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Reactions of tungsten and molybdenum alkylidyne complexes $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with the bidentate secondary phosphine $C_6H_4(PH_2)_2$-1,2; crystal structure of the phospha-allyl complex $[W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$

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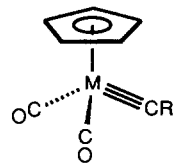
Abstract

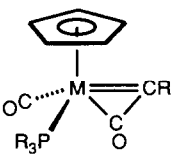
The reaction of the alkylidyne complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with rac-$C_6H_4(PMePh)_2$-1,2 gives only one of the possible diastereoisomers of the η^1-ketenyl complex $[W\{\eta^1\text{-}C(C_6H_4Me\text{-}4)=C=O)\}\{C_6H_4(PMePh)_2\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$. The reactions of the complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4, Me, C_6H_4OMe-2, and $C_6H_4CH_2OMe$-2) and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with the bidentate primary phosphine $C_6H_4(PH_2)_2$-1,2 give the metalla-phosphine complexes $[M\{\sigma,\eta^3\text{-}C_6H_4(PH_2)(PC\{OH\}CHR)\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ (M = W or Mo) which in the case of the R = $C_6H_4CH_2OMe$-2 derivative exists as a pair of isomers. The molecular structure of $[W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ has been established by an X-ray diffraction study, which shows that the central phosphorus atom of the chelate chain is part of a phospha-allyl moiety. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the new compounds are reported and discussed.

Introduction

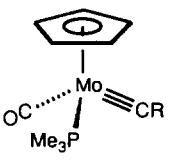
The alkylidyne complexes $[M(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (M = W, Ia; M = Mo, Ib) react with one equivalent of a variety of tertiary phosphine ligands (PR_3) to give the η^2-ketenyl derivatives $[M(\eta^2\text{-}RCCO)(CO)(PR_3)(\eta\text{-}C_5H_5)]$ (II) [1,2], which in the case of the Mo complex IIb readily decarbonylates, affording the phosphine substituted alkylidyne complex $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (III) [3]. The complex IIa reacts reversibly with a further equivalent of PMe_3 to give the η^1-ketenyl complex $[W(\eta^1\text{-}RCCO)(CO)(PMe_3)_2(\eta\text{-}C_5H_5)]$ (IV). The related reactions of Ia with the bidentate phosphine ligands $Me_2P(CH_2)_nPMe_2$ ($n = 1$ or 2) [4], and the photochemically activated reaction with $Ph_2P(CH_2)_2PPh_2$ (dppe) [5], give comparatively stable η^1-ketenyl derivatives Va–Vc. However, it has been established that the dppe derivative Vc may lose one equivalent of dppe giving a binuclear η^2-ketenyl derivative [5]. In contrast, we have previously reported that Ia reacts with



	M	R
(Ia)	W	C_6H_4Me-4
(Ib)	Mo	C_6H_4Me-4
(Ic)	W	Me
(Id)	W	C_6H_4OMe-2
(Ie)	W	$C_6H_4CH_2OMe$-2



	M
(IIa)	W
(IIb)	Mo



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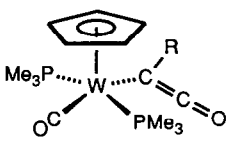

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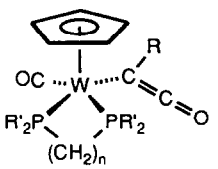
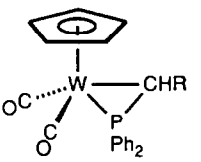


	n	R'
(Va)	1	Me
(Vb)	2	Me
(Vc)	2	Ph



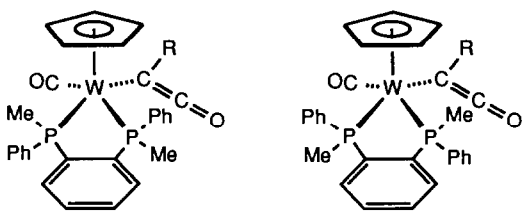
(VI)

the secondary phosphine PPh_2H to give the complex $[W\{\eta^2\text{-}C(HR)(PPh_2\}(CO)_2(\eta\text{-}C_5H_5)]$ (VI) [6]. Formation of the phosphine methanide ligand in the latter complex involves hydrogen migration from phosphorus to the μ-CR moiety together with concomitant P–C bond formation. It therefore seemed probable that treatment of the mononuclear alkylidyne complexes $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = W, Ia and Ic–Ie; M = Mo, Ib) with the bidentate primary phosphine ligand $C_6H_4(PH_2)_2$-1,2 [7] would afford unstable η^1-ketenyl derivatives which might subsequently undergo new hydrogen migration and P–C coupling reactions. The reactions of Ia with rac-$C_6H_4(PMePh)_2$-1,2 [8] were also studied so that the behaviour of primary and tertiary bidentate phosphine ligands with an o-phenylene backbone could be compared. Some of the work described in this paper has been the subject of a previous communication [9].

Results and discussion

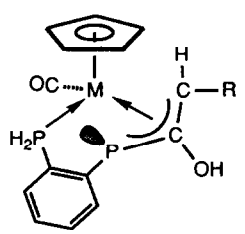
Treatment of an Et_2O solution of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (Ia) with one equivalent of rac-$C_6H_4(PMePh)_2$-1,2 affords good yields of the yellow η^1-ketenyl complex $[W\{\eta^1\text{-}C(C_6H_4Me\text{-}4)=C=O\}\{C_6H_4(PMePh)_2\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ (VII). The complex VII is very stable and unlike the related dppe derivative Vc, it shows no tendency to lose a phosphine ligand and form dimeric species. This no doubt

