Inorganica Chimica Acta, *119* (1986) 165–169

Complexes of Diphosphaferrocenes with Lewis Acids and Cu(I), Ag(I) Salts

R. M. G. ROBERTS*, J. SILVER* and A. S. WELLS

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, U.K.

(Received March 19, 1986)

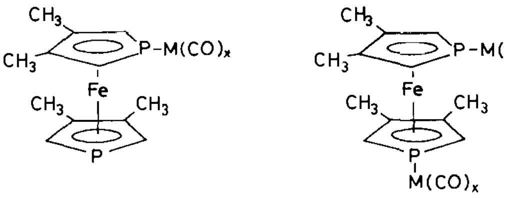
Abstract

Complexes of diphosphaferrocenes have been prepared using (a) Lewis acids $BF_3 \cdot Et_2O$, $AlCl_3$ and (b) Cu(I) and Ag(I) salts. The ^{31}P spectra showed that $BF_3 \cdot Et_2O$ complexes at phosphorus (characterised by a large downfield shift of 103 ppm) whereas all the other adducts involved binding at iron (characterised by large upfield shifts of 36–94 ppm). Deep purple adducts were isolated and characterised for the reaction of 2,2′,5,5′-tetraphenyldiphosphaferrocene with silver trifluoroacetate and triflate and also with copper(I) iodide. Similar complexes were isolated from 3,3′,4,4′-tetramethyldiphosphaferrocene. ^{57}Fe Mössbauer spectroscopy of the adducts showed that unlike the ferrocene system, quadrupole splittings generally decreased on iron complexation. The results are discussed in terms of current MO theory of ferrocene and diphosphaferrocene.

Introduction

η^5-Cyclopentadienyl metal complexes are known to form adducts with Lewis acids. Both ferrocene [1, 2] and ruthenocene [1] form complexes with $HgCl_2$ via metal–metal interactions. Stronger Lewis acids, such as $SnCl_4$, oxidise ferrocene to ferricinium species. By contrast, [2]-ferrocenophane forms stable adducts [3] of the type $\{[C_2H_4(C_5H_4)_2Fe^+]_2SnCl_2\}[SnCl_5^-]_2$ where two FeSn bonds are present. These complexes show very large quadruple splittings (*QS* = 3.49 mm s^{-1}) which result from bonding of the tin moiety via e_{2g} iron based orbitals. Ferrocene and ruthenocene are also weak Brönsted bases and can be metal–protonated in strong acid [4]. The protonated ferrocene derivatives also show high *QS* values.

Heterocyclic ferrocene analogues such as phospha- and azaferrocenes carry lone pairs of electrons on the heteroatom which do not contribute to metal–ligand bonding and are thus available for complexation with other metals. There are, therefore, two Lewis base sites in these species. We have recently studied protonation of mono- and diphosphaferrocenes in trifluoromethanesulphonic acid (triflic acid) [5] and have shown that metal rather than phosphorus protonation occurs. The P lone pair in π bonded phosphacyclopentadienyl (PC_p) ligands is less reactive than those in phosphines [6]. However, some P-bonded σ complexes are known, mainly with low oxidation state metal carbonyls and ruthenium(II) chloride



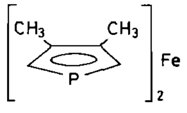
M= Fe, x = 4 ; M = Cr, Mo, W, x = 5

Although the P atom in these systems is a poor σ donor the PC_p ring acts as a good π acceptor inducing back bonding from the electron rich $M(CO)_x$ groups.

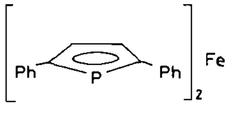
This report deals with complexation of diphosphaferrocenes with some common Lewis acids together with Cu(I) and Ag(I) salts.

