Journal of Organometallic Chemistry, 348 (1988) 361–367
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Stabilisation of novel phosphine ligands by P-complexation with tungsten pentacarbonyl

François Mercier, François Mathey,
DCPH, Ecole Polytechnique, 91128 Palaiseau, Cedex (France)

Clara Afiong-Akpan * and John F. Nixon
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, Sussex (Great Britain)

(Received November 30th, 1987)

Abstract

The novel phosphines PH_2Cl, $PHCl_2$, PH_2F, PHFCl, $PH(NEt_2)F$ and $PH(OH)_2$ have been stabilised by ligation to $[W(CO)_5]$. The analogous PF_2H, complex is also described. ^{31}P, ^{19}F, and ^{1}H NMR parameters for these and related compounds are presented and discussed.

Introduction

Trifluorophosphine and its derivatives have been widely used as ligands, particularly towards transition metals in low oxidation states [1,2]. With the exception of PH_2F all members of the series $PF_{3-n}H_n$ $(n = 0–3)$ have been isolated and chemically studied.

Recently Mercier and Mathey [3] reported the stabilisation of phosphinous acid PH_2OH and some of its derviatives by P-complexation to $[W(CO)_5]$. Here we report the extension of this method to the ligation of $PH(OH)_2$ and a wider variety of fluoro- and chloro-phosphines, several of which have not yet been observed in the free state.

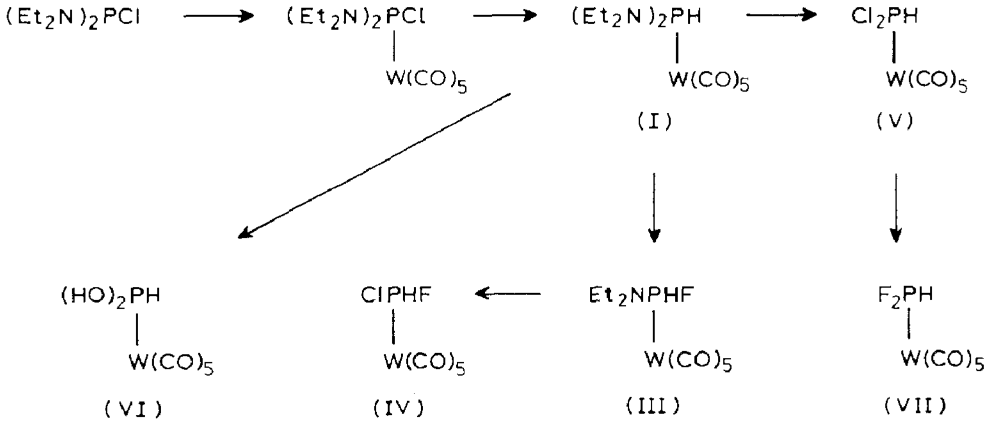
Results and discussion

The starting complexes for the syntheses outlined in Scheme 1 are $[W(CO)_5(Et_2N)_2PH]$ (I) and $[W(CO)_5Et_2NPH_2]$ (II) which have been previously reported [3,4]. Treatment of I with an excess of PhCOF in refluxing benzene affords

---

* Present address: Chemistry Department, Nigerian Defence Academy, Kaduna, Nigeria.