reflects the additional stability confered on the complex by the rigid *o*-phenylene backbone of the bidentate phosphine ligand. The complex VII was readily identified by comparison of it's spectroscopic data with that of the complexes Va–Vc [4,5]. It shows a strong IR absorption at 2019 cm^{-1} assigned to the ketenyl C=O stretch and a band at 1838 cm^{-1} for the W–CO ligand (Table 1). The $^{13}C\{^1H\}$ NMR spectrum has resonances at δ 161.2 (d, J(PC) 5) and −8.9 ppm (d, J(PC) 10) which are characteristic of the η^1-ketenyl C=*C*=O and *C*=C=O carbon atoms (Table 2). The complex VII has chiral centres at tungsten and phosphorus and in principle, could exist as enantiomeric mixtures of the two diastereoisomers VIIa and VIIb. Remarkably, the reaction of Ia with rac-$C_6H_4(PMePh)_2$-1,2 is completely stereospecific and gives only one of the two possible diastereoisomers. This is most clearly seen in the $^{31}P\{^1H\}$ NMR spectrum which shows only two resonances at δ 38.4 (J(WP) 198) and 41.4 ppm (J(WP) 337) for the two inequivalent phosphorus atoms (Table 3). In the absence of a single crystal X-ray diffraction study it was not possible to establish whether the diastereoisomer formed in this reaction had structure VIIa or VIIb.



(VIIa) R = C_6H_4Me-4 (VIIb)

The complex Ia does not react with the primary bidentate phosphine $C_6H_4(PH_2)_2$-1,2 at room temperature but in refluxing Et_2O a smooth reaction occurs affording bright orange crystals of [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)] (VIIIa). The reactions of $C_6H_4(PH_2)_2$-1,2 with the complexes Ib and Ic gave somewhat poorer yields of the analogous products VIIIb and VIIIc.



	M	R
(VIIIa)	W	C_6H_4Me-4
(VIIIb)	Mo	C_6H_4Me-4
(VIIIc)	W	Me

The structure of VIIIa was established by a single crystal X-ray diffraction study (Fig. 1) and selected bond lengths and angles are given in Table 4. The tungsten atom carries a cyclopentadienyl ring and a single terminal carbonyl ligand. One of the phosphorus atoms of the bidentate phosphine ligand has coupled with the carbonyl and the alkylidyne ligands to afford a η^3-phospha-allyl moiety –P(2)–C(2)(OH)–C(10)H(C_6H_4Me-4). The comparatively long W–P(2) (2.506(1) Å), W–C(2) (2.317(4) Å) and W–C(10) (2.322(4) Å) separations are consistent with these atoms having a significant π-interaction with the tungsten atom and the correspond-

Table 1

Analytical and other data

Compound	Colour	Yield (%)	ν_{max}(CO) [a] (cm^{-1})	Analysis (Found (calcd.) (%))	
				C	H
[W{η^1-C(C_6H_4Me-4)=C=O)}{C_6H_4($PMePh)_2$-1,2}(CO)(η-C_5H_5)] (VII)	yellow	91	2019s [b]	56.0 (56.8)	4.6 (4.5)
[W{σ,η^3-C_6H_4(PH_2)(PC{OH}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)] (VIIIa)	yellow	90	1862s, br	45.5 (45.5)	3.7 (3.7)
[Mo{σ,η^3-C_6H_4(PH_2)(PC{OH}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)]·(CH_2Cl_2) (VIIIb)	orange	33	1851s, br	48.5 (48.3)	4.4 (4.0)
[W{σ,η^3-C_6H_4(PH_2)(PC{OH}CHMe)1,2}(CO)(η-C_5H_5)]·(CH_2Cl_2) (VIIIc)	orange	40	1854s, br	34.1 (34.4)	3.5 (3.2)
[W{σ,η^3-C_6H_4(PH_2)(PC{OH}CH{C_6H_4OMe-2})-1,2}(CO)(η-C_5H_5)]·(CH_2Cl_2) (IX)	orange	50	1861s, br	39.6 (40.5)	4.2 (3.4)
[W{σ,η^3-C_6H_4(PH_2)(PC{OH}CH{$C_6H_4CH_2$OMe-2})-1,2}(CO)(η-C_5H_5)]·(0.5CH_2Cl_2) (Xa) [c]	yellow	15	1862s, br	42.9 (43.4)	4.1 (3.7)
[W{σ,η^3-C_6H_4(PH_2)(PC{OH}CH{$C_6H_4CH_2$OMe-2})-1,2}(CO)(η-C_5H_5)] (Xb) [c]	orange	15	1879s, br	–	–

[a] In CH_2Cl_2. [b] ν(C=O) 1838s cm^{-1}. [c] Isomers, see text.

ingly short P(2)–C(2) (1.782(6) Å) and C(2)–C(10) (1.413(6) Å) separations suggest some delocalisation within the P(2)–C(2)–C(10) fragment. Based upon spectroscopic data, Mathey has proposed that the $RPCHCH_2$ ligand in [W(η^3-$RPCHCH_2$)(CO)(η-C_5H_5)] (R = $C_6H_2(CMe_3)_3$-2,4,6) adopts an η^3-phospha-allyl bonding mode which is very similar to that observed for the –PC(OH)CH(C_6H_4Me-4) moiety in VIIIa [10].