Discussion and Results

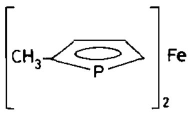
Two readily available diphosphaferrocenes were chosen for detailed study – the 3,3′,4,4′-tetramethyl derivative **I** [7] and the 2,2′,5,5′-tetraphenyl derivative **II** [7]. In some cases other substituted derivatives were used.



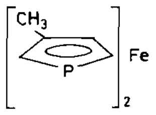
I



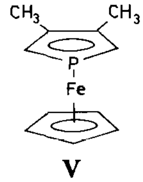
II



III



IV



V

---

*Authors to whom correspondence should be addressed.

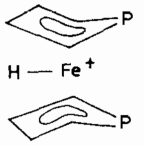
0020-1693/86/$3.50

TABLE I. ^{31}P Chemical Shifts[a] (δ in ppm relative to 85% H_3PO_4, +ve downfield) for Metal Complexes of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene(I)

Complex	$\delta\,^{31}P$
I	−72.0
$I\cdot Fe(CO)_4$	+32.4, −63.6
$I\cdot[Fe(CO)_4]_2$	+35
$I\cdot W(CO)_4$	−47.7, −66.54
$I\cdot[W(CO)_4]_2$	−46.25
$I\cdot Mo(CO)_5$	−23.49, −67.17
$I\cdot[Mo(CO)_5]_2$	−22.02
$I\cdot Cr(CO)_5$	+11.69, −67.71
$I\cdot[Cr(CO)_5]_2$	+13.57
$I\cdot Cr(CO)_5Mo(CO)_5$	+13.57 (Cr), −21.95 (Mo)
$I\cdot Cr(CO)_5W(CO)_5$	+14.17 (Cr), −46.79 (W)
$I\cdot Mo(CO)_5W(CO)_5$	−21.2 (Mo), −46.56 (W)
$I\cdot Mn_2(CO)_9$	+22, −66.95
$I\cdot[Mn_2(CO)_9]_2$	+29
$I\cdot RuCl_2$	+12.29, −72.87
$[PPh_3RuCl_2]_2$	+55.76 (PPh_3) + 17.73 (Ru)

[a] Data from refs. 6 and 8.

^{31}P NMR enables the site of complexation to be assigned unambiguously. Table I lists the ^{31}P shifts of a number of known complexes of I. In all cases marked downfield shifts occur typical of phosphorus complexation. In contrast protonation of iron causes large upfield shifts of 60–70 ppm for diphosphaferrocenes and 140–180 ppm for monophosphaferrocenes. In addition in some instances metal–phosphorus coupling is observed ($^1J_{W-P} = 257$ Hz in $I\cdot[W(CO)_5)$ [8]. The upfield shifts in iron protonated phosphaferrocenes [5] is thought to be due to increased PC_p ring puckering about the $C_\alpha C_\alpha{}'$ axis. The PC_p ligands in I are not planar, the P atoms being bent away from the iron atom. Metal protonation will undoubtedly cause considerable ring tilt and increased puckering as depicted below.



Lewis Acid Adducts

Diphosphaferrocenes readily formed adducts with Lewis acids. However, their structure varied with the strength of the Lewis acid. Table II lists the ^{31}P NMR of these derivatives.

I, when treated with $BF_3\cdot OEt_2$* in $CDCl_3$, gave a deep purple solution whose intensity increased with time. The rate of formation of the adduct could be followed using ^{31}P NMR. The spectrum of the adduct comprised two signals, one (−62.2 ppm) slightly downfield from free I (−72 ppm) [8] and the other considerably downfield at +31.0 ppm, the latter being very close to the value observed for $I-Fe(CO)_4$ [9]. The high field phosphorus signal appeared as a triplet with a $^2J_{PH}$ value of 36 Hz typical of the phosphaferrocene systems. The low field signal (+31.0 ppm) was a broad singlet probably caused by unresolved P–B coupling. I therefore appears to react with BF_3 to form a phosphorus bonded adduct. Even in the presence of excess $BF_3\cdot OEt_2$ only the mono adduct was formed which suggests that complexation of one P site deactivates the other. The reaction of $BF_3\cdot OEt_2$ with V, gave a deep red complex which also showed low field ^{31}P

