me*)	273						18
R = $CH(CO_2Et)_2$; L = PPh_3	^{13}C (A)	33.2	42.0	69.7	47.8, 52.1 (N*Me*)							
L = py	^{1}H (A)		2.5–2.8 (m)		2.86, 2.92 (N*Me*)	276						18
	^{13}C (A)	28.5	41.3	71.6	49.5, 54.0 (N*Me*)							

Table I (*Continued*)

complex	NMR[a] nucleus (solv)[b]	α	β	γ	other	IR (M–halogen), cm^{-1}	X-ray[c] M–halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
 18													
X = Cl; L = Me_2SO	^1H (B)	1.95 (m) 2.36 (dd)	3.99 (m)	3.37 (NCH_2)	2.85, 3.06 (N*Me*) 1.15, 1.19 (C*Me*)								20
X = Br; L = Me_2SO	^1H (B)	1.86–2.11 2.35	4.06 (m)	3.35 (NCH_2)	2.79, 3.02 (N*Me*) 1.15, 1.18 (C*Me*)	220 (Pd–Br)							20
X = Cl; L = py	^1H (A)	1.68–2.33 2.58	4.27 (m)	3.27 (NCH_2)	2.97, 3.53 (N*Me*) 1.18, 1.20 (C*Me*)								20
 19													
R = C_6H_5; X = Cl	^1H (A)	2.8	0.90 (C*Me*)			243, 298							23
R = Et; X = Cl	^1H (A)	2.5	1.15 (C*Me*)			240, 300							23
R = Me; X = Cl	^1H (A)	2.5	1.15 (C*Me*)	1.82 (C*Me*)		238, 297	2.34/2.54	2.023 (6) [79.8]	1.518 (8) [109.6]	1.516 (9) [108.1]	1.271 (4) [114.6]	1.997 [119.4]	23
R = Me; X = Br	^1H (A)	2.55	1.18 (C*Me*)	1.84 (C*Me*)		1655 (C=N)							23
R = Me; X = I	^1H (A)	2.55	1.19 (C*Me*)	1.84 (C*Me*)		1650 (C=N)							23
													
X = Cl; Q = PPh_3	^1H (A)	2.12 (d)	0.90 (C*Me*)		2.98 (N*Me*)	285							23
X = Cl; Q = PMe_2Ph	^1H (A)	2.35 (d)	1.15 (C*Me*)		2.85 (N*Me*)	283							23
X = Br; Q = PPh_3	^1H (A)	2.23 (d)	0.90 (C*Me*)		3.03 (N*Me*)								23
X = Br; Q = PMe_2Ph	^1H (A)	2.43 (d)	1.05 (C*Me*)		2.90 (N*Me*)								23
X = Q = diphos	^1H (A)	2.68 (dd)	1.05 (C*Me*)		2.5 (N*Me*)								23
X = Q = acac	^1H (A) ^{31}P (A)	2.95	1.15 (C*Me*)		2.82 (N*Me*) 33.85			1.991 (5)	1.506 (6)	1.274 (7)	1.483 (5)	2.027 (4)	23
 33													
X = Cl; R = Me	^1H (A)	3.15	1.02 (C*Me*)		2.86 (N*Me*)	255, 304							23
	^1H (E)	3.11	1.12 (C*Me*)		2.89 (N*Me*)								24
X = Cl; R = Ph	^1H (E)	3.35	1.26 (C*Me*)		3.55 (N*Me*)		2.334 (5)	1.985 (12) [80.7 (7)]	1.47 (3) [115 (1)]	1.51 (2) [111 (1)]	1.31 (1) [114 (1)]	1.996 (13) [119 (1)]	24, 166
X = Br; R = Me	^1H (A)	3.20	1.05 (C*Me*)		2.92 (N*Me*)								23
X = I; R = Me	^1H (A)	3.20	1.05 (C*Me*)		2.98 (N*Me*)								23

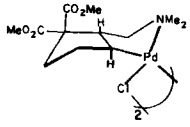


	^{1}H (E)	2.14	1.23 (C*Me*)	1.85 (C*Me*)	3.13 (N*Me*)							24



35

X = Cl; Y = Me	^{1}H (B)			1.94 (C*Me*)		207, 230						25
monomers: py	^{1}H (A)			1.93 (C*Me*)		231, 247, 288 (X = Cl) 203, 271 (X = Br)						25
PPh_3	^{1}H (A)			1.99 (C*Me*)		250, 296 (X = Cl) 200, 268 (X = Br)						25
X = Cl; Y = OMe	^{1}H (B)			1.93 (C*Me*)		240, 252						25
monomers: PPh_3	^{1}H (A)			2.05 (C*Me*)		276, 292						25
X = Cl; Y = NH_2	^{1}H (B)			1.88 (C*Me*)		232, 269						25



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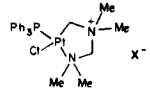
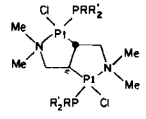
trans isomer												
monomer: PPh_3	^{1}H (A)	2.16	2.55	2.23, 2.60	2.89, 2.92 (N*Me*)							26
	^{13}C (A)	46.0	55.5	63.1	47.8, 51.9 (N*Me*)							
cis isomer												
monomer: PPh_3	^{1}H (A)	1.90	3.41	2.24, 2.24	2.89, 2.92 (N*Me*)							26
	^{13}C (A)	48.6	51.1	65.3	48.1, 52.2 (N*Me*)							



40

X = Cl	^{1}H (C)	3.30	3.14 (N*Me*)	4.28	3.15 (N*Me*)		2.362 (2)	2.017 (5) [82.2 (2)]	1.478 (7) [108.9 (3)]	1.482 (7) [106.9 (4)]	1.510 (6) [111.8 (4)]	2.134 (4) [108.2 (3)]	29
X = BF_4	^{1}H (C)	3.26	3.09 (N*Me*)	4.08	3.14 (N*Me*)								29



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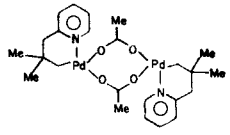
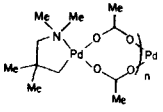
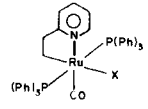
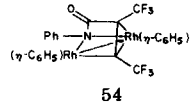
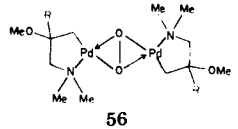
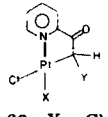
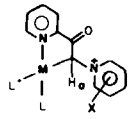
R = Ph; R^1 = Me	^{13}C (A)	35.4	35.4	72.3	46.2, 51.1 (N*Me*)	267						30
	^{31}P (A)				−14.9 (P)							
R = R^1 = Et	^{31}P (A)				4.5 (P)	255	2.420 (4)	2.067 (12) [83.6 (4)]	1.560 (16) [105.4 (7)]	1.509 (18) [105.5 (9)]	1.518 (16) [108.8 (9)]	2.180 (9) [105.8 (7)]	30