The solution spectroscopic data for VIIIa–VIIIc are consistent with the structure established in the solid state for VIIIa by X-ray diffraction. The data for VIIIa is typical of this series of complexes and is discussed below. The IR spectrum of VIIIa shows a single band at 1862 cm^{-1} which is attributed to the terminal carbonyl ligand. The ^1H NMR spectrum shows the expected aromatic resonances and the presence of the PH_2 hydrogen atoms is confirmed by the observation of two doublet resonances at δ 6.24 (J(PH) 359) and 6.5 (J(PH) 337) ppm which show characteristically large J(PH) coupling constants. The hydroxyl and CH hydrogen atoms of the allyl moiety, –PC(OH)CH(C_6H_4Me-4), are assigned to resonances at δ 2.76 and 3.72 ppm respectively. The latter signal appears as a doublet of doublets due to coupling with the two phosphorus atoms (J(PH) 12 and 2). The proton coupled ^{31}P NMR spectrum is particularly informative and shows resonances at δ −52.6 (s, WP, J(WP) 60) and −28.3 ppm (dd, WPH_2, J(HP) 359, 337, J(WP) 308). The allylic phosphorus atom has an unusually shielded chemical shift and a comparatively small J(WP) coupling constant of 60 Hz. Mathey has noted that both of these features are characteristic of π-phospha complexes [11–13] and has reported that J(WP) = 0 for the major isomer of the complex [W(η^3-$RPCHCH_2$)(CO)(η-C_5H_5)]. The residual W–P coupling of 60 Hz observed for the allylic phosphorus atom in VIIIa may reflect distortions from planarity in the allyl moiety which could arise from the geometrical constraints of the chelate ring system. In the $^{13}C\{^1H\}$ NMR spectrum, doublet resonances at δ 142.1 (J(PC) 54) and 32.5 ppm (J(PC) 37) are assigned to the COH and CHR carbon atoms of the phospha-allyl ligand. The analogous CH and CH_2 resonances in the major isomer of the complex [W(η^3-$RPCHCH_2$)(CO)(η-C_5H_5)] occur at δ 69.7 (d, J(PC) 65) and 29.9 ppm (d, J(PC) 70), respectively. These values are comparable for the *C*HR and CH_2 carbon atoms but the COH carbon in VIIIa is appreciably more deshielded than the CH carbon atom in [W(η^3-$RPCHCH_2$)(CO)(η-C_5H_5)]. This difference may reflect the presence of the hydroxyl ligand. However, it should be noted that the COH resonance in VIIIa (and VIIb and VIIIC also) lies within the envelope of the aromatic carbon resonances and it's assignment must therefore be treated with caution in the absence of corroborating data for a wider range of similar complexes.

The reactions of the complexes [W(≡CR)(CO)$_2$(η-C_5H_5)] (R = C_6H_4OMe-2, Id, and $C_6H_4CH_2$OMe-2, Ie) with $C_6H_4(PH_2)_2$-1,2 were also investigated to establish how the methoxyl substituents would affect the course of the reaction. Treatment of the complex [W(≡CC_6H_4OMe-2)(CO)$_2$(η-C_5H_5)] (Id) with one equivalent of the bidentate phosphine $C_6H_4(PH_2)_2$-1,2 gave moderate yields of the complex [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{C_6H_4OMe-2})-1,2}(CO)(η-C_5H_5)] (IX). The $^{13}C\{^1H\}$ NMR data for compound IX suggest it has a structure which is closely related to that of the complexes VIIIa–VIIIc. In the ^1H NMR spectrum the chemical shifts for the CH (δ 4.10) and OH (δ 3.25) protons are appreciably more deshielded than those found at δ 3.72 (CH) and 2.76 ppm (OH) in the C_6H_4Me-4 derivative VIIIa. These data suggest that the methoxyl substituent of the C_6H_4OMe-2 ring may

Table 2

^{1}H and ^{13}C NMR data [a]