TABLE II. ^{31}P NMR Data for Compexes Described in this Work

Compound	Solvent	Reactant	$\delta\,^{31}P$[a]	$\Delta\delta$[b]
I	$CDCl_3$	BF_3OEt_2	+31.0[c], −62.6	+103, +9.8
V	$CDCl_3$	BF_3OEt_2	+22.70	+104.7
II	$CDCl_3$	$AlCl_3$	−137.4	−76.4
II	DMF	CF_3CO_2Ag	−133.3	−72.3
I	CH_3CN	CF_3SO_3Ag	−140.8[d]	−68.8
II	CH_3CN	CF_3SO_3Ag	−146.3	−85.3
III	CH_3CN	CF_3SO_3Ag	−145.1, −148.9	−91.1, −90.0
IV	CH_3CN	CF_3SO_3Ag	−139.2, −155.3	−80.9, −96.5
I	CH_3CN	CF_3SO_3Ag[e]	−165.6[e]	
II	CH_3CN	CF_3SO_3Ag[e]	−153.2	
I	DMF	CF_3SO_3Ag[e]	−160.5	
I	DMF	CuI	−144.4	−72.4
I	CH_3CN	CF_3SO_3Cu	−153.50[f]	−81.5
II	CH_3CN	CF_3SO_3Cu	−108.61	−47.6

[a] To 85% H_3PO_4, +ve downfield. [b] $\Delta\delta = \delta$ uncomplexed − δ complexed. [c] $^2J_{PH} = 36$ Hz. [d] $^2J_{PH} = 28$ Hz. [e] Solid isolated from benzene. [f] $^2J_{PH} = 34$ Hz.

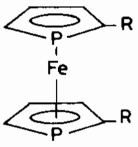
---

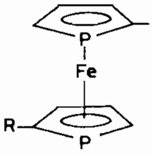
*Complex formation was very slow using aged BF_3OEt_2 samples.

signals (+22.7 ppm) indicative of P complexation. As with **I**, $^2J_{PH}$ was not observed. **I** and **V** in the presence of $AlCl_3$ or $SnCl_4$ underwent rapid oxidation, whereas **II** did not react with either BF_3OEt_2 or $SnCl_4$ in $CHCl_3$, presumably due to a reduction in σ bonding capacity of the phosphorus by the adjacent phenyl groups and increased steric hindrance to complexation. The electron withdrawing phenyl substituents also inhibit oxidation. The stronger Lewis acid $AlCl_3$ dissolved in solutions of **II** in $MeNO_2$ and MeCN† to form deep purple solutions whose ^{31}P NMR spectrum showed a broad singlet 76.4 ppm upfield from **II** itself. This is similar to the change in shift for **II** in CF_3SO_3H (75.8 ppm) where iron protonation occurs [5]. Thus in contrast to $BF_3{\cdot}OEt_2$, $AlCl_3$ forms an iron bound species. **II** could be recovered unchanged by the addition of aqueous Na_2CO_3 provided exposure to $AlCl_3$ was limited, otherwise extensive decomposition occurred over 4–5 h.