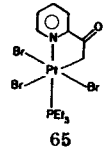
Table I (*Continued*)

complex	NMR[a] nucleus (solv)[b]	α	β	γ	other	IR (M–halogen), cm^{-1}	X-ray[c] M–halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
 44													
anti isomer	^{1}H (A)	1.81 (q)	0.44, 0.82 (C*Me*)	2.48 (q)	8.93 (6-py*H*)								31
syn isomer	^{1}H (A)	2.16	0.82, 0.90 (C*Me*)	2.69	8.24 (6-py*H*)								31
monomer: acac	^{1}H (A)	2.08	0.87 (C*Me*)	2.18	9.08 (6-py*H*)	1400, 1590 (*O,O'*-acac)							31
 45													
anti/syn (3:2)	^{1}H (A)[d]	2.40 (q)	1.33, 1.36 (C*Me*)	2.45	2.83, 3.01 (N*Me*)								32
	^{13}C (A)[e]	35.9	43.8	80.3	54.3 (N*Me*)								
 53													
X = Cl	^{1}H (A)	1.65 (t)	2.58 (t)			1888 (C=O)							35, 36
	^{13}C (A)	13.5	42.5	151.2	166.9 (6-py*C*)								
X = Br	^{1}H (A)	1.75 (t)	2.64 (t)			1900 (C=O)							36
	^{13}C (A)	13.4	42.5	166.8	152.4 (6-py*C*)								
 54													
	^{13}C			178.5				2.02/2.148	1.45 (1)	1.48 (1)	1.41 (1)	2.169/2.049	37
 56													
R = Me	^{1}H (A)	1.95	1.15 (C*Me*)	2.52	2.60, 2.85 (N*Me*)								38
													
60: X = Cl; Y = SMe_2	^{1}H	4.69 (*J* = 106)			9.30 (6-py*H*)	290, 334							40
61: X = SMe_2; Y = Cl	^{1}H	5.19 (*J* = 76)			9.64 (6-py*H*)		2.397 (3)	1.987 (10) [83.1 (3)]	1.53 (1) - [110.9 (6)]	1.49 (1) [113.4 (9)]	1.36 (1) [114.5 (8)]	2.044 (7) [115.6 (6)]	40



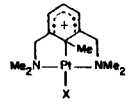
63

M = Pt; L = Cl;	^{1}H (F)	6.42 (J = 142)			9.34 (6-py*H*)							42
X = 4-Me	^{13}C (G)	68.0	200.4	153.3	145.6 (6-py*H*)	291, 330						
M = Pd; L = Cl;	^{1}H (F)	6.91			9.00 (6-py*H*)	296, 336						42
X = 4-Me												
M = Pt; L = Cl;	^{1}H (F)	6.36 (J = 143)			9.36 (6-py*H*)	290, 337						42
X = 3,5-Me$_2$	^{13}C (G)	69.3	200.3	153.4	143.2 (6-py*C*)							
M = Pd; L = Cl;	^{1}H (F)	6.36			9.36 (6-py*H*)	290, 337						42
X = 3,5-Me$_2$												
64: M = Pt;							2.001 (1)	1.39 (2)	1.44 (2)	1.41 (2)	1.99 (1)	41
L = $(H_2NCH_2)_2$;							[80.0 (5)]	[117.4 (9)]	[112.3 (10)]		[115.4 (9)]	
X = 3,5-Me$_2$												



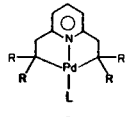
65

	^{1}H (A)	4.3 (J = 56)			10.0 (6-py*H*)							43
	^{31}P				6.55 (P)							



70

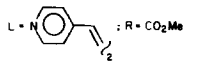
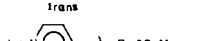
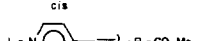
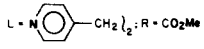
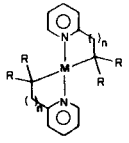
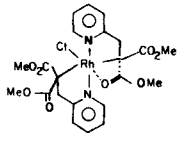
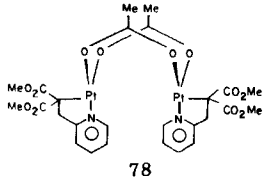
X = Cl (OTf$^-$)	^{1}H (A)	3.12 (C*Me*, J = 10)		3.84, 4.81	2.51, 2.88 (N*Me*)							44
X = Br (OTf$^-$)	^{1}H (A)	3.13 (C*Me*, J = 11)		3.85, 4.82	2.52, 2.88 (N*Me*)							44
X = I (OTf$^-$)	^{1}H (A)	3.12 (C*Me*, J = 9)		4.13, 4.83	2.61, 3.05 (N*Me*)							44
X = C$_6$H$_4$Me(*o*) (I$^-$)	^{1}H (A)	3.39 (C*Me*, J = 9)		4.05, 4.99	2.42, 2.61 (N*Me*)	2.005 (9) (Pt–C) [101.4] [Pt–C–Me]	2.293 (9) [85.4 (3)] [85.7 (3)]	1.35 (1) 1.44 (1) [89.1 (6)] [87.0 (5)]	1.44 (1) 1.54 (1) [118.1 (8)] [115.4 (8)]	1.53 (1) 1.49 (1) [104.7 (7)] [107.5 (8)]	2.094 (7) 2.090 (7) [106.6 (5)] [103.8 (5)]	44
X = C$_6$H$_4$Me(*p*) (I$^-$)	^{1}H (H)	3.32 (C*Me*, J = 8)		4.13, 5.00	2.46, 2.54 (N*Me*)							44
X = C$_6$H$_4$Me(*p*) (OTf$^-$)	H (A)	3.32 (C*Me*, J = 8)		3.86, 4.90	2.68, 2.78 (N*Me*)							44
X = I (BF_4^-)	^{1}H (H)	3.27 (C*Me*, J = 8)		3.97, 5.08	2.69, 3.15 (N*Me*)	2.581 (17) (Pt–I) [104.2] (Pt–C–Me)	2.183 (7) [87.1 (3)] [85.0 (3)]	1.40 (1) 1.40 (1) [88.9 (5)] [93.4 (5)]	1.48 (1) 1.51 (1) [116.3 (7)] [116.6 (7)]	1.50 (1) 1.50 (1) [106.3 (6)] [104.3 (6)]	2.106 (6) 2.123 (6) [103.2 (4)] [106.8 (5)]	44, 45