VII	2.18 (s, 3H, Me-4); 2.34 (d, 3H, PMe, *J*(PH) 9); 2.50 (d, 3H, PMe, *J*(PH) 9); 4.76 (s, 5H, C_5H_5); 6.26 (d, 2H, C_6H_4, *J*(HH) 8); 6.75 (d, 2H, C_6H_4Me-4, *J*(HH) 8); 7.10–7.40 (m, 14H, PC_6H_4P and C_6H_5)	237.5 (d, WCO, *J*(PC) 17); 161.2 (d, C=O, *J*(PC) 5); 127.6–152.9 (m, C_6H_5, C_6H_4Me-4 and PC_6H_4P); 88.6 (C_5H_5); 20.9 (Me-4); 19.8 (d, PMe, *J*(PC) 39); 19.7 (d, PMe, *J*(PC) 24); -8.9 (d, *C*=C=O, *J*(PC) 10)
VIIIa	2.28 (s, 3H, Me-4); 2.76 (s, 1H, OH); 3.72 (dd, 1H, C*H*C_6H_4Me-4, *J*(PH) 12, 2); 5.02 (s, 5H, C_5H_5); 6.24 (d, 1H, PH_2, *J*(PH) 359); 6.50 (d, 1H, PH_2, *J*(PH) 337); 7.01 (d, 2H, C_6H_4Me-4, *J*(HH) 8); 7.32 (d, 2H, C_6H_4Me-4, *J*(HH) 8); 7.43–8.13 (m, 4H, PC_6H_4P)	233.1 (d, WCO, *J*(PC) 19); 140.2 (d, COH, *J*(PC) 54); 128.8–143.7 ($C^{1,4}$, C_6H_4Me-4, and 6C, PC_6H_4P); 127.7 ($C^{2,6}$, C_6H_4Me-4); 126.7 ($C^{3,5}$, C_6H_4Me-4); 86.5 (C_5H_5); 32.5 (d, *C*HC_6H_4Me-4, *J*(PC) 37); 21.5 (Me-4)
VIIIb	2.29 (s, 3H, Me-4); 2.88 (s, 1H, OH); 3.62 (d, 1H, C*H*C_6H_4Me-4, *J*(PH) 11); 4.99 (s, 5H, C_5H_5); 5.83 (d, 1H, PH_2, *J*(PH) 354); 6.32 (d, 1H, PH_2, *J*(PH) 327); 7.21 ($(AB)_2$, 4H, C_6H_4Me-4, *J*(HH) 8); 7.50–8.12 (m, 4H, PC_6H_4P)	244.9 (d, MoCO, *J*(PC) 27); 140.3 (d, COH, *J*(PC) 50); 129.7–144.1 ($C^{1,4}$, C_6H_4Me-4, and 6C, PC_6H_4P); 128.9 ($C^{2,6}$, C_6H_4Me-4); 128.3 ($C^{3,5}$, C_6H_4Me-4); 89.8 (C_5H_5); 45.0 (d, *C*HC_6H_4Me-4, *J*(PC) 36); 21.2 (Me-4)
VIIIc	1.98 (d, 3H, Me, *J*(HH) 6); 2.43 (s, 1H, OH); 2.83 (m, 1H, C*H*Me, *J*(HH) 6, *J*(PH) 11, 2); 5.05 (d, 5H, C_5H_5, *J*(PH) 1); 6.21 (dd, 1H, PH_2, *J*(PH) 363, 2); 6.53 (d, 1H, PH_2, *J*(PH) 331); 7.41–8.10 (m, 4H, PC_6H_4P)	234.3 (dd, WCO, *J*(PC) 18, 4); 145.5 (dd, 1C, PC_6H_4P, *J*(PC) 41, 39); 141.5 (dd, 1C, PC_6H_4P, *J*(PC) 54.3); 137.4 (d, COH, *J*(PC) 80); 135.6 (m, 1C, PC_6H_4P); 133.6 (1C, PC_6H_4P); 130.5 (dd, 1C, PC_6H_4P, *J*(PC) 6, 2); 129.2 (d, 1C, PC_6H_4P, *J*(PC) 7); 86.4 (C_5H_5); 28.7 (d, *C*HMe, *J*(PC) 32); 17.7 (d, Me, *J*(PC) 9)
IX	3.25 (s, 1H, OH); 3.81 (s, 3H, OMe); 4.10 (d, 1H, C*H*C_6H_4OMe-2, *J*(PH) 12); 5.12 (s, 5H, C_5H_5); 6.26 (dd, 1H, PH_2, *J*(PH) 366, 6); 6.53 (d, 1H, PH_2, *J*(PH) 336); 6.75–7.05 (m, 3H), C_6H_4OMe-2); 7.43–8.13 (m, 4H, PC_6H_4P); 7.76 (m, 1H, C_6H_4OMe-2)	233.5 (d, WCO, *J*(PC) 9); 155.7 (1C, C_6H_4-OMe-2); 145.5 (m, 1C, PC_6H_4P), 141.0 (d, 1C, PC_6H_4P, *J*(PC) 55); 136.1, 135.9 (2m, 2C, PC_6H_4P); 134.2 (d, 1C, PC_6H_4P, *J*(PC) 11), 133.6 (1C, C_6H_4OMe-2); 129.9 (dd, COH, *J*(PC) 87, 7); 129.2 (1C, C_6H_4OMe-2); 129.0 (1C, PC_6H_4P); 125.0, 120.0, 109.9 (3s, 3C, C_6H_4OMe-2); 86.7 (C_5H_5); 55.3 (OMe); 26.3 (d, *C*HC_6H_4OMe-2, *J*(PC) 4)
Xa	3.40 (s, 3H, OMe); 3.83 (dd, 1H, C*H*$C_6H_4CH_2$OMe-2, *J*(PH) 12, 2); 4.53 (AB, 2H, CH_2OMe, *J*(HH) 11); 5.16 (s, 5H, C_5H_5); 6.21 (dd, 1H, PH_2, *J*(PH) 365.2); 6.53 (d, 1H, PH_2, *J*(PH) 337); 7.10–7.25 (m, 3H, $C_6H_4CH_2$OMe-2); 7.44–8.14 (m, 4H, PC_6H_4P); 7.77 (m, 1H, $C_6H_4CH_2$OMe-2)	233.4 (d, WCO, *J*(PC) 20); 146.2 (m, 1C, PC_6H_4P); 142.9, 142.8 (2C, $C_6H_4CH_2$OMe-2); 140.3 (d, 1C, PC_6H_4P, *J*(PC) 55); 136.1 (d, 1C, PC_6H_4P, *J*(PC) 53); 135.9 (1C, $C_6H_4CH_2$-OMe-2); 135.4 (m, 1C, PC_6H_4P); 133.4 (1C, PC_6H_4P); 132.7 (1C, $C_6H_4CH_2$OMe-2); 130.0 (dd, COH, *J*(PC) 95, 7); 129.6 (1C, PC_6H_4P), 127.6, 125.0 (1C, $C_6H_4CH_2$OMe-2); 86.9 (C_5H_5); 77.8 (CH_2); 57.9 (OMe); 33.2 (d, 1C, *C*H$C_6H_4CH_2$OMe-2, *J*(PC) 40)
Xb	2.47 (s, 1H, OH); 3.51 (s, 3H, OMe); 4.58 (s, 5H, C_5H_5); 4.59 (AB, 2H, CH_2OMe, *J*(HH) 11); 4.87 (d, 1H, C$C_6H_4CH_2$OMe-2, *J*(PH) 15); 6.10	230.7 (dd, WCO, *J*(PC) 22, 3); 147.9 (1C, $C_6H_4CH_2$OMe-2); 146.0 (m, 1C, PC_6H_4P); 137.4 (d, 1C, PC_6H_4P, *J*(PC) 53); 135.9 (m, 1C, PC_6H_4P); 134.0 (d, 1C, PC_6H_4P, *J*(PC)

Table 2 (continued)

Xb	(dd, 1H, PH_2, J(PH) 366, 3); 6.28 (d, 1H, PH_2, J(PH) 342); 6.88–7.24 (m, 4H, $C_6H_4CH_2OMe$-2); 7.44–8.28 (m, 4H, PC_6H_4P)	77); 131.8, 130.5 (2s, 2C, PC_6H_4P); 130.3 (dd, COH, J(PC) 111, 7); 128.7, 127.5, 123.4, 122.8, 122.5 (5s, 5C, $C_6H_4CH_2OMe$-2); 88.3 (C_5H_5); 77.0 (CH_2); 58.7 (OMe); 37.2 (d, $CHC_6H_4CH_2OMe$-2, J(PC) 6)

[a] Chemical shifts in ppm, coupling constants in Hz, with measurements at room temperature unless otherwise indicated. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 ppm), with measurements in CD_2Cl_2/CH_2Cl_2.