Silver(I) Complexes

Ag salts normally oxidise ferrocenes and this was found for the reaction of **I** with CF_3CO_2Ag though no well defined phosphaferricinium derivative could be isolated. This confirms the instability of such species as shown by cyclic voltammetry [10]. On the other hand **II** reacted with CF_3CO_2Ag to give a stable purple 1:1 adduct which was insoluble in most organic solvents. (**II**$\cdot CF_3CO_2Ag$) was sparingly soluble in DMF or DMSO but solutions were not very stable. ^{31}P NMR spectra of freshly made saturated DMF solution showed a broad singlet 72.3 ppm upfield from free **II** which is a very similar shift to that of the $AlCl_3$ adduct suggesting the presence of an Fe–Ag bond. Much more stable solutions of adducts could be prepared using silver triflate (CF_3SO_3Ag). In addition the solubility of the adduct was greatly increased. The purple solution of adducts of **I**–**IV** were stable for several hours in dry MeCN, but the addition of water led to rapid oxidation. The ^{31}P NMR results for **I** → **IV** (Table II) parallel those obtained for CF_3CO_2Ag and the upfield shifts being even more marked. These results remove the possibility that, for **II**, $AlCl_3$ complexation occurred on the phenyl rings. The upfield shifts ($\Delta\delta$) of the Ag^+ adducts are greater than those of the iron protonated analogues [5] and are probably due to the larger size of the Ag^+ ion which causes more distortion of the PC_p ring on binding to the iron. The actual magnitudes of $\Delta\delta$ do not follow the expected trend. **I** has the most basic Fe atom but shows the smallest upfield shift when complexed. It is likely that as for the iron–protonated species, the Ag^+ enters the structure in a direction remote from the P atoms. This would result in steric hindrance from the four β methyl groups. **II**–**IV** having fewer β substituents thus interact more strongly with Ag^+. Both **III** and **IV** occurs as interactable mixtures of structural isomer.





The ^{31}P NMR spectra of the Ag complexes under broad band decoupling showed two high field signals of approximately equal intensity indicating that both isomers formed adducts. In all the complexes hitherto described, no P–Ag coupling was detected which eliminates P–Ag bonding (typical $^1J_{^{31}P-^{107}Ag}$ = 200–700 Hz). Although the isolation of solid adducts from MeCN solution proved difficult we were able to obtain a 1:1 adduct for both **I** and **II** from CF_3SO_3Ag in benzene. The somewhat different ^{31}P shifts suggest a slightly different structure in MeCN probably due to complexation by the solvent which has a strong affinity for Ag^+. The Fe–Ag interaction is, however, still present.

Copper(I) Complexes

Both **I** and **II** formed 1:1 adducts with CuI in MeCN, though the latter was formed very slowly. Both adducts were insoluble in most solvents but [**I**$\cdot$CuI] dissolved sparingly in DMF to give a solution with ^{31}P shifts comparable to those of the Ag adduct thus implying Fe–Cu bonding. [**II**$\cdot$CuI] was completely insoluble. However, ^{57}Fe Mössbauer spectra indicated a similar structure (*vide infra*). As for the silver analogues, copper(I) triflate* gave better results with similar large upfield ^{31}P shifts and no evidence of P–Cu coupling (usually 1100–1500 Hz). The Cu triflate complexes proved impossible to isolate from solution.

^{57}Fe Mössbauer Spectra

The formation of metal–metal bonds in ferrocene systems is characterised by large increases in quadrupole splitting (*QS*). Both the $HgCl_2$ and $SnCl_4$ adducts of [2]-ferrocenophane show increases in *QS* of 0.6 and 0.9 mm s^{-1} [3] respectively relative to ferrocene. These increments have been attributed to redistribution of the electrons in the iron-based HOMO (e_{2g}) necessary for metal–metal bond formation. Diphosphaferrocenes (DPF) show reduced *QS* values relative to ferrocene [11] due to electron withdrawal by the PCp ligands and substituent effects are similar to those in ferrocene. Metal protonated diphosphaferrocenes usually show exalted *QS* values. The Mössbauer data for the adducts

---

† **II** is insoluble in $MeNO_2$, and MeCN but addition of $AlCl_3$ rapidly causes dissolution.

*CF_3SO_3Cu is isolated as $[CF_3SO_3Cu]_2C_6H_6$ but in MeCN it probably exists as $[Cu(MeCN)_4]^+CF_3SO_3^-$.

