

Figure 12. Structure drawing of $[\text{Pd}(\text{dmpz})_2(\text{Hdmpz})_2]$, **246**. [Based on data from (45).]

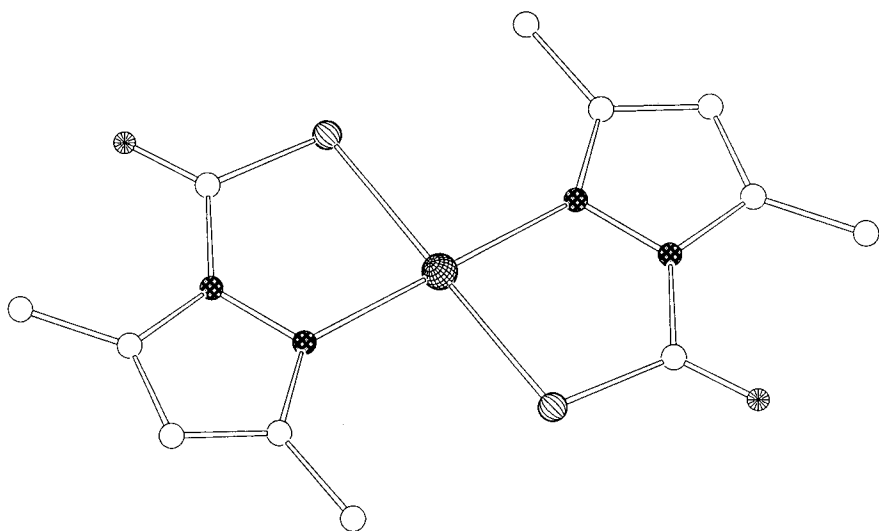


Figure 13. Structure drawing of $[\text{Pd}\{\text{SC}(\text{O})\text{dmpz}\}_2]$, **247**. [Based on data from (181).]

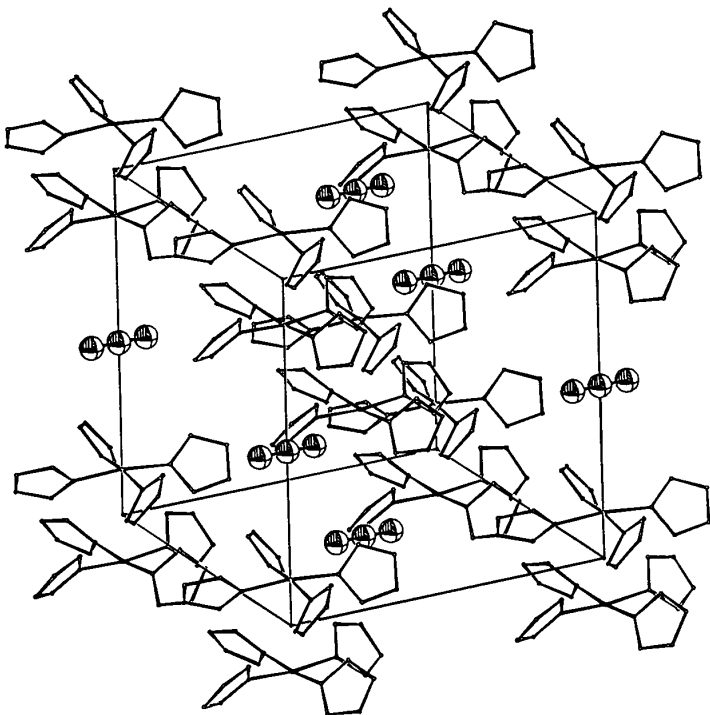


Figure 14. Unit cell diagram of $[\text{Pd}(\text{dmpz})_2(\text{Hdmpz})_2] \cdot \text{COS}$, **248**, showing clathrated, uncoordinated, COS molecules. [Based on data from (181).]

tributed to the still elusive $\eta^1\text{-S}$ coordination mode of the COS molecule. A structural characterization of **248** was performed by X-ray powder diffraction (XRPD) methods (181). This study showed that in **248** the identity of the $[\text{Pd}(\text{dmpz})_2(\text{Hdmpz})_2]_2$ molecules is essentially retained, while, unexpectedly, COS molecules are hosted in the crystal lattice as nonbonded fragments (Fig. 14).

VI. COMPLEXES CONTAINING THE $\text{M}(\mu\text{-pz}^*)_3\text{M}$ OR $\text{M}(\mu\text{-pz}^*)_4\text{M}$ CORE

Only a few examples of these unusual species have been reported. Recently, the synthesis and structural characterization of the hydroperoxo complex $[(\text{C}_5\text{Me}_5)\text{Ir}(\mu\text{-pz})_3\text{Rh}(\text{OOH})(\text{dppe})](\text{BF}_4)$, **249**, were described (182). This complex was obtained by protonation of the heterodinuclear complex $[(\text{C}_5\text{Me}_5)(\text{pz})\text{Ir}(\mu\text{-pz})_2\text{Rh}(\text{dppe})]$ (96) in the presence of dioxygen. An interest-

TABLE XIII

List of Structurally Characterized Transition Metal Complexes Containing Monodentate pz* Ligands

Complex	Formula	Reference
31	[Zn(dmpz) ₂ (Hdmpz)] ₂	42
44	[Co(dmpz) ₂ (Hdmpz)] ₂	72
78	[(C ₅ Me ₅)(pz)Ir(μ-pz) ₂ Ag(PPh ₃)]	96
218	<i>cis</i> -[Pt(dppz)(PPh ₃) ₂ Cl]	14
222	<i>trans</i> -[Ir(dfmpz)(CO)(PPh ₃) ₂]	168
227	[(dppe)Pt(dmpz) ₂]	173
229	[Cu(dcmpz) ₂ (py) ₂]	40
230	[{Rh(C ₅ Me ₅)(pz)} ₂ (μ-pz) ₂]	52
233	K{[HB(dmpz) ₃]}VCl ₂ (dmpz)	177
234	[(C ₅ Me ₅)Ir(dmpz) ₂ (Hdmpz)]	95
237	[Ru(<i>p</i> -cymene)(pz)(Hpz) ₂]	7
242	[Pd(C ₆ F ₅) ₂ (pz)(Hpz)(NBu ₄)	180
243	[Pt(C ₆ F ₅) ₂ (pz)(Hpz)(NBu ₄)	180
244	[Pt(pz) ₂ (Hpz) ₂] ₂	44
246	[Pd(dmpz) ₂ (Hdmpz) ₂]	45

ing feature of Complex **249** is the existence of a triply pyrazolate bridge connecting the two transition metal atoms. This structural feature is usual in the chemistry of tris(pyrazolyl)borato transition metal complexes, but extremely rare in bi- or polynuclear pyrazolate bridged transition metal compounds (4, 5, 12).

In 1969 Trofimenko (183) prepared the triply bridged anionic complex [(CO)₃Mn(μ-pz)₃Mn(CO)₃]⁻, from BrMn(CO)₅ and Na(pz). The structure was assigned on the basis of IR and NMR data. The nickel nitrosyl complex [(NO)Ni(μ-dmpz)₃Ni(NO)]⁻ had been reported 10 years later (184). The two Ni(NO) moieties are bridged by three dmpz ligands, with the nickel atom existing in a distorted tetrahedral coordination geometry.

In 1985, it was reported that the direct reaction of Rh₂(O₂CCH₃)₄ with Na(dmpz) in MeCN afforded the quadruply bridged pyrazolate complex [Rh₂(μ-dmpz)₄(MeCN)₂], **250** (185). The formulation of this unprecedented compound was supported by an X-ray crystal structure analysis (185). The MeCN ligands can be removed by heating under vacuum to give [Rh₂(dmpz)₄], which in turn formed adducts with different neutral monodentate ligands yielding species of the general formula [Rh₂(dmpz)₄(L)₂] (L = py or Hdmpz).

VII. COMPLEXES CONTAINING *endo*-BIDENTATE PYRAZOLATE LIGANDS

In 1981, the synthesis and the first structure analysis of a compound with an *endo*-bidentate pyrazolate anion, [U(C₅H₅)₃(η²-pz)], **251**, were reported (186).

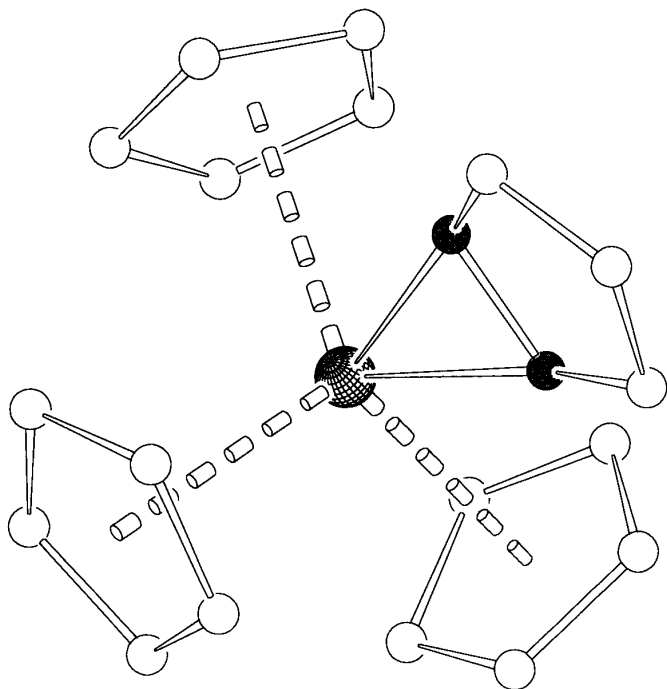


Figure 15. Structure drawing of $[U(C_5H_5)_3(\eta^2\text{-pz})]$, **251**. [Based on data from (186).]