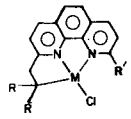


72

L = py; R = COMe	^{1}H (A)		4.0		1.90 (CO*Me*)							
L = py; R = CO_2Et	^{1}H (A)		3.85				2.140 (5)	1.556 (6)	1.482 (7)	1.348 (5)	1.967 (5)	46,
	^{13}C (A)	51.0	42.8	169.6			[81.8 (1)]	102.8 (3)	[111.1 (4)]	[114.5 (4)]	[117.9 (3)]	47
	^{1}H (A)		3.8		8.65 (pyra*H*)	2.050 (3)	2.175 (3)	1.558 (4)	1.486 (5)	1.332 (4)	1.978 (3)	48
L•N ; R•CO_2Et						(Pd–N2)	2.143 (3)	1.539 (5)	1.492 (5)	1.351 (4)	1.978 (3)	
							[80.9 (1)]	[101.8 (1)]	[111.1 (3)]	[118.6 (3)]	[118.6 (1)]	
							[80.5 (1)]	[102.5 (1)]	[110.4 (3)]	[114.2 (3)]	[117.8 (1)]	
L•N ; R•CO_2Me	^{1}H (A)		3.87		3.40 (O*Me*)							48

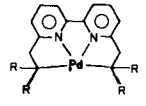
Table I (*Continued*)

complex	NMR[a] nucleus (solv)[b]	α	β	γ	other	IR (M-halogen), cm^{-1}	X-ray[c] M–halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
	^{1}H (A)		3.86		3.68, 3.74, 3.98, 4.04 (OCH_3)								48
	^{1}H (A)		3.88		3.41 (O*Me*); 7.25 (= H)								48
trans 	^{1}H (A)		3.81		3.43 (O*Me*); 6.72 (= H)								48
cis 	^{1}H (A)		3.82		3.37 (O*Me*)								48
	^{1}H (A)		3.87		3.41 (O*Me*); 3.01 (pyCH_2)								48
 **73**: $n = 1$ **74**: $n = 2$													
R = CO_2Me; M = Pd; $n = 1$	^{1}H (A)		3.75		9.06 (6-py*H*)			2.156 (2)	1.522 (4)	1.498 (4)	1.338 (4)	2.040 (3)	49
	^{13}C (A)	53.6	43.1 (t)	171.8				[79.6 (1)]	[100.3 (2)]	[110.7 (2)]	[114.2 (2)]	[125.6 (2)]	
$n = 1$; R = CO_2Me; M = Pt	^{1}H (A)		3.66		9.25 (6-py*H*)			2.159 (6) 2.142 (6) [80.6 (2)] [80.4 (2)]	1.548 (8) 1.531 (8) [101.6 (4)] [101.3 (4)]	1.500 (9) 1.474 (9) [109.8 (5)] [110.8 (6)]	1.376 (8) 1.363 (8) [114.8 (5)] [114.5 (6)]	2.013 (5) 2.021 (5) [115.1 (4)] [114.8 (4)]	53
R = CO_2Me; M = Pd; $n = 2$	^{1}H (A)							2.190 (9)	1.535 (12)	1.480 (13)	1.340 (10)	2.038 (7)	50
	^{13}C (A)	45.6	28.6 (t)	42.4 (t)	162.8			[84.5 (3)]	[109.9 (6)]	[111.0 (8)]	[116.0 (7)]	[120.3 (6)]	
 77													
	^{1}H (A)		2.97, 3.69		9.09 (6-py*H*)			2.052 2.097	1.539 1.537	1.507 1.486	1.338 1.356	2.006 2.044	52
	^{13}C (A)	31.7, 30.4	57.3	167.6	152.4 (6-py*C*)			[81.7] [81.8]	[105.4] [108.2]	[111.0] [111.0]	[112.7] [115.4]	[117.5] [116.4]	
 78													
	^{1}H (A)		2.97, 3.75		8.26 (6-py*H*)			2.055 (14) 2.073 (14) [81.05 (5)] [83.0 (5)]	1.563 (19) 1.559 (19) [105 (1)] [108 (1)]	1.488 (19) 1.466 (18) [109 (1)] [107 (1)]	1.375 (17) 1.368 (17) [114 (1)] [121 (1)]	2.019 (10) 1.983 (13) [115.3 (9)] [113.0 (10)]	53



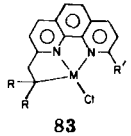
81

R = CO_2Et; X = Cl; M = Pd	^{1}H (E)		3.93		4.29 (C*H*)	322, 353	2.313 (2)	2.089 (9) [82.8 (3)]	1.551 (12) [106.1 (6)]	1.495 (14) [112.1 (7)]	1.345 (11) [114.1 (8)]	1.971 (6) [118.5 (5)]	54, 55
	^{13}C (A)	45.4	**47.6**	**169.2**									
R = CO_2Et; X = OAc; M = Pd	^{1}H (A)		**3.65**		1.96 ($COCH_3$)		2.047	2.066 [83.8]	1.62 [107]	1.47 [111]	1.35 [116]	1.969 [118]	55



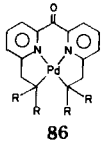
82

R = CO_2Me	^{1}H (A)		**4.02**		3.77 (O*Me*)								55
R = CO_2Et	^{1}H (E)		**3.90**					2.152 (5)	1.581 (7)	1.505 (7)	1.328 (6)	1.979 (4)	55
	^{13}C (A)	47.4	**48.0**	169.6				2.141 (5) [82.5 (2)] [81.5 (2)]	1.534 (7) [103.6 (3)] [105.3 (3)]	1.514 (7) [112.0 (4)] [112.4 (4)]	1.334 (6) [113.8 (4)] [113.2 (4)]	1.983 (3) [119.8 (3)] [119.9 (3)]	
R = CO_2-*i*-Pr	^{1}H (A)		3.88		4.94 (OC*H*)								55