TABLE III. ^{57}Fe Mössbauer Parameters (Isomer Shifts, *IS* quadrupole Splitting *QS* both in mm s^{-1} at 80 K) for Diphosphaferrocene Complexes

Compound	Phase[a]	*IS*	*QS*	Δ*QS*[b]
I	S	0.48(1)	1.87(1)	
I·$AgOSO_2CF_3$	S	0.50(1)	1.79(1)	−0.08
I·$AgOSO_2CF_3$	FSS	0.53(1)	1.74(1)	−0.13
I·CuI	S	0.51(1)	1.61(2)	−0.26
I·BF_3	FSS	0.48(1)	1.89(1)	+0.02
II	S	0.54(1)	1.54(2)	
II·$AgOSO_2CF_3$	S	0.54(1)	1.62(1)	+0.08
II·$AgOSO_2CF_3$	FSS	0.53(1)	1.54(2)	0.00
II·$AgOCOCF_3$	S	0.55(1)	1.53(1)	+0.01
II·$AlCl_3$	FSS	0.56(1)	1.50(2)	−0.04
II·CuI	S	0.53(1)	1.33(1)	−0.21
III	S	0.51(1)	1.79(1)	
IV	S	0.50(1)	1.82(1)	
IV·$AgOSO_2CF_3$	FSS	0.53(1)	1.77(1)	−0.05

[a] S = solid, FSS = complex prepared in solution as for ^{31}P NMR spectroscopy and quench cooled to 80 K using CH_3CN as solvent except for BF_3 where $CHCl_3$ was used. [b] Δ*QS* = *QS* (complex) − *QS* (parent).

described above appear in Table III. It is apparent that for the silver and aluminium to iron bonds that unlike ferrocene the *QS* values are relatively less affected by this metal–metal bonding, whereas for the copper–iron bonds the *QS* values are lowered by around 0.2 mm s^{-1} than that of the parent DPF. These effects are probably due to the decreased basicity of the iron atom in the DPF system leading to relatively weaker interactions. In addition, the degree of ring tilt is difficult to assess and its contribution to *QS* values problematical. Small ring tilt angles (~10°) appear to cause small reductions in *QS* [12] but larger values (23°) actually result in enhanced *QS* [13].

For **II**, protonation results in an increase in *QS* of 0.23 mm s^{-1}. For the metal adducts described above, *QS* values fall as the Lewis acidity drops (*viz.* Δ*QS* for Cu(I) complexes are ~ -0.2 mm s^{-1}).

This different behaviour of the phosphaferrocenes relative to ferrocene is perhaps not surprising since the ordering of molecular orbitals is different for the two systems. Both ferrocene [14, 15], phosphaferrocenes [16, 17] have been the subject of detailed MO calculations. From these studies major differences are found for ferrocene (FcH) [15] and DPF [16]. Although both systems have high-lying metal based orbitals a_{1g} (−10.75, −8.76 eV) and e_{2g} (−11.22, −10.01 eV for FcH and DPF respectively) the ligand-based e_{1g} orbitals are very different. For FcH, the e_{1g} at −10.94 eV has 23.5% metal (d_{xz}, d_{yz}) characters and 74.7% (58.5% π, 16.2% σ) ligand character [15]. The corresponding orbital for DPF at −11.88 eV has only 5% metal orbital (d_{xz}, $d_{x^2-y^2}$) contribution with 93% ligand character (66% σ_p and 27% π_p). It therefore represents a rather different type of bonding (mainly Fe–P interactions) and hence will only weakly transmit to the iron atom electron density changes arising from PC_p ring substitution. Most of the ligand–metal bonding arises from low-lying e_1 orbitals at −14.45 eV (18% d_{xz}, d_{yz}; 49% π_p, 6% σ_p) and −14.57 eV (20% d_{xz}, d_{yz}; 40% π_c 30% π_p). These orbitals are unlikely to be involved in ring substitution processes since they are far from being frontier orbitals. It is generally considered that the e_{2g} orbitals are used in forming metal–metal bonds. These orbitals have a somewhat different composition in FcH and DPF, the former having a higher Fe orbital content. In addition e_{2g} for DPF appears to be of significantly higher energy than that of FcH which suggests that DPF should react more easily with Lewis acids.