0022-328X/88/$03.50

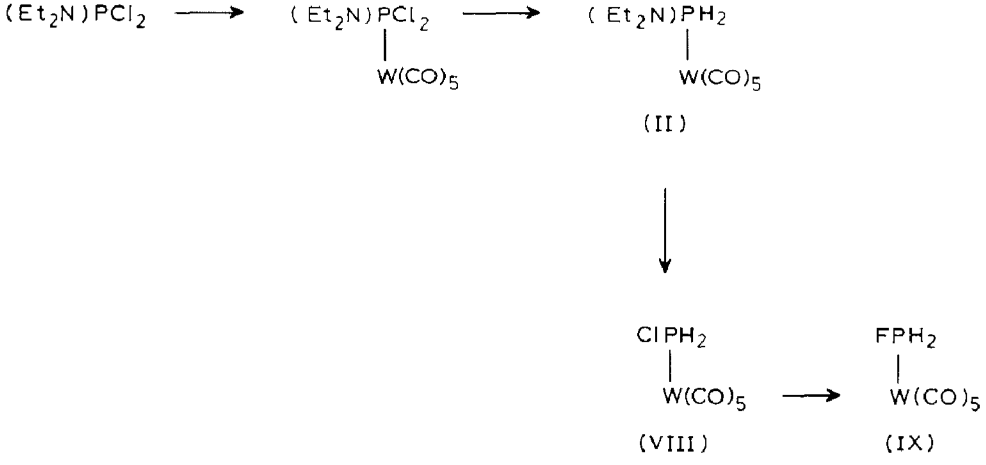


Scheme 1

$[W(CO)_5PHF(NEt_2)]$ (III) in 80% yield. The formulation of III is supported by its mass spectrum and confirmed by its characteristic ^{31}P, ^{19}F, and ^{1}H NMR spectra; the ^{31}P and ^{19}F NMR spectra, both show the expected doublet of doublet patterns, each exhibiting further ^{183}W satellites, (δ(P) +138 ppm (rel H_3PO_4), ^1J(PF) 952 Hz; ^1J(PW) 410 Hz, ^1J(PW) 312.7 Hz, δ(F) −72.3 ppm (rel CCl_3F) ^2J(FW) 18 Hz, ^2J(FH) 69 Hz).

Bubbling HCl gas through a benzene solution of III at room temperature yields the complex $[W(CO)_5PHFCl]$ (IV) in 50% yield as a distillable oil, (b.p. 70 °C/0.2 mm Hg), which is very sensitive towards hydrolysis (δ(P) +148.5 ppm, ^1J(PF) 1025 Hz, ^1J(PH) 405 Hz, ^1J(PW) 366 Hz; δ(F) −87.7 ppm, ^2J(FW) 9.4 Hz, ^2J(FH) 56.4 Hz).

Similar treatment of I with HCl gas rapidly gives the distillable liquid complex $[W(CO)_5(PHCl_2)]$ (V) (b.p. ~ 120 °C/0.2 mm Hg) (40% yield), whose ^{31}P and ^{1}H NMR spectra consist of 1/1 doublets (δ(P) +69 ppm, ^1J(PH) 403 Hz, ^1J(PW) 336.9 Hz). On the other hand, 2*N* aqueous HCl reacts with I at room temperature to give the novel phosphonous acid complex $[W(CO)_5(PH(OH)_2)]$ (VI) (δ(P) +116.2 ppm,