Table 3

^{31}P NMR data

Compound	$\delta(^{31}P)$ [a]
VII [b]	38.4 (s, PPhMe, J(WP) 198); 41.4 (s, PPhMe, J(WP) 337)
VIIIa	−52.6 (s, WP, J(WP) 60); −28.3 (dd, WPH_2, J(HP) 359, 337, J(WP) 308)
VIIIb [b]	−15.6 (d, MoP, J(PP) 4); 4.6 (d, $MoPH_2$, J(PP) 4)
VIIIc	−47.6 (br, WP, J(WP) 61); −29.2 (dd, WPH_2, J(HP) 363, 331, J(WP) 307)
IX	−51.9 (br, WP, J(WP) 61); −27.9 (dd, WPH_2, J(HP) 366, 336, J(WP) 309)
Xa	−56.7 (br, WP, J(WP) 59); −27.1 (dd, WPH_2, J(HP) 366, 337, J(WP) 301)
Xb	−39.3 (d, WP, J(HP) 15); −29.2 (dd, WPH_2, J(HP) 366, 342 J(WP) 305)

[a] Hydrogen-1 coupled unless otherwise noted. Small J(PH) coupling constants (ca. <15 Hz) were generally not well resolved. Chemical shifts are positive to high frequency of 85% H_3PO_4 (external). [b] Hydrogen-1 decoupled spectrum.

undergo hydrogen-bonding interactions with the CH and OH protons of the phospha-allyl moiety, as shown in IXa and IXb. Rapid rotation of the C_4H_4OMe-2 ring on the NMR time scale could interconvert IXa and IXb and lead to the single set of resonances observed for the CH and OH hydrogen atoms. If such a fluxional process is occuring it must have a very low activation energy because the ^1H NMR

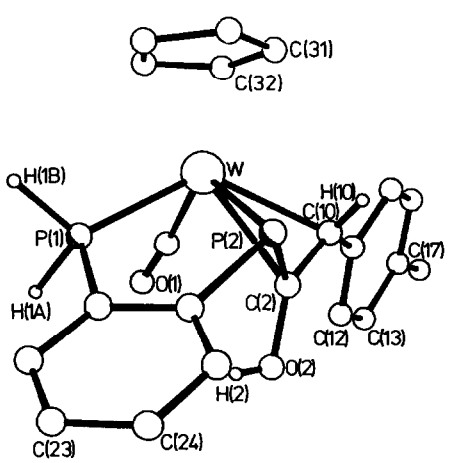


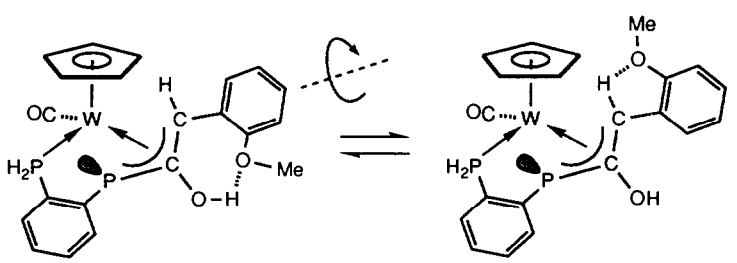
Fig. 1. The molecular structure of [W(σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)] (VIIIa) showing the crystallographic numbering scheme.

Table 4

Selected internuclear distances (Å) and angles (°) for [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)] (VIIIa) with esd's in parentheses

W–P(1)	2.396(1)	W–P(2)	2.506(1)
W–C(1)	1.946(5)	W–C(2)	2.317(4)
W–C(10)	2.332(4)	P(1)–H(1a)	1.35(6)
P(1)–H(1b)	1.37(7)	P(1)–C(21)	1.815(5)
P(2)–C(2)	1.782(6)	P(2)–C(26)	1.838(5)
C(1)–O(1)	1.166(6)	C(2)–O(2)	1.397(6)
C(2)–C(10)	1.413(6)	O(2)–H(2)	0.64(8)
C(10)–H(10)	0.90(6)	C(10)–C(11)	1.489(8)
P(1)–W–P(2)	79.0(1)	P(1)–W–C(1)	78.6(1)
P(2)–W–C(1)	119.7(1)	P(1)–W–C(2)	91.5(1)
P(2)–W–C(2)	43.1(1)	C(1)–W–C(2)	82.5(2)
P(1)–W–C(10)	126.3(1)	P(2)–W–C(10)	65.9(1)
C(1)–W–C(10)	84.8(2)	C(2)–W–C(10)	35.5(2)
W–P(1)–H(1a)	121(3)	W–P(1)–H(1a)	117(2)
H(1a)–P(1)–H(1b)	102(4)	W–P(1)–C(21)	114.7(1)
H(1a)–P(1)–C(21)	98(2)	H(1b)–P(1)–C(21)	102(3)
W–P(2)–C(2)	62.8(1)	W–P(2)–C(26)	108.6(1)
C(2)–P(2)–C(26)	103.0(3)	W–C(1)–O(1)	175.8(4)
W–C(2)–P(2)	74.1(2)	W–C(2)–O(2)	126.8(3)
P(2)–C(2)–O(2)	128.0(4)	W–C(2)–C(10)	72.5(2)
P(2)–C(2)–C(10)	110.3(3)	O(2)–C(2)–C(10)	121.1(5)
C(2)–O(2)–H(2)	98(7)	W–C(10)–C(2)	72.1(3)
W–C(10)–H(10)	98(5)	C(2)–C(10)–H(10)	104(4)
W–C(10)–C(11)	121.4(2)	C(2)–C(10)–C(11)	129.7(4)
H(10)–C(10)–C(11)	120(5)	P(1)–C(21)–C(22)	124.1(3)
P(1)–C(21)–C(26)	116.0(3)	C(22)–C(21)–C(26)	120.0(4)
P(2)–C(26)–C(21)	120.6(3)	P(2)–C(26)–C(25)	119.6(3)
C(21)–C(26)–C(25)	119.6(4)		

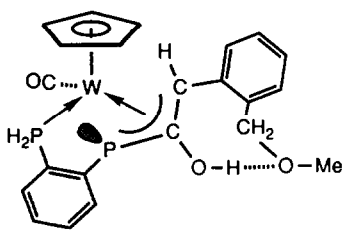
spectrum was found to be unaltered even at $-100\,^{\circ}C$. It is therefore possible that comparatively strong hydrogen-bonding interactions may lead to a static structure for the complex as shown in IXb.