This compound was readily prepared from $[U(C_5H_5)_3Cl]$ and $Na(pz)$. The U—N distances are 2.40 and 2.36 Å. The reason for such a 0.04-Å difference appeared unclear. The molecular structure consists of discrete $U(C_5H_5)_3(pz)$ molecules in which the $U^{(IV)}$ ion is coordinated by three η^5 - (C_5H_5) rings and by the two nitrogens of the pyrazolate group (Fig. 15).

In 1982, the same authors reported on other examples of the endo-bidentate pz^* ligand. The reaction between $[U(C_5Me_5)_2Cl_2]$ and stoichiometric amounts of $Na(pz)$ afforded $[U(C_5Me_5)_2Cl(\eta^2\text{-pz})]$, **252**, or $[U(C_5Me_5)_2(\eta^2\text{-pz})_2]$, **253** (187). These compounds were characterized by IR, 1H NMR, vis and mass spectra, and by single-crystal X-ray diffraction.

Recently, the synthesis and X-ray crystal structure analysis of a cationic zirconocene complex containing an endo-bidentate pyrazolate, were reported (188) (Fig. 16). The complex $[(C_5H_5)_2Zr(thf)(\eta^2\text{-pz})](BF_4)$, **254**, was obtained by treating dimethylzirconocene with one molar equivalent of Hpz and, subsequently, with $(Bu_3NH)(BPh_4)$. Complex **254** contains a η^2 -pyrazolate(*N,N'*) li-

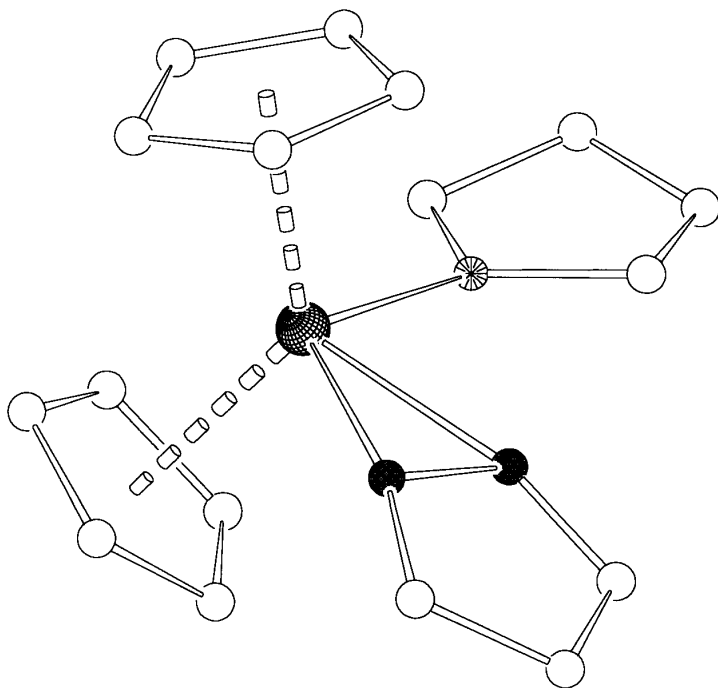
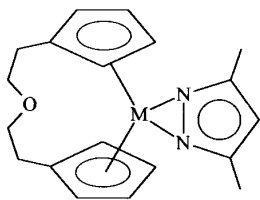


Figure 16. Structure drawing of the $[(C_5H_5)_2Zr(thf)(\eta^2-pz)]^+$ cation **255**. [Based on data from (188).]

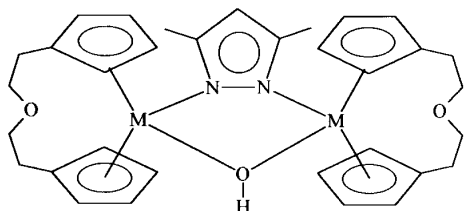
gand bonded to zirconium. Both nitrogen centers are nearly equidistant from zirconium. The preparation of a related zirconium endo-bidentate pyrazolate complex, $[(C_5H_5)_2Zr(Hpz)(\eta^2-pz)](BPh_4)$, **255**, was also reported. Its structure was proposed by means of 1H NMR evidences (188).

The reaction of $[O(CH_2CH_2C_5H_4)_2MCl]$ ($M = Y$ or Lu) with $Na(dmpz)$ gave the species $[O(CH_2CH_2C_5H_4)_2M(dmpz)]$ ($M = Y$, **256**; Lu , **257**) probably containing the dmpz group as an endo-bidentate ligand (189). Complexes **256** and **257** were shown to be highly sensitive toward air and water. Their partial hydrolysis gave the mixed-bridged complexes **258** and **259**, whose X-ray crystal structures were determined.

Complexes of the formula $Nd(pz)_3$, or $[Nd(dmpz)_3(thf)]_2$, were obtained in poor yields by the reaction of neodymium metal with $Hg(C_6F_5)_2$ and either Hpz or $Hdmpz$ in THF at room temperature. The X-ray crystal structure of the dmpz derivative showed that the compound is a centrosymmetric dimer with two



M = Y, 256; Lu, 257



M = Y, 258; Lu, 259

bridging dmpz ligands and two symmetrically bridging thf ligands. Each neodymium atom is eight-coordinate with four nitrogen atoms from terminal η^2 -dmpz ligands, one nitrogen from each bridging dmpz ligand and two oxygens from bridging thf molecules (190).

Monomeric tris-(η^2 -pyrazolate)-lanthanoid complexes with the bulky 3,5-di(*t*-butyl)pyrazolate ligand, of general formula $[M(t\text{-Bu}_2\text{pz})_3(\text{thf})_2]$ ($M = \text{La, Nd, Gd, or Er}$), were obtained by reaction of $\text{Hg}(\text{C}_6\text{F}_5)_2$ and 3,5-*t*-BupzH with an excess of lanthanoid metal in THF at room temperature. The X-ray crystal structure of the neodymium derivative was also reported (191).

Reaction of lanthanoid trichlorides, MCl_3 ($M = \text{Y, Ho, Yb, or Lu}$), with $\text{Na}(\text{dmpz})$ yielded complexes of the formula $[\text{M}_3(\mu\text{-dmpz})_6(\eta^2\text{-dmpz})_3(\mu_3\text{-O})\text{Na}_2(\text{thf})_2]$ and $[\text{M}_3(\mu\text{-dmpz})_6(\eta^2\text{-dmpz})_3(\mu_3\text{-O})\text{Na}_2(\text{Hdmpz})_2]$. The X-ray crystal structures of $[\text{Yb}_3(\mu\text{-dmpz})_6(\eta^2\text{-dmpz})_3(\mu_3\text{-O})\text{Na}_2(\text{thf})_2]$ and $[\text{Ho}_3(\mu\text{-dmpz})_6(\eta^2\text{-dmpz})_3(\mu_3\text{-O})\text{Na}_2(\text{Hdmpz})_2]$ revealed trigonal bipyramids containing an oxygen atom at the center, three lanthanoid atoms at the equatorial positions, and two sodium atoms at the apical vertices. Holmium and ytterbium each are heptacoordinated by four nitrogen atoms of the bridging pyrazolate ligands, two nitrogen of the endo-bidentate pyrazolate ligand, and the central oxygen atom (192).

Transition metal complexes containing the pyrazolate group as anionic non-coordinating ligand, although rare, have been reported (5). They are undoubtedly of lesser importance and will not be further discussed.

VIII. COMPLEXES CONTAINING DINUCLEATING FUNCTIONALIZED PYRAZOLATE LIGANDS

The synthesis, characterization, and properties of a large series of metal complexes built by pyrazole based dinucleating ligands possessing two chelating arms attached to the 3- and 5-positions of the pyrazole ring were reported. Such ligands were designed with the aim of preparing dinuclear complexes with

an appropriate metal-metal separation that is very important in studies on functional models for some bimetallic biosites (Fig. 17).

The ability of the trianion of pyrazole-3,5-dicarboxylic acid (H_3PZ^1) to form dinuclear complexes was utilized in the preparation of a family of anionic complexes of rhodium(I) and iridium(I), using cod, CO, and PPh_3 as ancillary ligands (193). The X-ray crystal structure of the complex $[Rh_2(CO)_4(PZ^1)](NBu_4)$, **260**, was determined. Stacking interactions in some of the rhodium and iridium anionic carbonyl complexes in the solid state have been inferred from the dramatic change of color with changes in the counteranion. The electrochemical oxidation of **260** produced a red solid analyzing as the mixed-valence compound $[Rh_2(CO)_4(PZ^1)]$. Bulk magnetic measurements on the red solid showed that it is diamagnetic, indicating either a strong spin-spin coupling or a metal-metal bond between the formally Rh(II) centers from two different molecules.

The same electrochemical oxidation, carried out on the iridium complexes $[Ir_2(CO)_4(PZ^1)](R_4N)$ ($R = Bu$ or Pr), gave dark conducting materials that analyzed as $[Ir_2(CO)_4(PZ^1)](R_4N)_{0.5}$ (193). Conductivity measurements for the latter species gave values that are 1000 times higher than the values found for the most conducting unoxidized precursor (the Me_4N^+ salt of the iridium complex).

Divalent metal complexes of the general formula $(Bu_4N)_2[M_2(PZ^1)_2]$ ($M = Pt, Pd, Ni,$ and Cu) were prepared by reacting H_2PtCl_4 , $PdCl_2$, $Ni(NO_3)_2$, and $Cu(NO_3)_2$ with H_3PZ^1 in the presence of Bu_4NOH (194). The structure of both copper and palladium complexes were determined as tetrabutylammonium salts (194) (Fig. 18).

Dicopper(II) complexes of the general formula $[Cu_2(PZ)(N_3)(H_2O)] \cdot H_2O$ were obtained from all the ligands $H_3PZ^1-H_3PZ^4$, with deprotonation of both the pyrazole and amide taking place (195). It is presumed that both the pyrazolate and azide groups function as bridges to two copper ions. The end-to-end mode of coordination seems the most plausible for the bridging azide ion in the present complexes. The corresponding complex with an acetate group was isolated only with H_3PZ^4 , $[Cu_2(PZ^4)(O_2CMe)] \cdot 2MeOH$. Infrared data support the presence of $MeCOO^-$ ion as a bridging group (195).