Scheme 2

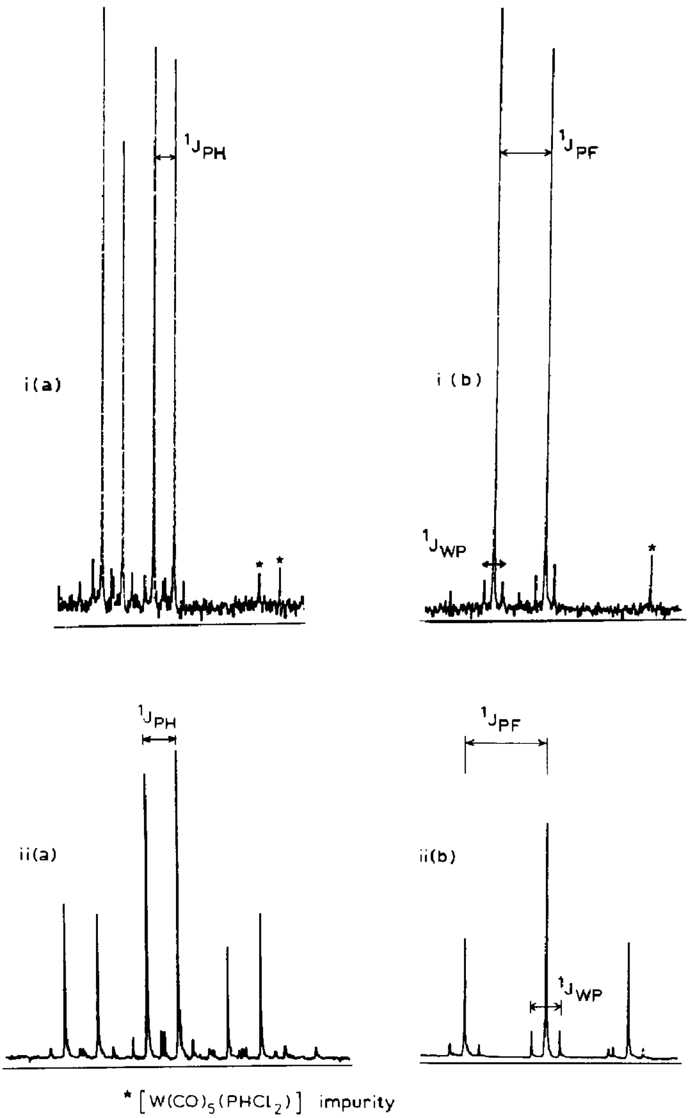


Fig. 1. (a) ^{31}P and (b) ^{31}P {^1H} NMR spectra for (i) [W(CO)$_5$(PHFCl)] (IV) and (ii) [W(CO)$_5$(PHF$_2$)] (VII).

^1J(PW) 312.5 Hz.) Fluorination of V to afford the corresponding PF_2H complex [W(CO)$_5$(PF$_2$H)] (VII) was achieved by use of AsF_3 but even under the mild reaction conditions small amounts of [W(CO)$_6$] are also formed. The ^{31}P and ^{19}F NMR spectra of VII showed the expected multiplet patterns (δ(P) 198.3 ppm, ^1J(PH) 423.2 Hz, ^1J(PF) 1064 Hz, ^1J(PW) 376 Hz, δ(F) 193.1 ppm ^2J(HF) 57.8 Hz). The $^{31}P\{^1H\}$ and ^{31}P NMR spectra of IV and VII which are typical of all the complexes reported in this paper are shown in Fig. 1.

In a similar way [W(CO)$_5$(P(Et$_2$N)H$_2$)] (II) was converted into [W(CO)$_5$(PH$_2$Cl)] (VIII) by treatment with gaseous HCl (δ(P) -19.1 ppm, ^1J(PH) 373.8 Hz, ^1J(WP) 267.0 Hz) [3]. Some additional NMR spectroscopic evidence for an $[AX_2]_2M$ spin system (A = phosphorus X = hydrogen M = tungsten) indicated the presence of

Table 1

NMR data for some $[W(CO)_5L]$ complexes

Complex	$\delta(P)$ [a]	$\delta(F)$ [b]	$\delta(H)$ [c]	$^1J(PH)$ [d]	$^1J(PF)$ [d]	$^2J(HF)$ [d]	$^1J(WP)$ [d]	Ref.
$[W(CO)_5(PCl_3)]$	−95.6	–	–	–	–	–	434.6 [f]	14
$[W(CO)_5(PHCl_2)]$	75.4	–	7.80	403.2	–	–	336.9	This work
$[W(CO)_5(PH_2Cl)]$	−19.1	–	–	373.8	–	–	267.0	This work
$[W(CO)_5(PHClF)]$	148.5	−87.7	9.80	415.0	1025	–	361.0	This work
$[W(CO)_5(PF_3)]$ [e]	–	7.9	–	–	1245	–	485.0	12
$[W(CO)_5(PHF_2)]$	198.3	193.1	7.50	423.2	1064	57.8	376.0	This work
$[W(CO)_5(PH_2F)]$	107.9	−204.8	4.70	376.7	791	50.5	284.4	This work
$[W(CO)_5(PH_3)]$	−183.0	–	2.51	341.0	–	–	215.8	14, 15
$[W(CO)_5(PH(OH)_2]$	116.2	–	8.53	378.4	–	–	312.5	This work
$[W(CO)_5(PH_2OH)]$	29.4	–	6.63	353.0	–	–	269.0	3

[a] In ppm relative to H_3PO_4. [b] In ppm relative to $CClF_3$. [c] In ppm relative to TMS. [d] In Hz. [e] $^2J(WF)$ 31 Hz. [f] The value of 213 Hz quoted in ref. 14 is incorrect, we have remeasured $^1J(WP)$ in this complex.