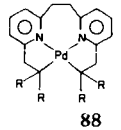
83

R = CO_2Me; R^1 = $CH_2CH(CO_2Me)_2$	^{1}H (A)		3.86			320, 342							55
	^{13}C (A)	45.1	48.5	168.7	51.9 (O*Me*)								
R = CO_2Et; R^1 = $CH_2CH(CO_2Et)_2$	^{1}H (A)		3.79										55
R = CO_2-*i*-Pr; R^1 = $CH_2CH(CO_2$-*i*-Pr$)_2$	^{1}H (A)		3.81				2.286 (3)	2.089 (10) [82.1 (3)]	1.557 (13) [105.6 (5)]	1.490 (13) [111.9 (9)]	1.336 (12) [112.6 (8)]	1.956 (7) [120.3 (5)]	55



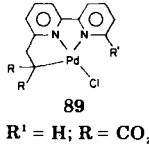
86

R = CO_2Et	^{1}H (A)		3.64			1674 (C=O)							57



88

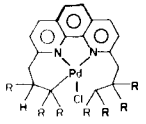
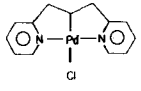
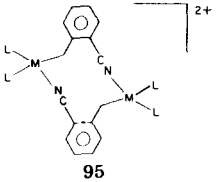
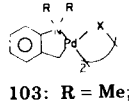
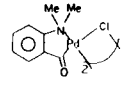
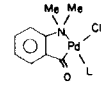
R = CO_2Me	^{1}H (A)		3.48		3.11 (CH_2)$_2$			2.108 2.090 [79.7] [78.3]	1.544 1.528 [103.1] [102.5]	1.484 1.484 [110.7] [110.8]	1.324 1.333 [114.9] [116.7]	2.112 2.184 [114.4] [109.7]	57

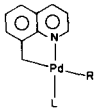


89

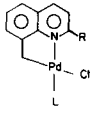
R^1 = H; R = CO_2Me	^{1}H (A)		3.83		8.81 (6-py*H*)		2.083	2.083 (3)				1.949/ 2.088	55
	^{13}C (A)	46.4	47.5	171.4	150.3 (6-py*C*)			[83.5 (1)]	[105.9 (2)]	[113.0 (2)]	[113.4 (3)]	[119.4]	

Table 1 (*Continued*)

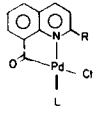
complex	NMR[a] nucleus (solv)[d]	α	β	γ	other	IR (M–halogen), cm^{-1}	X-ray[c] M–halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
R' = Me; R = CO_2Me	^1H (A)		3.62		2.98 (6-py*Me*)								57
	^{13}C (A)	46.7	47.5	169.3	26.7 (6-py*Me*)								
 92													
R = CO_2Me	^1H (A)			4.22	4.55 (C*H*)		2.329 (2)	2.090 (6) [95.0 (2)]	1.565	1.565 [111.0]	1.318 [120.5]	2.064 (5)	57
 93													
	^1H (A)	39.7 (sep)	2.53, 3.50 (d)			331							59
	^{13}C (A)	45.1	46.6										
 95													
M = Pt; L = diphos	^1H (A)	3.1 (J = 77)				2258 (C≡N)		2.13 (2)	1.54 (4)	1.46 (4)	1.41 (4)	2.02 (2)	62
						1050 (BF_4)		2.12 (2)	1.51 (3)	1.45 (3)	1.47 (3)	2.04 (2)	
$2BF_4^-$	^{31}P (A)				38.2, 51.1			[88.8 (8)] [89.4 (8)]	[108 (2)] [110 (1)]	[122 (2)] [125 (2)]	[119 (2)] [118 (2)]	[170 (3)] [176 (2)]	
													
103: R = Me; X = Cl	^1H (A)	3.39, 3.40			3.31 (N*Me*)	257, 315							64
	^{13}C (E)	22.71, 23.91			53.42 (N*Me*)								
102a: R = Me; X = OAc	^1H (A)	3.95, 4.01			3.30–3.43 (N*Me*)								64
	^{13}C (E)	22.7, 22.95			54.49 (N*Me*)								
monomer:	^1H (E)	3.36			3.25 (N*Me*)	275							64
X = Cl; L = py	^{13}C (E)	27.81			53.55 (N*Me*)								
X = Br; L = py						195							
X = Cl; L = PPh_3	^1H (E)	2.4			3.24 (N*Me*)	272							64
	^{13}C (E)	31.84			51.47 (N*Me*)								
 195													
	^{13}C (A)	191.2	127.5	156.0	45.6 (N*Me*)	1576 (C=O)							108
													
L = PPh_3	^{13}C (A)	210.7	142.3	157.4	52.6 (N*Me*)	1658 (C=O)							108



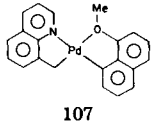
105: L = CO; R = Cl	^{1}H (A)	3.95			9.54 (2-quin*H*)	288						67
	^{13}C (A)	24.7	148.7	149.4								
106: L = $PPhMe_2$;	^{1}H (A)	3.50			9.18 (2-quin*H*)			2.074 (12)	1.514 (14)		1.414 (13)	2.150 (7)	67
R = $Mo(CO)_3(\eta\text{-}C_5H_5)$								[175.0 (02)]	[109.6 (08)]			[111.0 (6)]	
L = $PPhMe_2$;	^{1}H (A)	3.41			9.33 (2-quin*H*)								67
R = $Co(CO_4)$													
L = $Mo(CO)_3(\eta\text{-}C_5H_5)$;	^{1}H (A)	2.89			8.69 (2-quin*H*)								67
R = 4-MePy													
L = $Co(CO)_4$; R = py	^{1}H (A)	3.10			8.80 (2-quin*H*)								67
L = $Fe(CO)_3NO$;	^{1}H (A)	3.42			8.51 (2-quin*H*)	1704,							67
R = py						1682 (NO)							
L = $Mo(CO)_3(\eta\text{-}C_5H_5)$;	^{1}H (A)	3.89			9.07 (2-quin*H*)								67
R = CO													
L = $Co(CO)_4$; R = CO	^{1}H (A)	4.19			9.34 (2-quin*H*)								67
L = PEt_3; R = Cl	^{1}H (A)	3.12			9.58 (2-quin*H*)								70
	^{13}C	24.3 (d)	129.0	127.6	149.7 (2-quin*H*)								
115:	^{1}H (E)	3.02 (d)				161, 172	2.566 (1)	2.046 (6)				2.094 (5)	74,
L = $PPh_2CH_2CO_2Et$;	^{31}P (E)				28.7 (P)		(Pd–Br)	[81.92 (2)]					75
R = Br	^{13}C (E)	34.25											