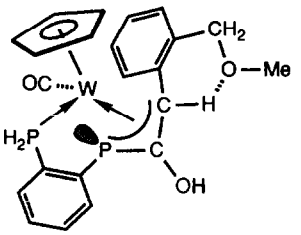
(IXa) (IXb)

The related reaction of the $C_6H_4CH_2OMe$-2 complex [W(≡$CC_6H_4CH_2OMe$-2)$(CO)_2$(η-C_5H_5)] (Ie) with $C_6H_4(PH_2)_2$-1,2 gave poor yields of two chromatographically separable isomers [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{$C_6H_4CH_2OMe$-2})-1,2}(CO)(η-C_5H_5)] (Xa and Xb) and a large number of minor unidentified by-products were also produced in this reaction. The spectroscopic data for the

complex Xa are similar to those of the complexes VIIIa–IX. In the ^{1}H NMR spectrum the resonances for the CH and OH protons are tentatively assigned to overlapping resonances at δ 3.8 ppm. The chemical shift for the CH proton is comparable with that found in the C_6H_4Me-4 derivative VIIIa and hence this proton does not appear to be involved in hydrogen-bonding interactions of the type found in the methoxyl complex IX. In contrast, the OH proton is extremely deshielded and this suggests that it may be strongly hydrogen-bonded to the oxygen atom of the CH_2OMe-2 substituent leading to a static structure of the type shown.



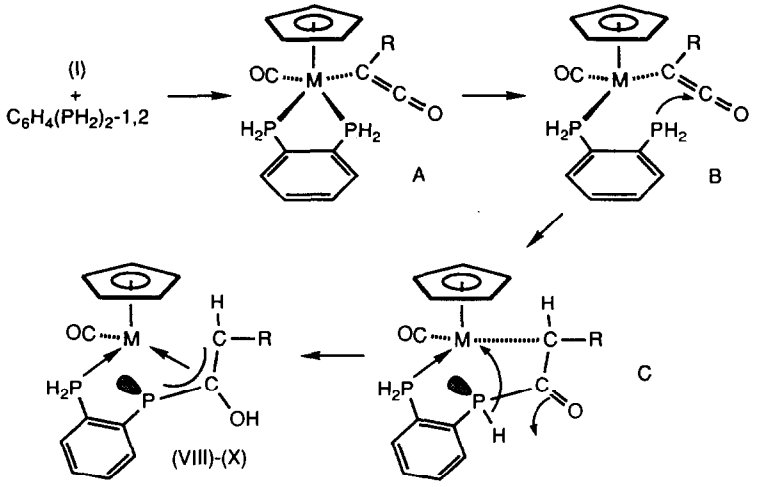
(Xa)



(Xb)

The spectroscopic data for the isomeric complex Xb are significantly different from those of the previously described complexes and it is tentatively assigned a structure with the CH hydrogen atom lying *syn* to the hydroxyl substituent which contrasts with the *anti*-configuration found in the complexes VIII-IX. The ^{1}H NMR spectrum of Xb shows resonances at δ 2.47 and 4.87 ppm which are due to the OH and CH protons, respectively. The chemical shift for the OH proton is comparable with that found in the C_6H_4Me-4 derivative VIIIa and hence this proton does not appear to be involved in hydrogen-bonding interactions. In contrast, the CH proton is extremely deshielded and this suggests that it may be strongly hydrogen-bonded to the oxygen atom of the CH_2OMe-2 substituent. The ^{1}H NMR spectrum also reveals an unusually shielded cyclopentadienyl resonance at δ 4.58 ppm which lies 0.58 ppm upfield of the equivalent signal in the C_6H_4Me-4 derivative VIIIa. If the structural assignment for Xb is correct, the cyclopentadienyl ring would be constrained to lie in close proximity to the *anti*-$C_6H_4CH_2OMe$-2 group and the diamagnetic field associated with the latter aromatic ring system could readily account for the observed shielding of the cyclopentadienyl protons.

A possible mechanism which accounts for the formation of the phospha-allyl complexes VIII-X is shown in Scheme 1. Initial attack of the bidentate primary phosphine on the alkylidyne complex presumably affords an unstable η^1-ketenyl intermediate **A** analogous to the stable complex $[W\{\eta^1\text{-}C(C_6H_4Me\text{-}4)=C=O)\}\text{-}\{C_6H_4(PMePh)_2\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)]$ (VII) isolated using the tertiary bidentate phosphine rac-$C_6H_4(PMePh)_2$-1,2. Dissociation of one end the the phosphine ligand in **A**, followed by nucleophilic attack at the β-carbon of the ketenyl ligand would give the cyclic keto-derivative **C**. Subsequent hydrogen migration from phosphorus to the oxygen atom of the ketone would then afford the observed phospha-allyl products The involvement of intermediates such as **B** is supported by the observation that ketenyl complexes such as IV and Vc are known to undergo facile dissociation of a phosphine ligand. Moreover, it has been shown [14] that the η^1-ketenyl complex $[W(\eta^1\text{-}RCCO)(CO)(PMe_3)_2(\eta\text{-}C_5H_5)]$ (VI, R = C_6H_4Me-4) reacts with NMe_2H to give the complex $[W(\eta^1\text{-}CRHC(O)NMe_2\}(CO)(PMe_3)_2(\eta\text{-}$



Scheme 1

C_5H_5)] in which the hydrogen atom of the amine has been transfered to the α-carbon of the ketenyl moiety and this provides a good precedent for the conversion of the ketenyl intermediate **B** to the cyclic ketone **C**.