By the same token, DPF should also be oxidised more readily if electron transfer occurs from Fe-based orbitals. This, however, is not found experimentally. Unfortunately at present there is no general agreement [16, 17] as to the ordering of energy levels in phosphaferrocenes which makes structure/reactivity correlations uncertain. What is beyond dispute is that the phosphorus lone pairs orbitals are low lying which explains why strong electrophiles such as metal ions and Lewis acids coordinate preferentially at iron. Coordination to phosphorus should induce backbonding and is the chosen site for zero oxidation state metal carbonyls. BF_3 cannot act as a π donor and thus coordinates to P rather than Fe. The Ag(I) adducts of diphosphaferrocenes are reasonably stable though stability is dependent on the counter ion and solvent. By contrast ferrocene always oxidises immediately when treated with CF_3SO_3Ag or CF_3CO_2Ag. The enhanced stability of the diphosphaferrocene silver adduct is undoubtedly due to the higher oxidation potentials found in the diphosphaferrocene system.

A final point of interest is the structure adopted by the diphosphaferrocene metal bonded adduct. For all cases the electrophile is probably located *trans* to the phosphorus atoms. The large radius of the phosphorus atom compared to a CH unit makes the metal orbitals less accessible, hence bonding occurs on the side of the molecule remote from the phosphorus atoms.

Experimental

Phosphaferrocenes were produced by literature methods as was $(CF_3SO_3Cu)_2C_6H_6$. Other reagents were made by standard procedures or supplied commercially.

All preparations were carried out under dry Ar using anhydrous solvents dried by standard methods. *In situ* complexation reactions were also carried out using anhydrous solvents. Phosphaferrocene/metal ion reactions were carried out in subdued light and isolated products stored in the dark.

^{1}H NMR spectra were obtained on a Varian EM360 reference external TMS. ^{31}P NMR spectra were run on a Bruker WP80 spectrometer (probe temperature 30 °C). The reference was 85% H_3PO_4. For non deuterated solvents an external D_2O lock was used. Chemical shifts were measured in ppm with a $+\delta$ indicating downfield shifts. Elemental analysis was performed by the Analytical Department, University of Manchester. Analytical data refers to products initially 'isolated'. Further attempts to purify the products via recrystallisation were unsuccessful.

2,2',5,5'-Tetraphenyldiphosphaferrocene/silver Triflate Complex

II (0.2 g, 0.38 mmol) was dissolved in dry benzene (50 cm^3) and filtered. Silver triflate (0.1 g, 0.38 mmol) was added and the mixture stirred for 0.5 h. The flask was left to stand for 1 h, whereupon the resulting dark purple precipitate was filtered off, washed with dry benzene ($\sim$150 cm^3) and dried *in vacuo*. Yield 0.21 g (71%). *Anal.* Found C, 48.5; H, 3.0; Ag, 13.0. Calc. for $C_{33}H_{24}AgF_3FeO_3P_2S$: C, 50.6; H, 3.1; Ag, 13.8%.

3,3',4,4'-Tetramethyldiphosphaferrocene/silver Triflate Complex

An identical procedure starting from **I** (0.2 g, 0.72 mmol) and silver triflate (0.19 g, 0.72 mmol) gave the title compound. Yield 0.31 g (80%). *Anal.* Found: C, 30.5; H, 3.4; Ag, 17.7. Calc. for $C_{13}H_{16}AgF_2FeO_3P_2S$: C, 29.1; H, 3.0; Ag, 20.2%.