L = PEt_3;	^{1}H (A)	3.16			3.66 (N*Me*)							69
R = CH=NMe	^{13}C (A)	24.7	148.7	129.7	49.8 (N*Me*)							
L = PEt_3; R = CH_2OH	^{1}H (A)	3.15			5.05 (CH_2O)							70
	^{13}C (A)	24.7	147.9	128.0	65.4 (CH_2O)							
					149.6 (2-quin*C*)							

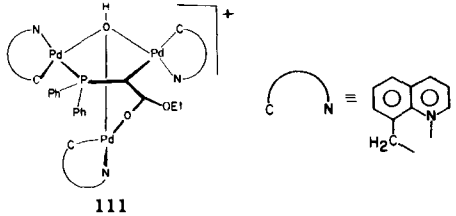


L = PPh_3	^{1}H (A)				10.14 (2-quin*H*)	1670 (C=O)						108
	^{13}C (A)	206.6	143.8	149.1	152.8 (2-quin*C*)							108
	^{31}P (A)				39.1 (P)							
L = PEt_3	^{13}C (A)	212.9	144.3	149.1	152.1 (2-quin*C*)							108



107

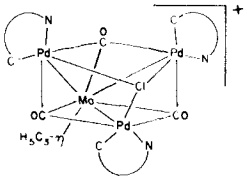
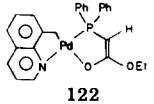
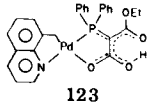
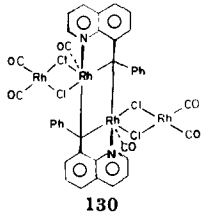
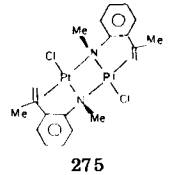
	^{1}H (A)	3.71			4.43 (O*Me*)			2.002 (7)	1.491 (8)	1.397 (7)	1.380 (9)	2.127 (6)	72
	^{13}C (E)	21.6			61.0 (O*Me*)			[82.8 (2)]	[109.7 (4)]		[116.2 (5)]	[111.5 (3)]	

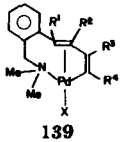


111

PF_6^-	^{1}H (E)	2.56, 3.29						2.03 (1)				2.15 (1)	74
	^{31}P (E)				33.7 (P)			[81.6 (5)]					

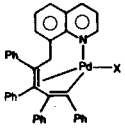
Table I (*Continued*)

complex	NMR[a] nucleus (solv)[b]	α	β	γ	other	IR (M–halogen), cm^{-1}	X-ray[c] M–halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
								2.06 (2) [86.2 (6)]				2.06 (2)	
								2.01 (1) [83.7 (6)]	1.51 (4) [108 (4)]	1.38 (4) [117 (3)]	1.37 (2) [116 (2)]	1.99 (1) [112 (2)]	
 113													
BF_4^-	^1H (E)	3.80				1065 (BF)	2.520 (2)	2.014 (9) [82 (5)]				2.097 (6)	74, 75
							2.525 (2)	2.023 (9) [81.6 (3)]				2.118 (6)	
							2.520 (2)	2.006 (9) [83.0 (3)]				2.089 (6)	
 122													
	^1H (E)	3.22 (d)											75
	^{31}P (E)				17.0								
	^{13}C (E)	20.77			179.96 (C=O)								
 123													
	^1H (E)	3.12 (d)						2.05 (2) [83.7 (10)]	1.50 (3) [107 (2)]	1.42 (3) [119 (2)]	1.40 (3) [115 (3)]	2.06 (3) [113 (2)]	75
 130													
	^1H (E)				8.28 (2-quin*H*)		2.364 (2) 2.368 (2)	2.083 (6)				2.099 (4)	78
 275													
	^1H (A)				3.40 (N*Me*)		2.318 (9)	2.09 (3) [85.6 (10)]	1.55 (4) [107 (2)]	1.39 (4) [116 (3)]	1.45 (3) [120 (3)]	2.07 (2) [110 (2)]	152
	^{13}C (A)	114.6	155.3	139.7									



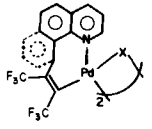
139

R = C_6H_5; X = Cl	^{1}H (E)			2.76	2.32, 2.70 (N*Me*)	320						88
R^1 = R^3 = Me; R^2 = R^4 = Ph; X = Cl	^{1}H (E)		1.58, 2.16 (C*Me*)	2.65, 2.76	2.64, 2.97 (N*Me*)	305						88
R^1 = R^3 = Me; R^2 = R^4 = Ph; X = Br	^{1}H (E)		1.54, 2.16 (C*Me*)	NA	2.71, 296 (N*Me*)	182–202	2.449 (2)	2.295 (14) [~99.6]	1.416 (22) [126.1 (0.9)]	1.519 (22) [125.6 (0.9)]	1.528 (20) [112.8 (0.8)]	2.247 (12) [110.2 (0.9)]	88
R^1 = R^4 = Me; R^2 = R^3 = Ph; X = Cl	^{1}H (E)	2.15/2.32 (C*Me*)		2.69, 2.82	2.60, 2.77 (N*Me*)	306	2.337 (4)	2.237 (13) [~101.4]	1.364 (20) [127.2 (1.1)]	1.530 (20) [124.9 (0.9)]	1.547 (15) [114.0 (0.8)]	2.222 (11) [110.6 (0.8)]	88



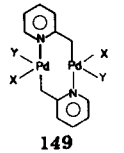
137

X = Cl				3.98, 4.16		312						88



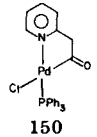
138: X = Cl
141: X = Cl; 

						317, 255						88
						315, 266						88



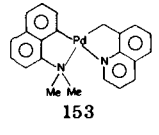
149

X = Cl; Y = PPh_3	^{1}H (E)	2.44 (t) 3.81 (d)				284 420 (Pd–P)	2.406 (2)	2.072 (5) [90.5 (2)]	. . . [115.6 (4)]	. . .	1.339 (9) [117.9 (5)]	2.104 (5) [1.215 (4)]	93
							2.405 (1)	2.071 (3) [90.7 (1)]	1.474 (5) [115.4 (2)]		1.344 (5) [117.8 (3)]	2.102 (3) [121.5 (4)]	93
X = H_2O; Y = PPh_3 ClO_4^-	^{1}H (E)	2.72 (t) 4.38 (dd)			7.76 (6-py*H*)	1600 (C=N)							33
	^{13}C (E)	26.2	164.2		151.1 (6-py*C*)								