Experimental

All experiments were carried out under nitrogen by Schlenk tube techniques. Light petroleum refers to the fraction of b.p. 40–60 °C. The compounds [W(≡CR)(CO)$_2$(η-C_5H_5)] (R = C_6H_4Me-4, Me, C_6H_4OMe-2, and $C_6H_4CH_2$OMe-2) and [Mo(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] were prepared using the methods described by Mayr [15], Stone [16], or Fischer [17]. The bidentate phosphines $C_6H_4(PH_2)_2$-1,2 and rac-C_6H_4(PMePh)$_2$-1,2 were prepared by the standard literature procedures [7,8]. Products were separated by column chromatography on alumina (Brockman activity III) or B.D.H. Florosil (100–200 mesh). NMR spectra were recorded with Jeol JNM FX90Q, GX270, and GX400 spectrometers, and IR spectra were recorded with Nicolet MX5 or Perkin–Elmer 1600 spectrophotometers.

Synthesis of the tungsten and molybdenum complexes

(i) A solution of the complex [W(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] (Ia) (0.126 g, 0.31 mmol) and rac-C_6H_4(PMePh)$_2$-1,2 (0.10 g, 0.31 mmol) in Et_2O (10 cm^3) was stirred for 3 h at room temperature. The resulting yellow precipitate was collected, washed with Et_2O (2 × 1 cm^3), and dried *in vacuo* to give yellow microcrystals of [W(η^1-C(C_6H_4Me-4)=C=O)}{C_6H_4(PMePh)$_2$-1,2}(CO)(η-C_5H_5)] (VII) (0.19 g).

(ii) A solution of [W(≡CC_6H_4Me-4)(CO)$_2$(η-C_5H_5)] (Ia) (1.0 g, 2.5 mmol) in Et_2O (7 cm^3) was treated with $C_6H_4(PH_2)_2$-1,2 (0.36 g, 2.5 mmol) and heated under reflux for 6 h. The solution was then stirred at room temperature for 48 h. The solvent was removed *in vacuo*. The brown residue was washed with n-hexane (3 × 5 cm^3) and dried *in vacuo* to yield yellow microcrystals of [W{σ,η^3-$C_6H_4(PH_2)$(P-C{OH}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)] (VIIIa) (1.2 g).

(iii) A solution of [Mo(≡CC_6H_4Me-4)$(CO)_2(\eta$-$C_5H_5)$] (Ib) (0.21 g, 0.64 mmol) in THF (20 cm^3) was treated with $C_6H_4(PH_2)_2$-1,2 (1 cm^3 of a 0.65 mmol cm^{-3} solution in EtOH, 0.65 mmol). The solution was refluxed for 2 days and solvent was removed *in vacuo*. The brown residue was dissolved in the minimum volume of CH_2Cl_2/hexane (3:2) and chromatographed on alumina (2 × 15 cm column) at −20 °C. Elution with the same solvent mixture afforded two minor orange bands which were discarded. The third yellow band was collected and solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2/hexane afforded orange microcrystals of the complex [Mo{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)] · (CH_2Cl_2) (VIIIb) (0.10 g).

(iv) A solution of [W(≡CMe)$(CO)_2(\eta$-$C_5H_5)$] (Ic) (0.10 g, 0.30 mmol) in THF (20 cm^3) was treated with $C_6H_4(PH_2)_2$-1,2 (0.7 cm^3 of a 0.43 mmol cm^{-3} solution in EtOH, 0.30 mmol) in EtOH. The solution was refluxed for 2 days and solvent was removed *in vacuo*. The brown residue was dissolved in the minimum volume of CH_2Cl_2/hexane (4:1) and chromatographed on alumina (2 × 15 cm column) at −20 °C. Elution with the same solvent mixture afforded an orange band which was discarded. The second orange band was collected and solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2/hexane afforded orange microcrystals of the complex [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CHMe)-1,2}(CO)(η-C_5H_5)] · (CH_2Cl_2) (VIIIc) (0.06 g).

(v) A solution of [W(≡CC_6H_4OMe-2)$(CO)_2(\eta$-$C_5H_5)$] (Id) (0.16 g, 0.37 mmol) in Et_2O (25 cm^3) was treated with $C_6H_4(PH_2)_2$-1,2 (0.60 cm^3 of a 0.65 mmol cm^{-3} solution in EtOH, 0.39 mmol). The solution was refluxed for 3 days and solvent was removed *in vacuo*. The brown residue was dissolved in the minimum volume of CH_2Cl_2/hexane (4:1) and chromatographed on alumina (2 × 15 cm column) at −20 °C. Elution with the same solvent mixture afforded a yellow band which was discarded. The second orange band was collected and solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2/hexane afforded orange microcrystals of the complex [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{C_6H_4OMe-2})-1,2}(CO)(η-C_5H_5)] · (CH_2Cl_2) (IX) (0.11 g).

(vi) A solution of [W(≡$CC_6H_4CH_2$OMe-2)$(CO)_2(\eta$-$C_5H_5)$] (Ie) (0.26 g, 0.42 mmol) in Et_2O (25 cm^3) was treated with $C_6H_4(PH_2)_2$-1,2 (1 cm^3 of a 0.43 mmol cm^{-3} solution in EtOH, 0.43 mmol). The solution was refluxed for 2 days and stirred at room temperature for a further 2 days. Solvent was removed *in vacuo* and the orange residue was dissolved in the minimum volume of CH_2Cl_2/hexane (2:3) and chromatographed on alumina (2 × 15 column) at −20 °C. Elution with the same solvent mixture afforded a yellow band which was discarded. The second yellow band was collected and solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2/hexane afforded yellow microcrystals of the complex [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{$C_6H_4CH_2$OMe-2})-1,2}(CO)(η-C_5H_5)] · (CH_2Cl_2) (Xa) (ca. 0.05 g). The third yellow band was also collected and solvent was removed *in vacuo*. Recrystallisation from CH_2Cl_2/hexane afforded yellow microcrystals of the complex [W{σ,η^3-$C_6H_4(PH_2)$(PC{OH}CH{$C_6H_4CH_2$OMe-2})-1,2}(CO)(η-C_5H_5)] · (CH_2Cl_2) (Xb) (ca. 0.05 g).