Two types of dinuclear complexes of the general formula $[M_2(PZ)(X)](BPh_4)_2$ (Type A) and $[M_2(PZ)_2](BPh_4)_2$ (Type B) were obtained by using ligands HPZ^5-HPZ^9 (196-198) (Table XIV).

X-ray crystal structures of the manganese(II) derivatives (PZ^7 or PZ^9) and of the copper(II)- PZ^5 complex were determined (196-198). All manganese(II) compounds showed catalytic activity toward disproportionation of H_2O_2 in DMF at $0^\circ C$. A probable mechanism for this reaction has also been proposed.

The reaction of H_3PZ^{10} with $CuCl_2 \cdot 2H_2O$ gave, according to the temperature, two different isomeric dinuclear compounds of the formula $[Cu_2(H_2PZ^{10})_2Cl_2] \cdot 2H_2O$. The molecular structures of the two isomers are closely related, differing only in hydrogen bonding (199).

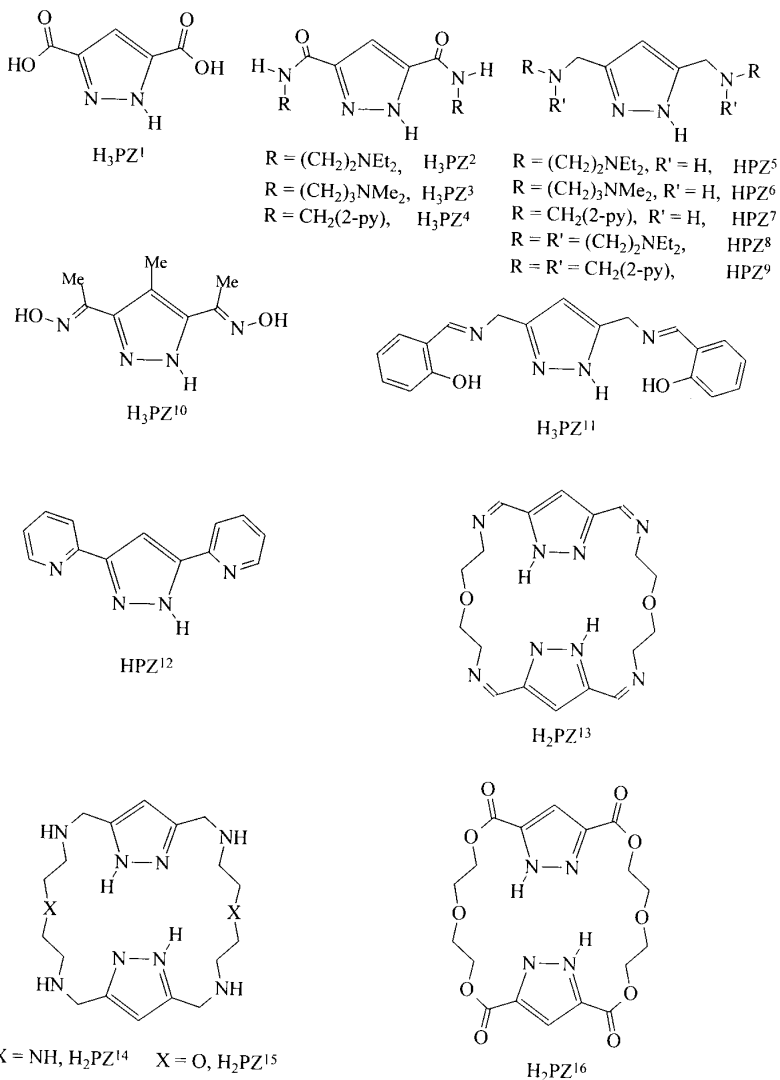


Figure 17. Drawings of the dinucleating functionalized pyrazolate ligands discussed in this chapter.

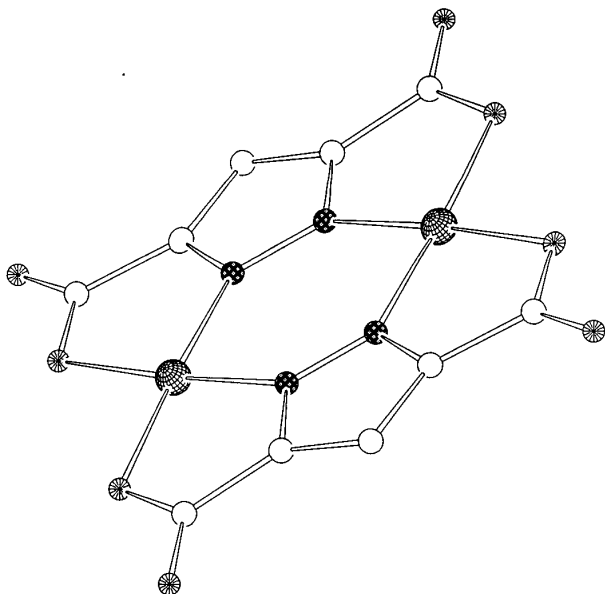


Figure 18. Structure drawing of the $[\text{Pd}_2(\text{PZ}')_2]^{2-}$ anion. [Based on data from (194).]

A manganese(III) complex, $[\text{Mn}_4(\text{PZ}^{11})_2(\text{MeO})_4(\text{MeOH})_4(\text{ClO}_4)_2]$, has been obtained from the dinucleating ligand H_3PZ^{11} and its crystal structure has been reported (200). The ligand H_3PZ^{11} may incorporate a pair of manganese ions by using its two tridentate coordination sites, that is, pyrazolate N and salicylideneaminate N and O. The bridge by the endogeneous pyrazolate group provides the $\text{Mn} \cdots \text{Mn}$ separation of about 3.48 Å. In DMF solutions, the complex exhibits a high catalase-like activity. The absorption spectrum in this solvent suggests that the complex structure differs from the tetranuclear structure found in the solid state.

TABLE XIV
Dinuclear Complexes of the General Formula $[\text{M}_2(\text{PZ})(\text{X})(\text{BPh}_4)_2]$ (Type A) and $[\text{M}_2(\text{PZ})_2](\text{BPh}_4)_2$ (Type B)

Metal	Type A		Type B	
	PZ	X	Metal	PZ
Mn	PZ^8	MeCOO^-	Cu	PZ^5
	PZ^9	PhCOO^-		PZ^6
Co, Cu	PZ^8	N_3^-	Mn	PZ^7

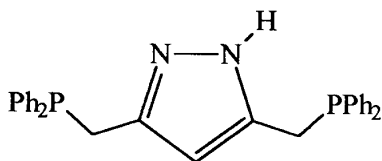
Reaction of 3,5-bis(pyridin-2-yl)pyrazole (HPZ²²) with metal nitrates, perchlorate, chlorides and bromides, yielded compounds of the general formula $[M(PZ^{12})]X \cdot nH_2O$ ($X = NO_3$, $M = Co, Cd, Ni, Zn, Cu$; $X = ClO_4$, $M = Cu$; $X = Cl$, $M = Mn, Ni, Co, Zn$; $X = Br$, $M = Ni, Co, Zn$) (201, 202). The nickel(II) derivative containing the NO_3^- anion has been known since 1969 and on the basis of spectroscopic and magnetic data was described as possessing a dinuclear structure (203). A tentative dinuclear structure was assigned to the other complexes of the type $[M(PZ^{12})]X \cdot nH_2O$ as well.

The crystal and molecular structure of $[Ni_2(PZ^{12})_2(MeOH)_4]Cl_2$ were determined (201), which confirms the previous assignment. More recently (204), the X-ray crystal structure of the $Cu^{(II)}/NO_3^-$ complex was solved; it revealed a tetranuclear arrangement, that is, $[Cu_4(PZ^{12})_4(H_2O)_4](NO_3)_4$ (204). However, this compound can be considered as composed of two weakly associated pairs of dimers, with $\pi(\eta^5)$ interdinuclear interactions.

Dinuclear copper(II) complexes, $[Cu_2(PZ^{13})(ClO_4)_2]$ and $[Cu(PZ^{14})(ClO_4)_2]$, were obtained from the 26-membered macrocycles containing two pyrazole rings, H_2PZ^{13} and H_2PZ^{14} (205). The X-ray crystallographic analysis of the PZ^{14} derivative demonstrates that inside the macrocyclic cavity, the two pyrazolate rings are simultaneously acting as exo-bidentate ligands linking both metal cations, with the $Cu \cdots Cu$ separation being 3.9 Å.

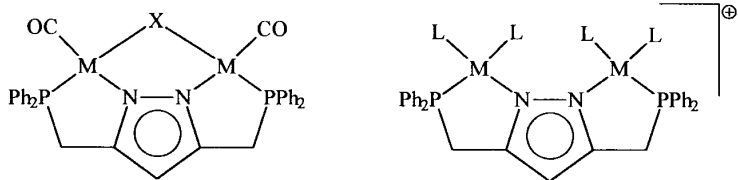
With the use of ¹³C NMR techniques, the formation of the related zinc(II) dinuclear complexes of the formula $[Zn_2(PZ)]^{2+}$, has been recently evidenced by treatment of $ZnCl_2$ with the ligands H_2PZ^{14} , H_2PZ^{15} , and H_2PZ^{16} (206, 207).

The PNNHP molecule, when deprotonated, behaves as a planar tetradentate ligand consisting of a central pyrazolate unit with symmetrically disposed methylenediphenylphosphine arms (PNNP). Its geometry provides for two metals to reside within a cooperative distance but does not allow for metal-metal bond formation (208).