150

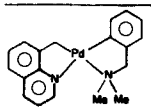
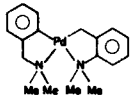
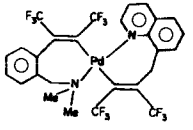
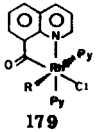
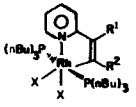
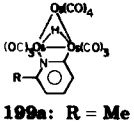
			4.11			292 427 (Pd–P)						93

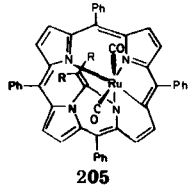


153

	^{1}H (E)	3.36			3.38 (N*Me*)							96
	^{13}C (E)	23.4			52.0 (N*Me*)							

Table I (*Continued*)

complex	NMR[a] nucleus (solv)[b]	α	β	γ	other	IR (M–halogen), cm^{-1}	X-ray[c] M–halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
 **154**													
	^1H (E)	3.25			2.79 (N*Me*)								96
	^{13}C (E)	21.9			49.8 (N*Me*)								
 **155**													
	^1H (E)	2.79			2.61, 3.03 (N*Me*)								96
	^{13}C (E)	21.8			49.6, 50.7 (N*Me*)								
 **158**													
trans N-donors	^1H (A)			2.95, 3.98	1.66, 2.63 (N*Me*)			2.016 (9) [90.31 (0.36)]			1.484 (13)	2.215 (8)	96 96
cis N-donors	^1H (A)			2.90, 3.99	1.67, 2.70 (N*Me*)			2.004 (10) [86.94 (0.35)]			1.321 (13)	2.119 (8)	
 **179**													
R = CH_2Ph	^1H (A)				10.28 (2-quin*H*)		2.545 (1)	1.949 (4)				2.042 (3)	103
 **189**													
$R^1 = R^2 = H$; X = Cl	^1H (A)	9.30	6.62		9.47 (6-py*H*)								105
	^{13}C (A)	186	129.3	168.2	151.5 (6-py*C*)								
$R^1 = H$; R^2 = Me; X = Br	^1H (A)	2.66 (*Me*)	6.42		9.70 (6-py*H*)								105
	^{13}C (A)	196.9	128.6	167.7	152.5 (6-py*H*)								
$R^1 = R^2$ = Me; X = Br	^1H (A)	2.64 (*Me*)	1.99 (*Me*)		9.86 (6-py*H*)								105
	^{13}C (A)	187.6	130.0	168.3	153.1 (6-py*H*)								
 **199a**: R = Me	^1H (A)				−14.34 (Os*H*)								113
204: R = 2-py								2.926 (4) (Os–Os)	2.118 (12) (OsC)		1.352 (14) (N–C)	2.058 (9)	113



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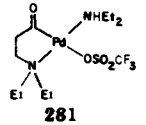
R = $C_6H_4Cl(p)$						2.086 (6)				2.206 (5)	115
						1.938 (11) [85.3 (4)]	1.52 (1) [113.0 (8)]	1.50 (1) [112.7 (10)]	1.47 (2) [112.1 (10)]	2.117 (8) [107.5 (6)]	156



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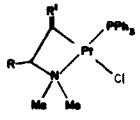
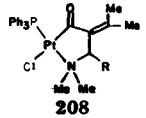


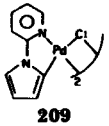
207

c: R = R¹ = H					2.396 (3)	2.055 (11) [70.6 (4)]	1.512 (18) [95.6 (8)]		1.584 (19) [102.4 (10)]	2.123 (7) [90.8 (7)]	117
a: R = H; R¹ = CMe_2	^{1}H (A)		2.87 (N*Me*)		2.370 (2)	2.002 (7) [68.6 (3)]	1.515 (10) [95.9 (4)]		1.538 (8) [99.0 (5)]	2.115 (5) [90.8 (4)]	116, 117



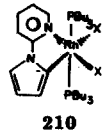
208

R = H	^{1}H (A)	3.53	3.09 (N*Me*)	265							116
R = Me	^{1}H (A)	3.58	3.04, 3.10 (N*Me*)	255							116



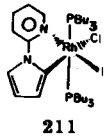
209

	^{1}H (A)		8.93 (6-py*H*)	226, 265							118



210

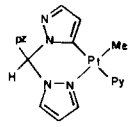
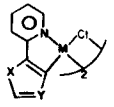
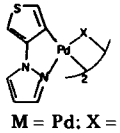
X = Cl	^{1}H (A)		9.47 (6-py*H*)	241, 279							118
X = Br	^{1}H (A)		9.61 (6-py*H*)								118

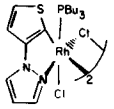


211

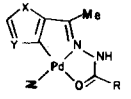
			9.78 (6-py*H*)	279							118

Table I (*Continued*)

complex	NMR[a] nucleus (solv)[b]	α	β	γ	other	IR (M-halogen), cm^{-1}	X-ray[c] M–halogen	Bd1 [1]	Bd2 [2]	Bd3 [3]	Bd4 [4]	Bd5 [5]	ref
													
213								1.969 (8) [89.0 (3)]				2.100 (8)	120
													
217													
a: X = S; Y = CH; M = Ir	^{1}H (E)				9.07 (6-py*H*)	224, 245							123
monomers: L = Me_2SO	^{1}H (B)				9.45, 9.77 (6-py*H*)	255							123
L = py	^{1}H (A)				7.94, 9.72 (6-py*H*)	243							123
L = PBu_3	^{1}H (A)				8.78, 9.77 (6-py*H*)	253							123
halogen = Br; L = PBu_3	^{1}H (A)				8.76, 9.91 (6-py*H*)								123
halogen = I; L = PBu_3	^{1}H (A)				8.75, 10.11 (6-py*H*)								123
b: X = S; Y = CH; M = Pd	^{1}H (B)				9.08 (6-py*H*)	217, 247							124
monomers: L = py	^{1}H (A)				9.35 (6-py*H*)	242							124
L = PBu_3	^{1}H (A)				9.36 (6-py*H*)	242							124
halogen = Br; L = py	^{1}H (A)				9.52 (6-py*H*)								124
halogen = Br; L = PBu_3	^{1}H (A)				9.63 (6-py*H*)								124
c: X = S; Y = CH; M = $Ru(CO)_2$	^{1}H (B)				9.27 (6-py*H*)	238, 279, 288							124
monomers: L = py	^{1}H (B)				9.37 (6-py*H*)	298							124
L = PBu_3	^{1}H (A)				8.38 (6-py*H*)	298							124
d: X = S; Y = CH; M = $RhPBu_3Cl$;	^{1}H (B)			9.38 (6-py*H*)	225, 273, 328								124
halogen = Br	^{1}H (B)				9.55 (6-py*H*)	204							124
e: X = CH; Y = S; M = Pd	^{1}H (B)				9.50 (6-py*H*)	248, 209							124
monomers: L = py	^{1}H (A)				9.32 (6-py*H*)	248							124
L = PBu_3	^{1}H (A)				9.37 (6-py*H*)	250							124
halogen = Br; L = py	^{1}H (A)				9.50 (6-py*H*)								124
halogen = Br; L = PBu_3	^{1}H (A)				9.60 (6-py*H*)								124
f: X = CH; Y = S; M = $RhPBu_3Cl$	^{1}H (B)				9.32 (6-py*H*)	228, 256, 343							124
													