small amounts of $[W(CO)_4(PH_2Cl)_2]$ in the reaction mixture ($\delta(P)$ +67.7 ppm, $^1J(WP)$ 229 Hz, $^1J(PH)$ 358.5 Hz, $^2J(PH)$ 23 Hz). Attempts to convert VIII into the dinuclear diphosphene complex $[(OC)_5W(PH=PH)W(CO)_5]$ by treatment with base were unsuccessful, but the reaction of VIII with AsF_3 readily gave the desired complex $[W(CO)_5(PH_2F)$ (IX) ($\delta(P)$ 107.9 ppm; $^1J(PH)$ 376.7 Hz, $^1J(PF)$ 791.4 Hz, $^1J(WP)$ 284.4 Hz, $\delta(F)$ −204.8 ppm, $^2J(HF)$ 50.5 Hz). Although PF_2H was already known [5–7], the stabilisation of PH_2F in IX thus completes the series of fluorophosphines $PF_{3-n}H_n$. Also noteworthy is the stabilisation by coordination of the as yet unknown free phosphines PFHCl, $PHCl_2$ and $PFH(NEt_2)$. Recently a $PHBr_2$ complex of manganese has been described by King and Fu [8].

Interestingly the $^1J(PF)$ value in the series of ligated compounds $PF_{3-n}H_n$ ($n = 0$–2) increases steadily from PH_2F to PF_3. Likewise in the mixed halogenophosphine complexes, $^1J(PH)$ increases as the sum of the electronegativities of the atoms attached to phosphorus increases, viz: $PH_3 < PH_2Cl < PH_2F < PHCl_2 <$ PHFCl $< PF_2H$, as does $^1J(PF)$ in the series $PFH_2 <$ PFHCl $< PF_2H < PF_3$.

It is also of interest to compare the magnitude of $^1J(PW)$ and $^1J(PH)$ in the complexes listed in Tables 1 and 2. Factors affecting the magnitude of $^1J(MP)$ in metal-phosphine complexes have been discussed at length by Nixon and Pidcock [9], Verkade [10], and Pregosin and Kunz [11]. It is generally accepted that changes in

Table 2

$^1J(WP)$ and $^1J(PH)$ for some complexes of the type $[W(CO)_5(PX_nH_{3-n})]$

Complex	$^1J(WP)$ [a]	$^1J(PH)$ [a]
$[W(CO)_5(PH)_3)]$	215.8	341.0
$[W(CO)_5(PH_2Cl)]$	267.0	373.8
$[W(CO)_5(PH_2OH)]$ [b]	269.0	353.0
$[W(CO)_5(PH_2F)]$	284.4	376.7
$[W(CO)_5[PH(OH)_2]$	312.5	378.4
$[W(CO)_5(PHCl_2)]$	336.9	403.2
$[W(CO)_5(PHFCl)]$	361.0	415.0
$[W(CO)_5(PHF_2)]$	376.0	423.2

[a] In Hz. [b] Data from ref. 3.

Table 3

${}^1J$(WP) (in Hz) data for some complexes of the type $[W(CO)_5(PX_nH_{3-n})]$

Compound	${}^1J$(WP)	Σx [a]
$[W(CO)_5(PH_3)]$	215.8	6.6
$[W(CO)_5(PH_2Cl)]$	267.0	7.6
$[W(CO)_5(PH_2F)]$	284.4	8.4
$[W(CO)_5(PHCl_2)]$	336.9	8.6
$[W(CO)_5(PHFCl)]$	361.0	9.4
$[W(CO)_5(PCl_3)]$	213.0	9.6
$[W(CO)_5(PHF_2)]$	376.0	10.2
$[W(CO)_5(PF_3)]$	485.0	12.0

[a] The sum of electronegativities of the substituents on phosphorus.

${}^1J$(MP) given by the expression in the equation below are largely dependent on changes in $|S_P(O)|^2$ and α_P^2 [9].

$${}^1J(\mathrm{MP}) = \gamma_P\gamma_M \cdot \frac{\hbar}{2\pi} \cdot \frac{256\pi^2}{9} \cdot \beta^2 \frac{|S_P(O)|^2 |S_M(O)|^2}{{}^3\Delta E} \frac{a^2(1-a^2)}{n} \alpha_P^2$$

Where γ_X is the magnetogyric ratio of nucleus X; $|S_X(O)|^2$ is the electron density in the *s*-orbital of atom X evaluated at the nucleus, a^2 is the *s*-character of the metal hybrid orbital, α_P^2 is the *s*-character of the phosphorus lone pair orbital, n is the number of ligands and ${}^3\Delta E$ is an average triplet excitation energy.