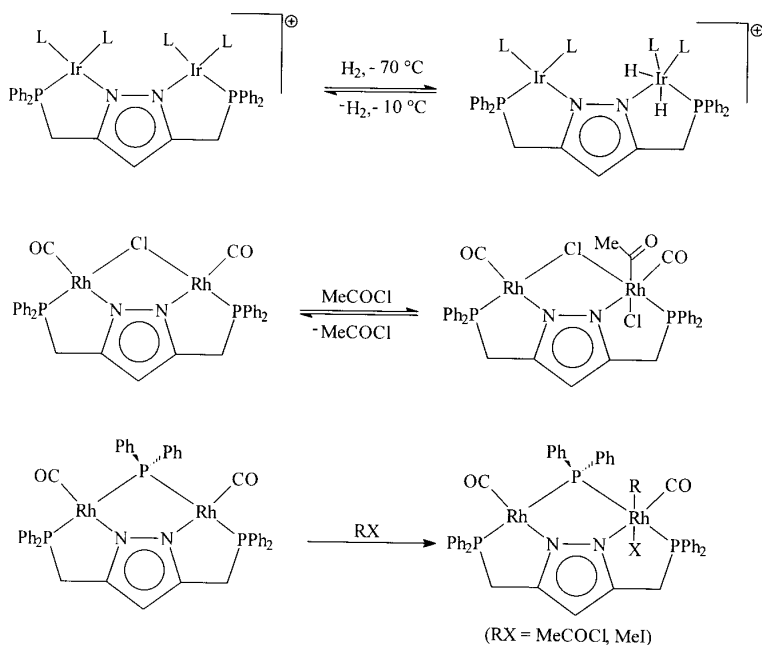
PNNHP

Two distinct classes of planar bimetallic complexes containing the PNNP ligand were isolated and characterized: the neutral $[M_2(PNNP)(\mu-X)L_2]$ and the cationic $[M_2(PNNP)(L)_4]^+$ (208).



Particular attention has been devoted to oxidative addition and reductive elimination reactions of $[M_2(PNNP)(\mu-X)L_2]$ with acyl and alkyl halides. Depending on the electron richness of the metals, a complete spectrum of possibilities was observed: from reversible single oxidative addition on one of the metals to irreversible double oxidative addition on both metals (2) (Scheme 12).

Oxidative addition to one metal leads to deactivation of the other one despite the fact that no metal-metal bonds are formed. The crystal structure of the

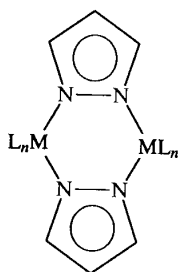


Scheme 12. Oxidative-addition reactions on complexes containing the functionalized pyrazolate ligand PNNP. Depending on the electron richness of the metals, reversible or irreversible addition takes place. [Adapted from (2).]

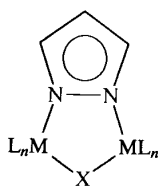
rhodium(I)/rhodium(III) complex $[\text{Rh}_2(\mu\text{-PPh}_2(\text{CO})_2)(\text{PNNP})(\text{Me})(\text{I})]$ was also determined (2). The bis(diene)species of rhodium and iridium are precursors for catalytic hydrogenation of alkenes and alkynes.

IX. CATALYTIC ACTIVITY OF HOMO- AND HETEROBRIDGED PYRAZOLATE COMPLEXES

Several studies were carried out in the last decade to test the catalytic activity of mononuclear pyrazole complexes as well as dinuclear and polynuclear species containing bridging pyrazolate groups. Particularly investigated were the pyrazolate complexes in which the $\text{M}(\mu\text{-pz}^*)_2\text{M}$ (Type A) or the " $\text{M}(\mu\text{-pz}^*)(\mu\text{-X})\text{M}$ " (Type B) framework is present.



Type A



Type B

Some evidence has been presented that the dinuclear structure is retained during the catalytic cycle in the case of homobridged Type A complexes. Indeed, studies on $(\mu\text{-pz}^*)_2$ complexes demonstrated the stability and flexibility of the six-membered cyclic core $\text{M}-[\text{N}-\text{N}]_2-\text{M}$. Such compounds generally exist in boat conformations, which thereby facilitate the interactions between the two metal centers, a factor that has important consequences on catalytic activity. In fact, pz^* is an extremely versatile ligand in that it is able to bridge an unusually wide range of intermetallic separations. It was suggested that the shorter metal-metal distances generally lead to higher reactivity (209). Accordingly, $[\text{Ir}(\mu\text{-dmpz})(\text{CO})_2]_2$ evidenced catalytic activity in hydrogenation reactions. The related compounds $[\text{Ir}(\mu\text{-mpz})(\text{CO})_2]_2$ and $[\text{Ir}(\mu\text{-pz})(\text{CO})_2]_2$, which possess a longer metal-metal separation, were shown to be inert for the same catalytic reactions (210). However, $[\text{Ir}(\mu\text{-dfmpz})(\text{cod})]_2$, which exhibits a metal-metal distance much shorter than the related dmpz derivative, $[\text{Ir}(\mu\text{-dmpz})(\text{cod})]_2$, was found to be inert as a hydrogenation catalyst (211). Photo-

electron spectroscopy studies carried out on a series of representative iridium dimer complexes, having a variety of metal-metal distances, led to believe that electronic interactions are of primary importance in determining the Ir_2 chemistry (211). The catalytic reactions that have been investigated to date can be referred to as (a) hydroformylation reactions, (b) hydrogen-transfer reactions, and (c) oxidation or oxygenation reactions. Moreover, it was found that some rhodium-pyrazolate complexes are able to promote the polymerization of monoaryl acetylenes.

A. Hydroformylation Reactions

The catalytic activity of the mixed-bridged dinuclear complex $[\text{Rh}_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$, **111**, in the selective hydroformylation of 1-hexene to afford the corresponding aldehydes was explored and the results were compared with those observed for the symmetrical pyrazolate-free precursor $[\text{Rh}_2(\text{CO})_2(\mu\text{-S-}t\text{-Bu})_2\{\text{P}(\text{OMe})_3\}_2]$ (117, 212). Very mild conditions (5 bar, 80°C) were chosen in both cases. Complex **111** exhibits lower activity; however, the selectivity is about the same as for the symmetrical precursor ($\sim 80\%$ heptanal and 20% 2-methylhexanal). Complex **111** does not give rise to a detectable dimerization and was found to be practically unchanged after reaction. A catalytic cycle in which all the intermediate species remain dinuclear was proposed for the hydroformylation of 1-hexene catalyzed by the symmetrical complexes $[\text{Rh}_2(\text{CO})_2(\mu\text{-S-}t\text{-Bu})_2\text{L}_2]$ [$\text{L} = \text{P}(\text{OMe})_3, \text{PPh}_3, \text{P}(\text{OPh})_3$] (213). This proposal is based mainly on the results obtained by varying the phosphorus ligands and on extended Hückel calculations carried out for several proposed intermediates. It is possible that Complex **111** could follow such a cycle (117).

It was also reported (214) that the same hydroformylation reaction can be achieved by various rhodium(I) double bridged pyrazolate complexes of the general formula $[\text{Rh}_2(\mu\text{-pz}^*)(\text{CO})_2\text{L}_2]$ ($\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3, \text{PPh}_3$; $\text{Hpz}^* = \text{Hpz}, \text{Hmpz}, \text{or Hdmpz}$). Good catalytic activity was found. The latter decreases in the sequence $\text{P}(\text{OPh})_3 > \text{P}(\text{OMe})_3 > \text{PPh}_3$ (214). The effect of the bridging pyrazolate ligand was also studied (215, 216).

Recently, the hydroformylation of 1-dodecene and cyclohexene by the dinuclear doubly bridged pyrazolate complexes $[(\text{PR}_3)(\text{CO})\text{Rh}(\mu\text{-pz}^*)]_2$, **46-49**, was reported (75). Thus, at 120°C and at a CO and H_2 pressure of 28 atm, these two olefins were transformed into the corresponding aldehydes with greater than 95% yield. All four complexes catalyze the transformation of 1-dodecene to 1-undecane-carboxaldehyde in preference to the iso compound, although this regioselectivity is rather poor (75).

Recently, it has been shown that Complexes **47** and **49** are able to catalyze the polymerization of $\text{Ph-C}\equiv\text{CH}$ and the substituted arylacetylenes $4\text{-HC}_6\text{H}_4\text{-C}\equiv\text{CH}$ ($\text{X} = \text{MeO}, \text{Me}, \text{or Cl}$) at 25°C in a stereoregular manner

(74). The cis-oriented poly(arylacetylenes) so formed, were found to depolymerize selectively at 200–225°C to the corresponding 1,3,5-triaryl-benzenes derivatives.

B. Hydrogen-Transfer Reactions

Some pyrazolate complexes were found to possess high catalytic activity for various hydrogen-transfer processes and to be of considerable value in synthesis. The heterodinuclear complexes $[(\text{CO})(\text{H})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})(\mu\text{-Cl})\text{M}(\text{diolefin})]$ ($\text{M} = \text{Rh}$ or Ir ; diolefin = cod or tfbb) catalyze the hydrogen transfer from isopropanol to cyclohexanone (101). The heterodinuclear complexes were shown to be more active catalysts than the mononuclear pyrazole compounds $[\text{Ru}(\text{H})(\text{Cl})(\text{Hpz})(\text{PPh}_3)_2]$ and $[\text{M}(\text{H})(\text{Cl})(\text{Hpz})(\text{diolefin})]$ (101).

Various hydrogenation catalysts based on $(\text{C}_5\text{Me}_5)\text{Rh}$ complexes with pyrazole-type ligands have been studied (217). Olefins such as cyclohexene and 1-hexene are hydrogenated under ambient conditions with $[\{\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}\}_2(\mu\text{-Cl})_2]$ in the presence of Hpz^* and NEt_3 ($\text{Hpz}^* = \text{Hpz}$, Hmpz , or Hdmpz). The catalytic activities are affected mainly by the pyrazole-type ligand. The activity decreases in the order $\text{Hdmpz} > \text{Hmpz} > \text{Hpz}$, and is highest for the combination $[\{\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}\}_2(\mu\text{-Cl})_2] + 2 \text{Hdmpz} + 2\text{Et}_3\text{N}$.