M = Pd; X = Cl	^{1}H (B)				8.65 (3-pyrz)	223, 252							125
X = Br	^{1}H (A)				7.94 (3-pyrz)	339							125
monomer:	^{1}H (B)				8.12 (3-pyrz)	210							125
L = py	^{1}H (A)				7.48 (3-pyrz)	252							125
L = PBu_3	^{1}H (A)				7.83 (3-pyrz)	250							125
X = I; L = PBu_3	^{1}H (A)				7.80 (3-pyrz)								125



	^{1}H (B)		8.72 (3-pyrz)	231, 274, 318	125
monomer: L = PBu_3	^{1}H (A)		8.13 (3-pyrz)	246, 313	125



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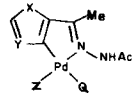
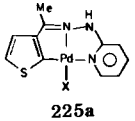
X = S; Y = CH; Z = Cl		2.05, 2.30 (C*Me*)	7.56, 7.83 (Thio*H*)	287, 363	126
X = S; Y = CH; Z = Br		2.08, 2.28 (C*Me*)	7.50, 7.79 (Thio*H*)	217	126



X = S; Y = CH; Z = py; Q = Cl	^{1}H (A)	2.18, 2.32 (C*Me*)	6.33, 7.40 (Thio*H*)	242	126
X = S; Y = CH; Z = py; Q = Br	^{1}H (A)	2.19, 2.32 (C*Me*)	6.35, 7.37 (Thio*H*)		126
X = S; Y = CH; Z = PBu_3; Q = Cl	^{1}H (A)	2.17, 2.34 (C*Me*)	6.95, 7.46 (Thio*H*)	293	126



225a

X = Cl	^{1}H (B)		7.98 (6-py*H*)	328	128
X = Br	^{1}H (B)		8.05 (6-py*H*)		128
X = I	^{1}H (B)		8.27 (6-py*H*)		128

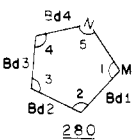
[a] In complexes having four-membered cyclometalated ring, the coordinating carbon is numbered α, while the carbon next to the coordinating nitrogen is numbered as γ. In six- and higher-membered cyclometalated rings, the coordinating carbon is numbered α, the carbon next to it is numbered β, and the carbon next to the coordinating nitrogen is numbered γ. For π-complexes, both the π-bonded carbons are numbered as α, while the carbon next to the coordinating nitrogen is numbered γ. [b] NMR solvents: A = $CDCl_3$; B = $(CD_3)_2SO$; C = CD_3CN; D = $C_6D_5NO_2$; E = CD_2Cl_2; F = SO_2; G = CD_3OD; and H = $(CD_3)_2CO$. [c] Bond distances are in angstroms. Bond angles [in brackets] are in degrees. [d] 14 °C. [e] 24 °C.

Metal–halogen vibrations occur in the region from 400 to 100 cm^{-1}. These signals are usually strong; thus the particular frequency and number of signals can be related to isomeric geometry, metal–halogen separation, and stereochemistry within the coordination sphere. The frequency of metal–halogen vibrations are of interest when the halogen is trans to a C-donor; numerous examples are shown in Table I. The absorption for a halogen trans to carbon is shifted to much lower energy than when trans to nitrogen. The stereochemistry of coordinated carbon and halogen can be ascertained as cis or trans simply by finding the number of peaks due to metal–halogen (one for trans and two for cis) in the 400–100 cm^{-1} region. σ-C-Donors have been found by this technique; controversy still remains as to which kind of C-donor, i.e., alkyl, alkenyl, aryl, benzyl, or acyl, is the strongest σ-donor. Limited evidence suggests that the σ-bonded acyl carbon may win out.[156]

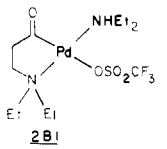
C. X-ray Structural Determinations

Numerous crystal structure determinations of these organometallics have been completed to date and have indicated a remarkable similarity between chelate rings. Unfortunately of the complexes herein reviewed, few correlatable series are yet available in which two or more types of pertinent spectral data have been reported. As X-ray crystallography becomes more routien, such comparative studies for example with ^{13}C NMR data will follow.

Table I lists key structural data, which deal directly with the chelate ring. The headings are defined by **280**. Below the bond lengths are the designated bond angles. In general, the five-membered metallacyclic ring is *not* flat preferring a pseudoenvelope conformation. The average N–metal distance in σ-complexes is 2.06 Å and in π-complexes is 2.09 Å. The C–metal distance averages 2.08 Å for a σ-bond and 2.14 Å for a π-bond. The structural analysis of **281** has revealed an unusually short C–Pd bond, which (1.938 Å) is even shorter than the ylide C–metal distance of **64**[41] and is the shortest C–Pd bond for a cyclometalated carbon yet reported.[156] The structural effect of this short bond is to force the trans ligands to exceptionally long bonding distances.[156]



280



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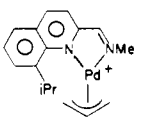
Of all the listed complexes for which X-ray data are available, the σ-complexes **4a** and **5** have the most ideal geometry. Thus, saturated five-membered ring appears to be well suited to form the expected bond angles in the chelate ring. Interestingly, **74** has bond angles which closely approach the expected or predicted angles, although it has a *six*-membered chelate ring; **74** exhibits totally comparable physical properties to the related five-membered analogue.