Both terms are influenced by the electronegativity of the substituent groups attached to phosphorus. The higher the sum of the electronegativities of these

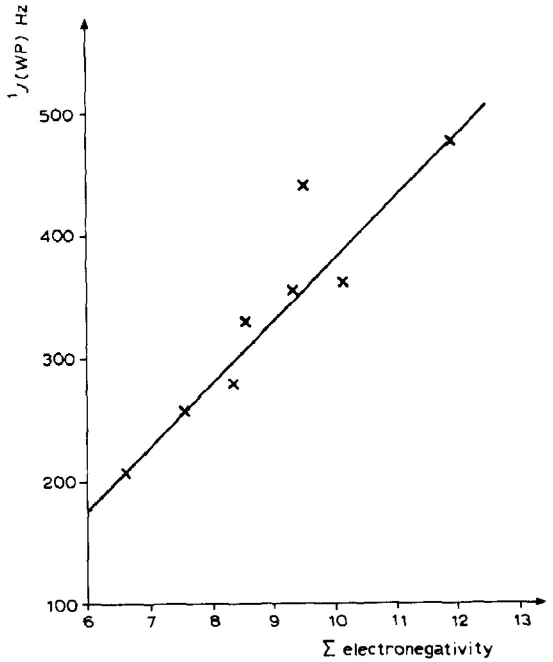


Fig. 2. Plot of ${}^1J$(WP) against Σ electronegativity of the substituents attached to phosphorus for complexes of the type $W(CO)_5(PX_nH_{3-n})$ listed in Table 3.

groups, Σx, the more s-character is diverted into the phosphorus lone pair orbital and hence the magnitude of $^1J(MP)$ increases. This is demonstrated by the steady increase in $^1J(WP)$ with Σx for the atoms directly bound to phosphorus in the complexes in Table 3 and Fig. 2. The steady changes in both $^1J(PW)$ and $^1J(PH)$ for complexes shown in Table 2 also underlines these relationships.

Experimental

All experiments were conducted by a combination of Schlenk and high-vacuum techniques. Manipulations were carried out under dry argon or dinitrogen. All solvents were dried by standard methods and were freshly distilled before use. ^{31}P, ^{19}F and ^1H NMR spectra were recorded on a Bruker WP80 or a Bruker WM360 spectrometer operating in the Fourier Transform mode. Mass spectra were obtained on a Shimadzu GCMS-QP1000 spectrometer.

Reaction of I with PhCOF

A solution of complex I (1.5 g) and PhCOF (0.5 g) in benzene (25 ml) was refluxed for 1 h, 40 min. After evaporation of the solvent, the residue was chromatographed (silica gel, Riedel de Haën 70-230 mesh) with toluene as eluant to afford complex III (1.1 g, 80%) (Found: C, 24.5; H, 2.5; F, 4.08. $C_9H_{11}FNO_5PW$ calcd.: C, 24.18; H, 2.48; F, 4.25%), ν(CO) decalin 2078s, 1964m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (t, 6H, $^3J(HH)$ 7.18 Hz) 3.38 (m, 4H, $^3J(HH)$ 7.18 Hz, $^3J(HP)$ 14.65 Hz) 8.22 (d of d, 1H, $^2J(HF)$ 69.07 Hz, $^1J(HP)$ 410.7 Hz) mass spectrum: (CI, (IC_4H_{10}), ^{184}W) m/e (relative intensity) 448 ($M^+ + 1$, 23%), 446 ($M^+ - H$, 30%), 427 ($M^+ - HF$, 23%), 124 ($Et_2NPFH + 1$, 37%) 72 ($Et_2NH + 1$, 100%). ^{31}P and ^{19}F NMR data are presented in the text.

Reaction of III with HCl gas

A benzene solution of complex III (0.9 g) was treated with HCl gas for 10 min at room temperature to afford IV, (0.4 g); ν(CO) (decalin) 2095s, 1992m, 1975vs cm^{-1}. The product was purified by distillation (b.p. 70 °C/0.2 mm Hg).

Mass spectrum: 410 (M^+, 42%); 326 ($M^+ - 3CO$, 44%); 298 ($M^+ - 4CO$, 96%); 270 ($M^+ - 5CO$, 100%), ^{31}P and ^{19}F NMR data are presented in the text.