C. Oxidation or Oxygenation Reactions

Recently, it has been found that the copper(I) homoleptic pyrazolate complexes $[\text{Cu}(\text{dmpz})_3]$, **6**, and $[\text{Cu}(\text{dppz})_4]$, **8**, are catalytically active in the oxidative coupling of primary aromatic amines to give the corresponding azobenzenes in the presence of O_2 at atmospheric pressure (17, 137).

The reaction proceeds with a selectivity of 100%. In the case of $[\text{Cu}(\text{dppz})_4]$, the oxidative coupling of a series of different para-substituted aromatic amines was investigated in order to study the influence of the para substitution on the activity of the catalytic system (137).

Complex **6** also exhibits catalytic activity in the oxidation reaction of various other substrates such as PPh_3 , dibenzylamine, and CO, with formation of triphenylphosphine oxide, *N*-benzylidenebenzylamine, and CO_2 , respectively.

The octanuclear copper(II) hydroxo complex $[\text{Cu}_8(\text{dmpz})_8(\text{OH})_8]$, **182**, has been identified as the active intermediate species when $[\text{Cu}(\text{dmpz})_3]$ is used (137). In the case of $[\text{Cu}(\text{dppz})_4]$, the intermediacy of a copper(II) imido species (17) has been proposed on the basis of chemical and spectroscopic evidences.

X. CONCLUSIONS

The pyrazolate group has been recognized as a particularly useful ligand that is capable of holding two or more metal ions in close proximity with formation of multimetallic transition metal systems. The increasing interest in this area is due to the high relevance of such complexes for multimetal-centered catalysis, biological mimicry, multielectron-transfer reactions, and metal-metal interactions. The extent of such interactions can be controlled by varying the metal-metal distance and the charge and π -donor/acceptor properties of the ligand used to bridge the metals.

The purpose of this review was to emphasize the remarkable progress in the coordination chemistry of the pyrazolate ligand in the last decade. Quite a lot of interesting and un hoped-for results were attained. These results are summarized below.

1. The metal-pyrazolate saga has been known since the pioneering work of Büchner in the nineteenth century. In the last few years, a definitive characterization of several binary complexes has been possible due to the advent of the recent method of ab initio structure determination from X-ray powder diffraction data. In this respect, it is likely that a number of new molecules and/or crystalline phases, which have so far escaped a complete characterization, will be structurally analyzed, thus confirming the variability of the coordination modes and stoichiometries attributable to "simple" pyrazolato complexes.
2. It is now widely accepted that the nuclearity of binary pyrazolate complexes, $[M(pz^*)_n]_m$, is dependent not only on the nature of the substituents present in the heterocyclic ring, but also on the synthetic strategy used. This important observation allows these systems to be prepared in a selective way.
3. As suggested by Trofimenko in his review articles, controlled extension of the " $M(pz^*)_2M$ " core to form polynuclear compounds may constitute an interesting area of research. In these last few years, many elegant examples of homo- and heteropolynuclear systems containing such fragment as well as mixed-bridging $(\mu\text{-}pz^*)(\mu\text{-}X)$ groups have been described. The synthesis and chemical and physical behavior of such compounds in larger sequences may represent a fascinating objective in the future. In particular, heteronuclear complexes are of crucial interest because of the special features of the reactivity, which might result from the presence of adjacent metals having different chemical properties (complexes containing electron-rich and electron-deficient metal centers).

4. The monodentate mode of coordination of the pz^* group has been now found in many structurally characterized transition metal compounds. Thus, complexes of the type $M(pz^*)$, $cis-M(pz^*)_2$, and $trans-M(pz^*)_2$ have been described. The utility of some of these species as building blocks for the preparation of heteronuclear complexes is well documented, although further studies are necessary in order to gain more insight into the properties of these systems.

ABBREVIATIONS

acac	Acetylacetonate
cod	Cycloocta-1,5-diene
cyclop	(1 <i>S</i> ,2 <i>S</i>)-(+) -1,2-Bis(diphebylphosphinomethyl)cyclohexane
<i>p</i> -cymene	<i>p</i> -Isopropyl-methylbenzene
dapm	(Diphenylarsino)(diphenylphosphino)methane
debd	1,6-Bis-(3,5-dimethylpyrazol-1-yl)-2,5-dimethyl-2,5-diazahexane
DMF	<i>N,N</i> -Dimethylformamide
dms	Dimethyl sulfoxide (ligand)
DMSO	Dimethyl sulfoxide (solvent)
dpa	1,2-Bis(diphenylarsino)ethane
dpam	Bis(diphenylarsino)methane
dppb	1,4-Bis(diphenylphosphino)butane
dpe	1,2-Bis(diphenylphosphino)ethane
dppm	Bis(diphenylphosphino)methane
dppp	1,3-Bis(diphenylphosphino)propane
ET	Electron transfer
Hdbpz	3,5-Di- <i>tert</i> -butylpyrazole
Hdcmpz	3,5-Dicarbomethoxy pyrazole
Hdfmpz	3,5-Bis(trifluoromethyl)pyrazole
Hdmepz	3(5),4-Dimethyl-5(3)-ethylpyrazole
Hdmpz	3,5-Dimethylpyrazole
Hdppz	3,5-Diphenylpyrazole
Hmpz	3(5)-Methylpyrazole
Hpz	Pyrazole
Hpz*	A general pyrazole
Htmpz	3,4,5-Trimethylpyrazole
IR	Infrared spectroscopy
nbd	Norbornadiene (bicyclo-[2.2.1]-heptadiene)
NMR	Nuclear magnetic resonance
phen	1,10-Phenanthroline

py	Pyridine
py ⁺	Pyridinium or substituted pyridinium
pz*	A general pyrazolate anion
tfbb	Tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-Dihydro-1,4-ethenonaphthalene)
tht	Tetrahydrothiophene
tmpz	Trimethylpyrazolate
XPS	X-ray photoelectron spectroscopy
XRPD	X-ray powder diffraction
4-XdmpzH	4-Substituted 3,5-dimethylpyrazole
4-XdppzH	4-Substituted 3,5-diphenylpyrazole
4-XpzH	4-Substituted pyrazole

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REFERENCES

1. See, for example, K. D. Karlin and J. Zubieta, Eds., *Biological and Inorganic Copper Chemistry*, Adenine Press, New York, 1986.
2. T. G. Schenck, C. R. C. Milne, J. F. Sawyer, and B. Bosnich, *Inorg. Chem.*, **24**, 2338 (1985).
3. J. Catalan, J. L. M. Abboud, and J. Elguero, *Adv. Heterocycl. Chem.*, **41**, 187 (1987).
4. J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta*, **26**, 71 (1978).
5. S. Trofimenko, *Progress in Inorganic Chemistry*, Wiley-Interscience, New York, 1986, Vol. 34, p. 115.
6. S. Trofimenko, *Chem. Rev.*, **72**, 497 (1972).
7. D. Carmona, J. Ferrer, L. A. Oro, M. C. Apreda, C. Foces-Foces, F. H. Cano, J. Elguero, and M. L. Jimeno, *J. Chem. Soc. Dalton Trans.*, 1463 (1990).
8. B. Bovio, G. Banditelli, and A. L. Bandini, *Inorg. Chim. Acta*, **96**, 213 (1985).
9. M. Mohan, M. R. Bond, T. Otieno, and C. J. Carrano, *Inorg. Chem.*, **34**, 1233 (1995).

10. W. Hüchel and H. Bretschneider, *Chem. Ber.*, **70**, 2024 (1937).
11. Q. Mingoia, *Gazz. Chim. Ital.*, **61**, 449 (1931).
12. S. Trofimenko, *Chem. Rev.*, **93**, 943 (1993).
13. N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia, and G. La Monica, *J. Am. Chem. Soc.*, **116**, 7668 (1994).
14. J. P. Fackler, Jr., R. G. Raptis, and H. H. Murray, *Inorg. Chim. Acta*, **193**, 173 (1992).
15. H. H. Murray, R. G. Raptis, and J. P. Fackler, Jr., *Inorg. Chem.*, **27**, 26 (1988).
16. R. G. Raptis, and J. P. Fackler, Jr., *Inorg. Chem.*, **27**, 4179 (1988).
17. G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi, and M. Moret, *Inorg. Chem.*, **33**, 1458 (1994).
18. E. Büchner, *Chem. Ber.*, **22**, 842 (1889).
19. H. Okkersen, W. L. Groeneveld, and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **92**, 945 (1973).
20. E. Keller, SCHAKAL 92: a computer program for the graphical representation of crystallographic models, University of Freiburg, Germany, 1992.
21. G. A. Ardizzoia, G. La Monica, N. Masciocchi, and M. Moret, unpublished results.
22. C. B. Singh, S. Satpathy, and B. Sahoo, *J. Inorg. Nucl. Chem.*, **33**, 1313 (1971).
23. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, **68**, 1444 (1990).
24. G. A. Ardizzoia, and G. La Monica, *Inorg. Synth.*, **31**, 299 (1997).
25. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, **70**, 2161 (1992).
26. M. K. Ehlert, A. Storr, and R. C. Thompson, *Can. J. Chem.*, **70**, 1121 (1992).
27. G. A. Ardizzoia, E. M. Beccalli, G. La Monica, N. Masciocchi, and M. Moret, *Inorg. Chem.*, **31**, 2706 (1992).
28. F. Bonati, A. Burini, B. R. Pietroni, and R. Galassi, *Gazz. Chim. Ital.*, **123**, 691 (1993).
29. J. Berthou, J. Elguero, and C. Rerat, *Acta Crystallogr.*, **B26**, 1880 (1970).
30. F. Krebs-Larsen, M. S. Lehmann, I. Sotofte, and S. E. Rasmussen, *Acta Chem. Scand.*, **24**, 3248 (1970).
31. J. A. S. Smith, B. Wehrle, F. Aguilar-Parrilla, H. H. Limbach, C. Foces-Foces, F. H. Cano, J. Elguero, A. Baldy, M. Pierrot, M. M. T. Khurshid, and J. B. Lacombe-McDouall, *J. Am. Chem. Soc.*, **111**, 7304 (1989).
32. A. L. Llamez-Saiz, C. Foces-Foces, F. H. Cano, P. Jiménez, J. Laynez, W. Meutermans, J. Elguero, H. H. Limbach, and F. Aguilar-Parrilla, *Acta Crystallogr.*, **B50**, 746 (1994).
33. F. Aguilar-Parrilla, G. Scherer, H. H. Limbach, C. Foces-Foces, F. H. Cano, J. A. S. Smith, C. Toiron, and J. Elguero, *J. Am. Chem. Soc.*, **114**, 9657 (1992).
34. R. G. Raptis, R. J. Staples, C. King, and J. P. Fackler, Jr., *Acta Crystallogr.*, **C49**, 1716 (1993).

35. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, **67**, 1970 (1989).
36. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, **69**, 432 (1991).
37. M. K. Ehlert, A. Storr, R. C. Thompson, F. W. B. Einstein, and R. J. Batchelor, *Can. J. Chem.*, **71**, 331 (1993).
38. J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta*, **24**, 123 (1977).
39. S. Emori and K. Sadakata, *Bull. Chem. Soc. Jpn.*, **67**, 1743 (1994).
40. M. Angaroni, G. A. Ardizzoia, G. La Monica, E. M. Beccalli, N. Masciocchi, and M. Moret, *J. Chem. Soc. Dalton Trans.*, 2715 (1992).
41. M. K. Ehlert, A. Storr, and R. C. Thompson, *Can. J. Chem.*, **71**, 1412 (1993).
42. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, **68**, 1494 (1990).
43. W. Burger and J. Strähle, *Z. Anorg. Allg. Chem.*, **529**, 111 (1985).
44. W. Burger and J. Stähle, *Z. Anorg. Allg. Chem.*, **539**, 27 (1986).
45. G. A. Ardizzoia, G. La Monica, S. Cenini, M. Moret, and N. Masciocchi, *J. Chem. Soc. Dalton Trans.*, 1351 (1996).
46. G. Minghetti, G. Banditelli, and F. Bonati, *J. Chem. Soc. Dalton Trans.*, 1851 (1979).
47. B. Bovio, F. Bonati, and G. Banditelli, *Inorg. Chim. Acta*, **87**, 25 (1984).
48. W. L. Driessen, F. Paap, and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, **114**, 317 (1995).
49. G. A. Ardizzoia, G. La Monica, M. A. Angaroni, and F. Cariati, *Inorg. Chim. Acta*, **158**, 159 (1989).
50. G. A. Ardizzoia, M. A. Angaroni, G. La Monica, N. Masciocchi, and M. Moret, *J. Chem. Soc. Dalton Trans.*, 2277 (1990).
51. B. F. Fieselmann and G. D. Stucky, *Inorg. Chem.*, **17**, 2074 (1978).
52. L. A. Oro, D. Carmona, M. P. Lamata, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, **97**, 19 (1985).
53. J. A. Bailey, S. L. Grundy, and S. R. Stobart, *Organometallics*, **9**, 536 (1990).
54. S. Trofimenko, *J. Org. Chem.*, **33**, 890 (1968).
55. G. A. Ardizzoia, M. Angaroni, G. La Monica, M. Moret, and N. Masciocchi, *Inorg. Chim. Acta*, **185**, 63 (1991).
56. T. N. Sorrell, *Tetrahedron*, **45**, 3 (1989).
57. A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti, and M. T. Pinillos, *Inorg. Chim. Acta*, **99**, 165 (1985).
58. R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem.*, **29**, 5003 (1990).
59. R. G. Raptis, H. H. Murray, and J. P. Fackler, Jr., *Acta Crystallogr.*, **C44**, 970 (1988).
60. G. Lopez, G. Garcia, J. Ruiz, G. Sanchez, J. Garcia, and C. Vicente, *J. Chem. Soc. Chem. Commun.*, 1045 (1989).

61. G. Lopez, G. Garcia, G. Sanchez, J. Garcia, J. Ruiz, J. A. Hermoso, A. Vegas, and M. Martinez-Ripoll, *Inorg. Chem.*, **31**, 1518 (1992).
62. G. Lopez, J. Ruiz, G. Garcia, J. M. Marti, G. Sanchez, and J. Garcia, *J. Organomet. Chem.*, **412**, 435 (1991).
63. G. López, G. Garcia, G. Sánchez, M. D. Santana, J. Ruiz, and J. Garcia, *Inorg. Chim. Acta*, **188**, 195 (1991).
64. G. López, J. Ruiz, G. Garcia, C. Vicente, J. Casabó, E. Molins, and C. Miravittles, *Inorg. Chem.*, **30**, 2605 (1991).
65. G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J. M. Marti, J. A. Hermoso, A. Vegas, and M. Martinez-Ripoll, *J. Chem. Soc. Dalton Trans.*, 53 (1992).
66. G. Lopez, J. Ruiz, G. Garcia, C. Vicente, V. Rodriguez, G. Sanchez, J. A. Hermoso, and M. Martinez-Ripoll, *J. Chem. Soc. Dalton Trans.*, 1681 (1992).
67. V. K. Jain, S. Kannan, and E. R. T. Tiekink, *J. Chem. Soc. Dalton Trans.*, 2231 (1992).
68. V. K. Jain and S. Kannan, *Polyhedron*, **11**, 27 (1992).
69. F. Bonati, H. C. Clark, and C. S. Wong, *Can. J. Chem.*, **58**, 1435 (1980).
70. V. K. Jain, S. Kannan, and E. R. T. Tiekink, *J. Chem. Soc. Dalton Trans.*, 3625 (1993).
71. M. Maekawa, M. Munakata, T. Kuroda, and Y. Nozaka, *Inorg. Chim. Acta*, **208**, 243 (1993).
72. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, and J. Trotter, *Can. J. Chem.* **71**, 1425 (1993).
73. R. Usón, L. A. Oro, M. A. Ciriano, M. R. Pinillos, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Organomet. Chem.*, **205**, 247 (1981).
74. I. Amer, H. Schumann, V. Ravindar, W. Baidossi, N. Goren, and J. Blum, *J. Mol. Cat.*, **85**, 163 (1993).
75. H. Schumann, H. Hemling, V. Ravindar, Y. Badrieh, and J. Blum, *J. Organomet. Chem.*, **469**, 213 (1994).
76. F. Barceló, P. Lahuerta, M. A. Ubeda, C. Foces-Foces, F. H. Cano, and M. Martinez-Ripoll, *J. Chem. Soc. Chem. Commun.*, 43 (1985).
77. F. Barceló, P. Lahuerta, M. A. Ubeda, C. Foces-Foces, F. H. Cano, and M. Martinez-Ripoll, *Organometallics*, **7**, 584 (1988).
78. G. W. Bushnell, D. O. K. Fjeldsted, S. R. Stobart, M. J. Zaworotko, S. A. R. Knox, and K. A. Macpherson, *Organometallics*, **4**, 1107 (1985).
79. L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc. Dalton Trans.*, 31 (1986).
80. L. A. Oro, D. Carmona, and J. Reyes, *J. Organomet. Chem.*, **302**, 417 (1986).
81. L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, **112**, 35 (1986).
82. D. Carmona, F. J. Lahoz, L. A. Oro, J. Reyes, and M. P. Lamata, *J. Chem. Soc. Dalton Trans.*, 3551 (1990).
83. K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, J. L. Atwood, and M. J. Zaworotko, *J. Am. Chem. Soc.*, **104**, 920 (1982).