Crystal structure determination

Crystals of VIIIa were grown from CH_2Cl_2–Et_2O mixtures as dark yellow prisms (crystal dimensions ca. 0.40 × 0.35 × 0.20 mm). Data were collected using a Nicolet

$P2_1$ diffractometer (293 K, Mo-K_α X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.71069 Å). Of the 3836 data collected (Wyckoff ω-scans, $2\theta \leqslant 50°$), 3216 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects. An empirical absorption correction was applied using a method based upon azimuthal scan data.

Crystal data for VIIIa. $C_{21}H_{20}O_2P_2W$, $M = 550.3$, triclinic, space group $P\bar{1}$, $a = 9.182(3)$, $b = 10.279(4)$, $c = 12.058(5)$ Å, $\alpha = 108.35(3)$, $\beta = 110.96(3)$, $\gamma = 73.53(3)°$, $U = 989.8(6)$ Å^3, $Z = 2$, $D_c = 1.85$ g cm^{-3}, $F(000) = 532$, μ(Mo-K_α) = 61.3 cm^{-1}.

The structure was solved by conventional heavy atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The important PH_2, OH, and C*H*(C_6H_4Me-4) hydrogen atoms were located from a final electron density difference synthesis and their positions were refined with fixed isotropic thermal parameters ca. $1.2 \times U_{eq}$ of the parent carbon atoms. All other hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters ca. $1.2 \times U_{eq}$ of the parent carbon atoms (C_6H_4, C_6H_4Me-4 and η-C_5H_5), or a common refined isotropic thermal parameter (Me-4). Final refinement by blocked-cascade matrix least-squares procedures were per-

Table 5

Atomic positional parameters (fractional coordinates $\times 10^4$) for compound VIIIa with esd's in parentheses

	x	*y*	*z*
W	1372(1)	1237(1)	3346(1)
P(1)	−706(1)	−78(1)	2261(1)
P(2)	2828(1)	−1160(1)	3613(1)
C(1)	693(5)	1634(4)	1742(4)
O(1)	192(4)	1863(4)	773(3)
C(2)	3182(5)	−532(4)	2530(4)
O(2)	3016(4)	−1159(4)	1294(3)
C(10)	3904(4)	648(4)	3126(4)
C(11)	4444(4)	1503(4)	2609(4)
C(12)	4346(5)	1275(5)	1388(4)
C(13)	4921(6)	2131(6)	1018(5)
C(14)	5595(5)	3216(6)	1818(5)
C(15)	5706(5)	3455(5)	3041(5)
C(16)	5157(5)	2607(5)	3433(4)
C(17)	6222(9)	4159(8)	1408(7)
C(21)	−60(5)	−1954(5)	2075(4)
C(22)	−1062(7)	−2919(6)	1416(5)
C(23)	−423(8)	−4340(6)	1331(5)
C(24)	1159(8)	−4807(6)	1893(6)
C(25)	2119(7)	−3842(5)	2552(5)
C(26)	1531(5)	−2415(4)	2639(4)
C(31)	2524(7)	2678(6)	5225(4)
C(32)	1489(7)	3487(5)	4440(5)
C(33)	−26(7)	3299(7)	4193(6)
C(34)	89(10)	2321(9)	4847(6)
C(35)	1674(10)	1983(7)	5497(5)

formed on Data General 'Eclipse' computer with the SHELXTL system of programs [18]. Final $R = 0.022$ ($R' = 0.024$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000\ 5\,|F|^2]$. The final electron density difference synthesis showed no peaks > 0.66 or < -0.70 eÅ^{-3}. Scattering factors with corrections for anomalous dispersion were taken from reference [19]. Atomic co-ordinates are listed in Table 5 and full listings of bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Structure factors are available from the authors.

Acknowledgements

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References

1 F.R. Kreissl, in R.B. King and J.J. Eisch, (Eds.), Organometallic Synthesis, Elsevier, New York, 1986, 241–249, and refs. therein; F.R. Kreissl, K. Eberl and W. Uedelhoven, Chem. Ber., 110 (1977) 3782.
2 J.C. Jeffery, C. Sambale, M.F. Schmidt and F.G.A. Stone, Organometallics, 1 (1982) 1597.
3 P.G. Byrne, M.E. Garcia, N.H. Tran-Huy, J.C. Jeffery and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 1243.
4 K. Eberl, W. Uedelhoven, H.H. Karsch and F.R. Kreissl, Chem. Ber., 113 (1980) 3377.
5 J.B. Sheridan, D.B. Pourreau and G.L. Geoffroy, Organometallics, 7 (1988) 289.
6 G.A. Carriedo, V. Riera, M. Luz Rodriguez and J.C. Jeffery, J. Organomet. Chem., 314 (1986) 139.
7 E.P. Kyba, S.-T. Liu and R.L. Harris, Organometallics, 2 (1983) 1877.
8 N.K. Roberts and S.B. Wild, J. Am. Chem. Soc., 101 (1979) 6254.
9 J.E. Denison, J.C. Jeffery, S. Harvey, P. Muller and K.D. Vinindra Weerasuria, J. Chem. Soc., Chem. Commun., (1990) 1023.
10 F. Mercier and F. Mathey, Organometallics, 9 (1990) 863.
11 F. Mathey, Nouv. J. Chim., 11 (1987) 585.
12 S. Holland, F. Mathey and J. Fischer, Polyhedron, 5 (1986) 1413.
13 B. Deschamps and F. Mathey, J. Chem. Soc., Chem. Commun., (1985) 1010.
14 F.R. Kreissl, W. Sieber and M. Wolfgruber, Angew. Chem., Int. Ed. Engl., 22 (1983) 493.
15 G.A. McDermott, A.M. Dorries and A. Mayr, Organometallics, 6 (1987) 925.
16 S.J. Dossett, A.F. Hill, J.C. Jeffery, F. Marken, P. Sherwood and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1988) 2453.
17 E.O. Fischer, T.L. Lindner, G. Huttner, P. Friedrich, F.R. Kreissl and J.O. Besenhard, Chem. Ber., 110 (1977) 3397.
18 G.M. Sheldrick, SHELXTL programs for use with the Nicolet X-ray system, 1986.
19 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.