Reaction of I with HCl gas

A benzene solution of I (1.5 g) was treated with HCl gas for 10 min at room temperature to afford V, ν(CO) decalin 2085s, 1972vs cm^{-1}. The product was purified by distillation (120 °C/0.2 mm Hg). Found: C, 14.2; H, 0.26; Cl, 16.0. $C_5HCl_2O_5PW$ calcd.: C, 14.1; H 0.23; Cl, 16.6%. ^1H NMR ($CDCl_3$) δ 9.16 (d of d $^1J(PH)$ 403.2 Hz). Mass spectrum: 428–426 (M^+, 56%); 393–391 ($M^+ - Cl$, 46%); 335 ($M^+ - (Cl + 2CO)$, 27%); 288–286 ($M^+ - 5CO$, 90%); 316–314 ($M^+ - 4CO$, 100%).

^{31}P NMR data are listed in the text.

Reaction of I with 2N aqueous HCl

A THF solution of I (1.0 g) was treated with 2*N* HCl (5 ml) at room temperature. The residue was chromatographed on silica gel (as above) with Et_2O as eluant to give VI (95%) ν(CO) (decalin) 2080s, 1945vs cm^{-1}. ^1H NMR $(CD_3)_2CO$ δ

8.53 ppm (d, 1H, ^{1}J(PH) 378.4 Hz). Mass spectrum: 390 (M^+, 14%); 362 (M^+ – CO, 5%); 306 (M^+ – 3CO, 65%); 250 (M^+ – 5CO) 100%.

Reaction of II with HCl gas

A benzene solution of (II) (0.278 g) cooled to 10 ° C was treated with HCl gas for 15 minutes. After removal of solvent, the residue was dissolved in toluene and the NMR spectra recorded. These showed the products to be an inseparable mixture of VIII and $[W(CO)_4(PH_2Cl)_2]$.

Reaction of VIII with AsF_3

An excess of AsF_3 was condensed on to solution of the above products and the formation of IX was subsequently established by NMR studies (see text).

Reaction V with AsF_3

Likewise an excess of AsF_3 was added to V (0.0705 g) in toluene (2 ml) at 0 ° C and VII was formed as the major product together with small amounts of $[W(CO)_6]$ which sublimed on to the walls of the reaction vessel.

References

1 J.F. Nixon, Adv. Inorg. Chem. Radio Chem., 29 (1985) 41.
2 J.F. Nixon, Adv. Inorg. Chem. Radio Chem., 13 (1979) 364.
3 F. Mercier and F. Mathey, J. Chem. Soc. Chem. Comm., (1984) 782.
4 F. Mercier and F. Mathey, Tetrahedron Lett., 27 (1986) 1323.
5 R.W. Rudolph and H.W. Schiller, J. Am. Chem. Soc., 90 (1968) 3581.
6 R.W. Rudolph and R.W. Parry, Inorg. Chem., 4 (1965) 1339; 6 (1967) 1070.
7 R.W. Rudolph and R.W. Parry, J. Am. Chem. Soc., 89 (1967) 1621.
8 R.B. King and W.K. Fu, Inorg. Chem., 25 (1986) 2384.
9 J.F. Nixon and A. Pidcock, in E. Mooney (Ed.), Ann. Reports on N.M.R. Spectroscopy, Vol. 2., Academic Press, London, 1969, p. 345.
10 J.G. Verkade, Coord. Chem. Revs., 9 (1972/73) 1.
11 P.S. Pregosin and R.W. Kunz, ^{31}P and ^{13}C N.M.R. of Transition Metal Phosphine Complexes, Springer Verlag, New York, 1979, No. 16 in Series 'N.M.R., Basic Principles and Progress'.
12 F. Ogilvie, R.J. Clark and J.G. Verkade, Inorg. Chem., 8 (1969) 1904.
13 R.L. Keiter and J.G. Verkade, Inorg. Chem., 8 (1969) 2115.
14 E. Moser, E.O. Fischer, W. Bathelt, W. Gretner, L. Knauss, and E. Louis, J. Organomet. Chem., 19 (1969) 377.
15 F. Nief, F. Mercier and F. Mathey, J. Organomet. Chem., 328 (1987) 349.