84. J. Powell, A. Kuksis, S. C. Nyburg, and W. W. Ng, *Inorg. Chim. Acta*, **64**, L211 (1982).
85. J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, and M. J. Zaworotko, *Inorg. Chem.*, **23**, 4050 (1984).
86. D. G. Harrison and S. R. Stobart, *J. Chem. Soc. Chem. Commun.*, 285 (1986).
87. R. D. Brost, and S. R. Stobart, *J. Chem. Soc. Chem. Commun.*, 498 (1989).
88. M. A. Ciriano, F. Viguri, L. A. Oro, A. Tiripicchio, and M. Tiripicchio-Camellini, *Angew. Chem. Int. Ed. Engl.*, **26**, 444 (1987).
89. R. D. Brost, D. O. K. Fjeldsted, and S. R. Stobart, *J. Chem. Soc. Chem. Commun.*, 488 (1989).
90. D. O. K. Fjeldsted, S. R. Stobart, and M. J. Zaworotko, *J. Am. Chem. Soc.*, **107**, 8258 (1985).
91. S. Trofimenko, *Inorg. Chem.*, **10**, 1372 (1971).
92. K. A. Beveridge, G. W. Bushnell, S. R. Stobart, J. L. Atwood, and M. J. Zaworotko, *Organometallics*, **2**, 1447 (1983).
93. M. A. Ciriano, M. A. Tena, and L. A. Oro, *J. Chem. Soc. Dalton Trans.*, 2123 (1992).
94. C. Tejel, M. A. Ciriano, L. A. Oro, A. Tiripicchio, and F. Ugozzoli, *Organometallics*, **13**, 4153 (1994).
95. D. Carmona, L. A. Oro, M. P. Lamata, J. Elguero, M. C. Apreda, C. Foces-Foces, and F. H. Cano, *Angew. Chem. Int. Ed. Engl.*, **25**, 1114 (1986).
96. D. Carmona, F. J. Lahoz, L. A. Oro, M. P. Lamata, and S. Buzarra, *Organometallics*, **10**, 3123 (1991).
97. D. Carmona, L. A. Oro, M. P. Lamata, M. L. Jimeno, J. Elguero, A. Belguise, and P. Lux, *Inorg. Chem.*, **33**, 2196 (1994).
98. R. Seeber, G. Minghetti, M. I. Pilo, G. Banditelli, and S. Zamponi, *J. Organomet. Chem.*, **402**, 413 (1991).
99. R. S. Farid, I. J. Chang, J. R. Winkler, and H. B. Gray, *J. Phys. Chem.*, **98**, 5176 (1994).
100. R. S. Farid, L. M. Henling, and H. B. Gray, *Acta Crystallogr.*, **C49**, 1363 (1993).
101. M. P. Garcia, A. M. Lopez, M. A. Esteruelas, F. J. Lahoz, and L. A. Oro, *J. Organomet. Chem.*, **388**, 365 (1990).
102. M. P. Garcia, A. M. Lopez, M. A. Esteruelas, F. J. Lahoz, and L. A. Oro, *J. Chem. Soc. Dalton Trans.*, 3465 (1990).
103. J. A. Cabeza, C. Lanzaduri, L. A. Oro, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Organomet. Chem.*, **322**, C16 (1987).
104. J. A. Cabeza, C. Lanzaduri, L. A. Oro, D. Belletti, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc. Dalton Trans.*, 1093 (1989).
105. F. Neumann and G. Süss-Fink, *J. Organomet. Chem.*, **367**, 175 (1989).
106. F. Neumann, H. Stoeckli-Evans, and G. Süss-Fink, *J. Organomet. Chem.*, **379**, 151 (1989).
107. S. J. Sherlock, M. Cowie, E. Singleton, and M. M. de V. Steyn, *J. Organomet. Chem.*, **361**, 353 (1989).

108. D. Carmona, J. Ferrer, R. Atencio, F. J. Lahoz, L. A. Oro, and M. P. Lamata, *Organometallics*, **14**, 2057 (1995).
109. M. T. Pinillos, A. Elduque, and L. A. Oro, *Polyhedron*, **11**, 1007, 1992.
110. M. T. Pinillos, A. Elduque, and L. A. Oro, *Inorg. Chim. Acta*, **178**, 179 (1990).
111. B. M. Louie, S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, **63**, 688 (1985).
112. M. T. Pinillos, A. Elduque, J. A. Lopez, F. J. Lahoz, and L. A. Oro, *J. Chem. Soc. Dalton Trans.*, 1391 (1991).
113. F. H. Cano, C. Foces-Foces, L. A. Oro, M. T. Pinillos, and C. Tejel, *Inorg. Chim. Acta*, **128**, 75 (1987).
114. M. T. Pinillos, A. Elduque, J. A. Lopez, F. J. Lahoz, L. A. Oro, and B. E. Mann, *J. Chem. Soc. Dalton Trans.*, 2389 (1992).
115. P. Kalck, J. M. Frances, P. M. Pfister, T. G. Southern, and A. Thorez, *J. Chem. Soc. Chem. Commun.*, 510 (1983).
116. A. Tiripicchio, F. J. Lahoz, L. A. Oro, and M. T. Pinillos, *J. Chem. Soc. Chem. Commun.*, 936 (1984).
117. C. Claver, P. Kalck, M. Ridmy, A. Thores, L. A. Oro, M. T. Pinillos, M. C. Apreada, F. H. Cano, and C. Foces-Foces, *J. Chem. Soc. Dalton Trans.*, 1523 (1988).
118. M. T. Pinillos, A. Elduque, L. A. Oro, F. J. Lahoz, F. Bonati, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc. Dalton Trans.*, 989 (1990).
119. L. A. Oro, D. Carmona, M. P. Garcia, F. J. Lahoz, J. Reyes, C. Foces-Foces, and F. H. Cano, *J. Organomet. Chem.*, **296**, C43 (1985).
120. M. P. Garcia, A. Portilla, L. A. Oro, C. Foces-Foces, and F. H. Cano, *J. Organomet. Chem.*, **322**, 111 (1987).
121. M. T. Pinillos, A. Elduque, E. Martin, N. Navarro, F. J. Lahoz, J. A. Lopez, and L. A. Oro, *Inorg. Chem.*, **34**, 111 (1995).
122. M. T. Pinillos, A. Elduque, E. Martin, N. Navarro, L. A. Oro, A. Tiripicchio, and F. Ugozzoli, *Inorg. Chem.*, **34**, 3105 (1995).
123. M. T. Pinillos, C. Tejel, L. A. Oro, M. C. Apreada, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc. Dalton Trans.*, 1133 (1989).
124. A. Elduque, L. A. Oro, M. T. Pinillos, C. Tejel, A. Tiripicchio, and F. Ugozzoli, *J. Chem. Soc. Dalton Soc. Trans.*, 2807 (1991).
125. G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J. M. Marti, and M. D. Santana, *J. Organomet. Chem.*, **393**, C53 (1990).
126. D. Carmona, A. Mendoza, J. Ferrer, F. J. Lahoz, and L. A. Oro, *J. Organomet. Chem.*, **431**, 87 (1992).
127. L. A. Oro, D. Carmona, M. P. Lamata, M. C. Apreada, C. Foces-Foces, F. H. Cano, and P. M. Maitlis, *J. Chem. Soc. Dalton Trans.*, 1823 (1984), and references cited therein.
128. D. Carmona, L. A. Oro, M. P. Lamata, M. P. Puebla, J. Ruiz, and P. M. Maitlis, *J. Chem. Soc. Dalton Trans.*, 639 (1987).
129. J. A. Bailey, S. L. Grundy, and S. R. Stobart, *Organometallics*, **9**, 536 (1990).

130. M. P. Lamata, D. Carmona, L. A. Oro, M. C. Aprea, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, **158**, 131 (1989).
131. D. Carmona, M. P. Lamata, M. Esteban, F. J. Lahoz, L. A. Oro, M. C. Aprea, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc. Dalton Trans.*, 159 (1994).
132. M. Valderrama, M. Scotti, J. Cuevas, D. Carmona, M. P. Lamata, J. Reyes, F. J. Lahoz, E. Onate, and L. A. Oro, *J. Chem. Soc. Dalton Trans.*, 2735 (1992).
133. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, and J. Trotter, *Inorg. Chem.*, **32**, 5176 (1993).
134. M. K. Ehlert, S. J. Rettig, A. Storr, A. C. Thompson, and J. Trotter, *Acta Crystallogr.*, **C50**, 1023 (1994).
135. M. Angaroni, G. A. Ardizzoia, T. Beringhelli, G. La Monica, D. Gatteschi, N. Masciocchi, and M. Moret, *J. Chem. Soc. Dalton Trans.*, 3305 (1990).
136. F. B. Hulsbergen, R. W. M. ten Hoedt, G. C. Verschoor, J. Reedijk, and A. L. Spek, *J. Chem. Soc. Dalton Trans.*, 539 (1983).
137. G. A. Ardizzoia, M. A. Angaroni, G. La Monica, F. Cariati, S. Cenini, M. Moret, and M. Masciocchi, *Inorg. Chem.*, **30**, 4347 (1991).
138. R. Robson, *Inorg. Nucl. Chem. Lett.*, **6**, 125 (1970).
139. P. A. Vigato, S. Tamburini, and D. E. Fenton, *Coord. Chem. Rev.*, **106**, 25 (1990) and references cited therein.
140. T. N. Doman, D. E. Williams, J. F. Banks, R. M. Buchanan, H. R. Chang, R. J. Webb, and D. N. Hendrickson, *Inorg. Chem.*, **29**, 1058 (1990). See also references cited therein.
141. W. Mazurek, B. J. Kennedy, K. S. Murray, M. J. O'Connor, J. R. Rodgers, M. R. Snow, A. G. Wedd, and P. R. Zwack, *Inorg. Chem.*, **24**, 3258 (1985).
142. Y. Nishida and S. Kida, *Inorg. Chem.*, **27**, 447 (1988).
143. D. Ajó, A. Bencini, and F. Mani, *Inorg. Chem.*, **27**, 2437 (1988).
144. K. Matsumoto, S. Ooi, W. Mori, and Y. Nakao, *Bull. Chem. Soc. Jpn.*, **60**, 4477 (1987).
145. P. Iliopoulos, K. S. Murray, R. Robson, J. Wilson, and G. A. Williams, *J. Chem. Soc. Dalton Trans.*, 1585 (1987).
146. M. G. B. Drew, P. C. Yates, F. S. Esho, J. Trocha-Grimshaw, A. Lavery, K. P. McKillop, S. M. Nelson, and J. Nelson, *J. Chem. Soc. Dalton Trans.*, 2995 (1988).
147. P. Iliopoulos, G. D. Fallon, and K. S. Murray, *J. Chem. Soc. Dalton Trans.*, 1823 (1988).
148. C. J. McKenzie and R. Robson, *Inorg. Chem.*, **26**, 3615 (1987).
149. M. Mikuriya, K. Nakadera, and T. Kotera, *Chem. Lett.*, 637 (1993).
150. L. A. Oro, D. Carmona, M. P. Puebla, M. P. Lamata, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, **112**, L11 (1986).
151. T. V. Ashworth, D. C. Liles, and E. Singleton, *J. Chem. Soc. Chem. Commun.*, 1317 (1984).
152. T. V. Ashworth, D. C. Liles, and E. Singleton, *Inorg. Chim. Acta*, **98**, L65 (1985).