Structural determinations have been used to confirm suspected molecular irregularities. Complex **5** demonstrated an unusual absorption (IR) for the aldehydic carbonyl group. The X-ray data for **5** have revealed that there was a large contribution due to the enolic resonance hybrid, in which the coordinated carbon had a geometry which was distorted toward sp^2 hybridization and the C(carbonyl)–C bond was appreciably shortened (1.460 Å; 1.505 Å was predicted).[17] X-ray results for **64** also showed the similar phenomenon for carbonyl–ylide C bond distance (1.39 Å), which is shortened even more drastically than in **5** and approaches C=C bond character.[41] X-ray determinations have been useful for delineating the geometry of π-bonded double bonds in relation to the coordination sphere and to confirm hypothesized metal–hydrogen interactions from spectral analysis.[148]

IV. Conclusions

In general, there are only four basic reactions that lead to cyclometallation. To date in the reviewed series, each involves initial N-coordination. The differentiation occurs in the second step, i.e., formation of the C–metal bond. Type I is a simple anionic displacement reaction, which encompasses nucleophilic attack on the metal by a stabilized carbanion, an aromatic ring, or a juxtaposed electron pair. Type II utilizes either a C–H or C–C insertion process (oxidative addition) involving a nonzero oxidation state for metal. For C–H insertion the resulting oxidized complex can either undergo reductive elimination of HX or remain in the oxidized state if the hydrido species is stable. For example, the benzyl group undergoes facile C–H bond insertion. Type II is generally differentiated from Type I because the pK_a of the C–H bond is sufficiently high to make this group relatively nonacidic; thus, the formation of a carbanion under typical conditions (i.e., weak base or no base) for cyclometalation is not likely. A corollary to Type II can be seen in the cyclopalladation of 8-isopropylquinoline where it has been shown that the C–H bond activation in the square-planar complexes involve short CH···M axial interactions. 8-Isopropylquinoline in **282** did not result in the cyclometalated



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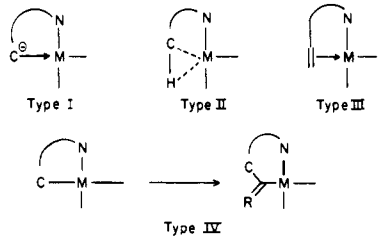
product even under forcing conditions probably due mostly to distortions in coordination forcing the isopropyl group out of the desired orientation for cyclization.[69,157] Newkome et al. have also observed similar type of distortions in the Pd(II) complexes of bipyridine systems.[55] Type III involves oxidative addition of a carbon group to a zerovalent metal. The carbon group may be a C–H, C–C, C–halogen, or C–metal system. Type IV is exemplified by a carbon group insertion into an already existing C–metal bond of a metallocyclic ring (Chart I).

There do not appear to be any a priori rules for predicting the stability of a metallocyclic system, since a myriad of carbons in diverse degrees of hybridization coordinate various metals to generate organometallics with wide-ranging stability characteristics. However, it is obvious that the five-membered ring size is the most common variable in the cyclometalated examples, yet reported. The reason for five-membered ring stability embraced by most researchers is that this ring size

CHART I. Types of Carbon–Metal Bond-Forming Reactions



should have the most ideal geometries (bond angles) of all the possible ring sizes. While the five-membered ring has been shown by X-ray structure determination to have fairly ideal geometries, the one X-ray structure of a six-membered ring in a Pd complex (**74**) also has relatively strain-free bond angles and lengths;[50] thus the enhanced mobility in larger ring may permit a chelate ring to approach the idealized orientation. Steric bulk both on the metallacyclic ring and in other coordinating ligands is another factor that gives stability to systems that otherwise are not stable.

The general reactivity of metallacyclic complexes has been studied in a limited fashion. Further studies aimed toward using the complexes as synthetic intermediates and catalyst[13] would be timely.

Note Added in Proof. Albinati et al.[159] have recently reported carbonylation and isonitrile insertion into the Pd–C bond of cyclopalladated benzylideneaniline Schiff's base complexes. The reaction conditions and products formed are similar to that of **147** and **149**. Many other interesting rhodium[160] and ruthenium[161] clusters have been synthesized by the cycloaddition of nitrenes, carbon monoxide, and an alkyne. Spectral data and X-ray crystal structures of these clusters have been reported.[160,161]

8-Quinolinyl alkyl ketones having β-hydrogens on the alkyl group react with $[(C_2H_4)RhCl]_2$ to afford 8-quinolinyl ethyl ketone; a similar reaction of 8-quinolinyl phenyl ketone with $[(C_2H_4)RhCl]_2$ generates styrene via ethylene insertion into a Rh–phenyl bond, then β-elimination of the phenylethyl complex.[162] 8-Quinolinecarboxaldehyde reacted with $PtP(C_6H_{11})_3$ to give (tricyclohexylphosphine)(quinolinecarbonyl) platinum hydride, which upon treatment with CCl_4 generated the corresponding chloro complex by $H^- \rightarrow Cl^-$ exchange.[164]

Recently, Crabtree et al. reported that a methyl C–H bond in the 8-methylqinoline (mq) complex, $[IrH_2(mq)\{P(C_6H_5)_3\}_2]SbF_6$, was nondissociatively bound to iridium via a 2-electron 3-center C–H–Ir bridge.[165] A similar reaction involving 7,8-benzoquinoline (bqH) and $[Ir(cod)(PPh_3)_2]^+$ in CH_2Cl_2 under a hydrogen atmosphere gave $[IrH(H_2O)(bq)(PPh_3)_2]SF_6$; analytical and spectroscopic data were reported.[166]

The reactivity of the C–Pd σ-bond in **231b** has been shown by carbonylation in the presence of long-chain diols to give α-keto esters, which readily undergo subsequent cyclopalladation.[167] Cyclopalladated ferrocene **231b** underwent bridge cleavage with $P(C_6H_5)_3$, $As(C_6H_5)_3$, $P(OC_6H_5)_3$, pyridine, and 1,2-bis(diphenylphosphino)ethane. Electrochemical and spectroscopic data for metalation complexes of [(dimethylamino)methyl]ferrocene were reported.[168] Photolysis of these complexes is also described.[169] It has been shown recently that aminopalladation and stoichiometric double carbonylation of alk-1-enes affords an entry into β,γ-unsaturated α-keto amides.[170]

V. Acknowledgment

We wish to thank in the initial phases of our studies in palladacycles Dow Chemical USA and later the LSU Center for Energy Studies and the National Science Foundation for partial support of our work reported in this review.

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