2,2',5,5'-Tetraphenyldiphosphaferrocene/silver Trifluoroacetate Complex

Finely ground **II** (0.3 g, 0.57 mmol) was suspended in a dry acetone solution of silver trifluoroacetate (50 ml, 0.13 g, 0.57 mmol) and stirred at room temperature for 1 h. The resulting purple solid was filtered off and washed with acetone ($\sim$150 cm^3). Yield 0.34 g (80%). *Anal.* Found. C, 54.6, H, 3.3; Ag, 13.9; Fe, 7.3. Calc. for $C_{34}H_{24}AgF_3FeO_2P_2$: C, 54.6; H, 4.3; Ag, 14.5; Fe, 7.5%. An identical procedure using 4 equivalents of silver trifluoroacetate resulted in rapid decomposition. After 5 min the solution was dark green in colour. The solution was filtered and the purple solid isolated, washed with acetone and dried. *Anal.* Found C, 60.5; H, 3.8; Ag, 8.9%.

2,2',5,5'-Tetraphenyldiphosphaferrocene/copper Iodide Complex

Finely ground **II** (0.2 g, 0.72 mmol) was stirred with finely ground copper(I) iodide in dry acetonitrile (100 cm^3) for 48 h at room temperature. The purple product was filtered off and washed with acetonitrile ($\sim$200 cm^3) and dried. Yield 0.23 (45%). *Anal.* Found. C, 49.9; H, 3.3; Cu = 7.4. Calc. for $C_{32}H_{24}CuFeIP_2$. C, 53.6; H, 3.3; Cu, 8.9%.

3,3',4,4'-Tetramethyldiphosphaferrocene/copper Iodide Complex

A similar procedure with **I** (0.25 g, 0.9 mmol) and copper(I) iodide (0.17 g, 0.9 mmol), reaction time 2 h gave the title compound as a brick red powder. Yield 0.21 g (50%). *Anal.* Found: C, 31.0; H, 3.4; Cu, 13.7. Calc. for $C_{12}H_{16}PO_2FeCuI$: C, 30.7; H, 3.4; Cu, 13.6%.

References

1 W. H. Morrison and D. N. Hendrickson, *Inorg. Chem*, *11,* 2912 (1972).

2 R M G Roberts and J Silver, *J. Organomet. Chem*, *209,* 385 (1981)

3 M Watanabe, H. Ichikawa, I. Motoyama and H. Sano, *Chem. Lett.*, 1009 (1983).

4 R M. G. Roberts, J Silver and R J. Ranson, *J. Organomet. Chem*, *219,* 233 (1981)

5 R M. G. Roberts, J Silver and A S. Wells, unpublished results

6 G de Lauzon, B Deschamps and F Mathey, *Nouv J Chim*, *4,* 683 (1980).

7 G. de Lauzon, B Deschamps, J. Fischer, F Mathey and A Mitschler, *J Am Chem. Soc.*, *102,* 994 (1980)

8 B. Deschamps, F. Mathey, J Fischer and J H. Nelson, *Inorg. Chem.*, *23,* 3455 (1984)

9 F Mathey, *J Organomet. Chem.*, *154,* C13 (1978)

10 P Lemoine, M Gross, P. Braunstein, F. Mathey, B. Deschamps and J H Nelson, *Organometallics*, *3,* 1303 (1984).

11 B Lukas, R M G Roberts, J Silver and A. S. Wells, *J Organomet. Chem.*, *256,* 103 (1983)

12 A G Nagy, I Dezsi and M Hillman, *J. Organomet. Chem.*, *117,* 95 (1976).

13 M Watanabe, H. Ichikawa, I Motoyama and H Sano, *Bull Chem. Soc. Jpn.*, *56,* 3291 (1983).

14 D W. Clack and K D Warren, *Inorg. Chim. Acta*, *30,* 251 (1978).

15 M. C. Bohm, *Z. Naturforsch Teil A*, *37,* 1193 (1982).

16 N. M. Kostić and R. F. Fenske, *Organometallics*, *2,* 1008 (1983).

17 C Guimon, D. Gonbeau, G. Pfister-Guillouzo, G. de Lauzon and F. Mathey, *Chem. Phys. Lett.*, *104,* 560 (1984).