153. M. O. Albers, S. F. A. Crosby, D. C. Liles, D. J. Robinson, A. Shaver, and E. Singleton, *Organometallics*, **6**, 2014 (1987).
154. R. Atencio, C. Bohanna, M. A. Esteruelas, F. J. Lahoz, and L. A. Oro, *J. Chem. Soc. Dalton Trans.*, 2171 (1995).
155. M. I. Bruce, M. G. Humphrey, M. R. Snow, E. R. T. Tiekink, and R. C. Wallis, *J. Organomet. Chem.*, **314**, 311 (1986).
156. J. R. Shapley, D. E. Samkoff, C. Bueno, and M. R. Churchill, *Inorg. Chem.*, **21**, 634 (1982).
157. L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, and F. H. Cano, *Inorg. Chim. Acta*, **112**, 35 (1986).
158. J. A. Cabeza, R. J. Franco, V. Riera, S. Garcia-Granda, and J. F. Van der Maelen, *Organometallics*, **14**, 3342 (1995).
159. C. P. Kubiak and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 6129 (1977).
160. L. A. Oro, D. Carmona, P. L. Perez, M. Esteban, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc. Dalton Trans.*, 973 (1985).
161. D. Carmona, L. A. Oro, P. L. Pérez, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc. Dalton Trans.*, 1427 (1989).
162. L. A. Oro, M. T. Pinillos, A. Tiripicchio, and M. Tiripicchio-Camellini, *Inorg. Chim. Acta*, **99**, L13 (1985).
163. C. J. Janke, L. J. Tortorelli, J. L. E. Burn, C. A. Tucker, and C. Woods, *Inorg. Chem.*, **25**, 4597 (1986).
164. C. Woods, L. J. Tortorelli, D. P. Rillema, J. L. E. Burn, and J. C. DePriest, *Inorg. Chem.*, **28**, 1673 (1989).
165. L. J. Tortorelli, C. Woods, and A. T. McPhaie, *Inorg. Chem.*, **29**, 2726 (1990).
166. L. J. Tortorelli, C. Woods, and C. F. Campana, *Acta Crystallogr.*, **C48**, 1311 (1992).
167. G. W. Bushnell, K. R. Dixon, D. T. Eadie, and S. R. Stobart, *Inorg. Chem.*, **20**, 1545 (1981).
168. A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti, F. Demartin, and M. Manassero, *J. Organomet. Chem.*, **269**, 91 (1984).
169. A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti, F. Demartin, and M. Manassero, *Inorg. Chem.*, **26**, 1351 (1987).
170. J. A. Bailey and H. B. Gray, *Acta Crystallogr.*, **C48**, 1420 (1992).
171. J. A. Bailey, V. M. Miskowski, and H. B. Gray, *Inorg. Chem.*, **32**, 369 (1993).
172. G. Minghetti, G. Banditelli, and F. Bonati, *J. Chem. Soc. Dalton Trans.*, 1851 (1979).
173. B. Bovio, F. Bonati, and G. Banditelli, *Gazz. Chim. Ital.*, **115**, 613 (1985).
174. W. P. Schaefer, W. B. Connick, V. M. Miskowski, and H. B. Gray, *Acta Crystallogr.*, **C48**, 1776 (1992).
175. F. Bonati and H. C. Clark, *Can. J. Chem.*, **56**, 2513 (1978).
176. A. L. Bandini, G. Banditelli, G. Minghetti, and F. Bonati, *Can. J. Chem.*, **57**, 3237 (1979).

177. E. Kime-Hunt, K. Spartalian, M. DeRusha, C. M. Nunn, and C. J. Carrano, *Inorg. Chem.*, **28**, 4392 (1989).
178. I. A. Degnan, W. A. Herrmann, and E. Herdtweck, *Chem. Ber.*, **123**, 1347 (1990).
179. M. M. Taqui Khan, P. S. Roy, K. Venkatasubramanian, and N. H. Khan, *Inorg. Chim. Acta*, **176**, 49 (1990).
180. G. Lopez, J. Ruiz, C. Vicente, J. M. Marti, G. Garcia, P. A. Chaloner, P. B. Hitchcock, and R. M. Harrison, *Organometallics*, **11**, 4090 (1992).
181. N. Masciocchi, M. Moret, A. Sironi, G. A. Ardizzoia, S. Cenini, and G. La Monica, *J. Chem. Soc. Chem. Commun.*, 1955 (1995).
182. D. Carmona, M. P. Lamata, J. Ferrer, J. Modrego, M. Perales, F. J. Lahoz, R. Atencio, and L. A. Oro, *J. Chem. Soc. Chem. Commun.*, 575 (1994).
183. S. Trofimenko, *J. Am. Chem. Soc.*, **91**, 5410 (1969).
184. K. S. Chong, S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, **57**, 3099 (1979).
185. A. R. Barron, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *Polyhedron*, **4**, 1131 (1985).
186. C. W. Eigenbrot, Jr., and K. N. Raymond, *Inorg. Chem.*, **20**, 1553 (1981).
187. C. W. Eigenbrot, Jr., and K. N. Raymond, *Inorg. Chem.*, **21**, 2653 (1982).
188. D. Röttger, G. Erker, M. Grehl, and R. Fröhlich, *Organometallics*, **13**, 3897 (1994).
189. H. Schuman, J. Loebel, J. Pickardt, C. Qian, and Z. Xie, *Organometallics*, **10**, 215 (1991).
190. G. B. Deacon, B. M. Gatehouse, S. Nickel, and S. N. Platts, *Austr. J. Chem.*, **44**, 613 (1991).
191. J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, H. Hemling, and H. Schumann, *Angew. Chem. Int. Ed. Engl.*, **32**, 874 (1993).
192. H. Schumann, P. R. Lee, and J. Loebel, *Angew. Chem. Int. Ed. Engl.*, **28**, 1033 (1989).
193. J. C. Bayon, C. Net, P. Esteban, P. G. Rasmussen, and D. F. Bergstrom, *Inorg. Chem.*, **30**, 4771 (1991).
194. J. C. Bayon, P. Esteban, G. Net, P. G. Rasmussen, K. N. Baker, C. W. Hahn, and M. M. Gumz, *Inorg. Chem.*, **30**, 2572 (1991).
195. T. Kamiyusuki, H. Okawa, E. Kitaura, M. Koikawa, N. Matsumoto, S. Kida, and H. Oshio, *J. Chem. Soc. Dalton Trans.*, 2077 (1989).
196. T. Kamiyusuki, H. Okawa, N. Matsumoto, and S. Kidá, *J. Chem. Soc. Dalton Trans.*, 195 (1990).
197. T. Kamiyusuki, H. Okawa, E. Kitaura, K. Inoue, and S. Kida, *Inorg. Chim. Acta*, **179**, 139 (1991).
198. M. Itoh, K. Motoda, K. Shindo, T. Kamiyusuki, H. Sakiyama, N. Matsumoto, and H. Okawa, *J. Chem. Soc. Dalton Trans.*, 3635 (1995).
199. B. Mernari, F. Abraham, M. Lagrenee, M. Drillon, and P. Legoll, *J. Chem. Soc. Dalton Trans.*, 1707 (1993).

200. K. Shindo, Y. Mori, K. Motoda, H. Sakiyama, N. Matsumoto, and H. Okawa, *Inorg. Chem.*, **31**, 4987 (1992).
201. J. Casabo', J. Pons, K. S. Siddiqi, F. Teixidor, E. Molins, and C. Miravittles, *J. Chem. Soc. Dalton Trans.*, 1401 (1989).
202. M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, and S. Kitagawa, *J. Chem. Soc. Dalton Trans.*, 4099 (1995).
203. P. W. Ball and A. B. Blake, *J. Chem. Soc. (A)*, 1415 (1969).
204. J. Pons, X. Lopez, J. Casabo', F. Teixidor, A. Caubet, J. Rius, and C. Miravittles, *Inorg. Chim. Acta*, **195**, 61 (1992).
205. M. Kumar, V. J. Aran, P. Navarro, A. Ramos-Gallardo, and A. Vegas, *Tetrahedron Lett.*, **35**, 5723 (1994).
206. M. Kumar, V. J. Aran, and P. Navarro, *Tetrahedron Lett.*, **34**, 3159 (1993).
207. C. Acerete, J. M. Bueno, L. Campayo, P. Navarro, M. I. Rodriguez-Franco, and A. Samat, *Tetrahedron Lett.*, **50**, 4765 (1994).
208. T. G. Schenck, J. M. Downes, C. R. C. Milne, P. B. Mackenzie, H. Boucher, J. Whelan, and B. Bosnich, *Inorg. Chem.*, **24**, 2334 (1985).
209. K. A. Beveridge, G. W. Bushnell, S. R. Stobart, J. L. Atwood, and M. J. Zaworotko, *Organometallics*, **2**, 1447 (1983).
210. S. Nussbaum, S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, **63**, 692 (1985).
211. D. L. Lichtenberger, A. S. Copenhaver, H. B. Gray, J. L. Marshall, and M. D. Hopkins, *Inorg. Chem.*, **27**, 4488 (1988).
212. P. Kalck, J. M. Frances, P. M. Pfister, T. G. Southern, and A. Thorez, *J. Chem. Soc. Chem. Commun.*, 510 (1983).
213. A. Dedieu, P. Escaffre, J. M. Frances, P. Kalck, and A. Thorez, *Nouv. J. Chim.*, **10**, 631 (1986).
214. P. Kalck, A. Thorez, M. T. Pinillos, and L. A. Oro, *J. Mol. Catal.*, **31**, 311 (1985).
215. C. Claver, P. Kalck, L. A. Oro, M. T. Pinillos, and C. Tejel, *J. Mol. Catal.*, **43**, 1 (1987).
216. R. Uson, L. A. Oro, M. T. Pinillos, M. Royo, and E. Pastor, *J. Mol. Catal.*, **14**, 375 (1982).
217. L. A. Oro, M. Campo, and D. Carmona, *J. Mol. Catal.*, **39**, 341 (1987).