Monocyclopentadienyl complexes of niobium, tantalum and tungsten containing heterodifunctional P,O ligands†

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The reactions of P,O type ligands with the half-sandwich complexes $[(\eta\text{-}C_5R_5)MCl_4]$ ($R_5 = H_5$, Me_5, ${}^iPrH_4$; M = Nb, Ta, W) have been investigated. Monodentate P-adducts were obtained with the β-amidophosphine $Ph_2PCH_2C(O)NPh_2$, whereas in the case of the keto ligand $Ph_2PCH_2C(O)Ph$ a spontaneous HCl elimination occurred to give direct access to the corresponding phosphinoenolate complexes. The crystal structures of $[(\eta\text{-}C_5H_5)NbCl_3\{PPh_2CH{\cdots}C({\cdots}O)Ph\}]$, $[(\eta\text{-}C_5H_5)TaCl_3\{PPh_2CH{\cdots}C({\cdots}O)Ph\}]$ and $[(\eta\text{-}C_5Me_5)TaCl_3\{PPh_2CH{\cdots}C({\cdots}O)Ph\}]$ have been determined. Interestingly, the acetamido derived phosphine $Ph_2PNHC(O)Me$ afforded O-adducts, which is an unusual bonding mode for a P,O ligand.

Introduction

Bifunctional P,O ligands, which combine a soft phosphine moiety and a hard oxygen function, such as ester, amide or ketone, remain the subject of numerous studies, owing to the various properties and/or applications of their transition-metal complexes.[1–4] In metal complexes with these P,O molecules both P-monocoordination and P,O chelation are commonly found. The P,O chelate ligands give stable metal complexes and due to the different properties of the P and O ligand atoms they can strongly influence the stereoelectronic properties at the metal centre.[3] Furthermore, in late transition metal complexes, the greater lability of the O-ligand atom favours fluxional processes resulting from reversible O-atom dissociation and recoordination.[1–4] The O-atom dissociation in these hemilabile ligands creates a vacant coordination site, and conversely weak O-association can give rise to stabilisation of an otherwise coordinatively unsaturated species. For this reason complexes with P,O ligands have been studied for their catalytic properties,[5–13] especially in reactions involving the activation of small molecules.[14–19]

In contrast to the wealth of late transition metal complexes synthesized, which contain a β-keto-, ester- or amidophosphine ligand, there have been only a few studies on the early transition-metal chemistry of these ligands and they have mainly focused on molybdenum. Thus, the half-sandwich complexes of the β-amidophosphine $Ph_2PCH_2C(O)NPh_2$ **1**, $[(\eta\text{-}C_5H_5)MoCl_2\{\mathbf{1}\text{-}\kappa^2P,O\}]$ or $[(\eta\text{-}C_5Me_5)MoCl_2\{\mathbf{1}\text{-}\kappa^2P,O\}][BF_4]$,[20] and of the keto-functionalised *N*-pyrrolylphosphine $Ph_2PNHC_4H_3\{C(O)Me\}\text{-}2$ (PpyrO), $[(\eta\text{-}C_5H_5)MoCl(CO)_2\{(PpyrO)\text{-}\kappa P\}]$ and $[(\eta\text{-}C_5H_5)Mo(CO)_2\{(PpyrO)\text{-}\kappa^2P,O\}][BF_4]$,[21] have been reported. More recently, we have described the synthesis of η-arene-molybdenum complexes, such as $[(\eta\text{-}C_6H_5R)Mo(\eta\text{-}C_3H_5)\{Ph_2PXHC(O)R'\text{-}\kappa^2P,O\}][PF_6]$ (R = H, Me; R′ = Ph, NPh_2, Me; X = N, C).[22,23] In these complexes, the P,O ligands act either as P-monodentate phosphine or as a P,O-chelate, whereas O-monocoordination, which may have been anticipated owing to the relatively hard nature of molybdenum *vs.* late transition metals, was not observed. Although ligands with carbonyl functions (ketones,[24–26] amides,[27,28] acids/esters[29,30]) are known to coordinate readily to groups 5 and 6 metals, there has been no example reported, to the best of our knowledge, when a phosphine donor is also present in the ligand. This also applies to somewhat related ligands, such as $R_2PNHP(O)R_2$,[31] or even when the P atom is not available for coordination as in $R_3P{=}NC(O)R'$.[32,33] We will present here a rare example of a P,O phosphine acting as a O-monodentate ligand in half-sandwich Nb, Ta and W complexes.

Anionic phosphino-enolates, formed from ketophosphines, are also a well-developed group of P,O ligands.[34–49] Interest in this chemistry partly stems from the fact that nickel phosphino-enolate complexes catalyze the oligomerisation of ethylene in α-olefins (Shell Higher Olefin Process).[34,40,50,51] Substitutional modification of the phosphino-enolate ligands can modify catalyst activity and the chain length distribution.[49–52] Numerous phosphino-enolate complexes of group 8–10 metals have been synthesized and their reactivity studied.[35–39,41–46,49,53–58] For example, Rh(I) complexes in this class are efficient catalysts for the transfer dehydrogenation of alkanes to alkenes.[59]

As for their neutral counterparts, the early transition metal chemistry of anionic P,O ligands has been little investigated. The η-arene-molybdenum complexes $[(\eta\text{-}C_6H_5R)Mo(\eta\text{-}C_3H_5)\{Ph_2PX{\cdots}C({\cdots}O)Ph\text{-}\kappa^2P,O\}]$ or $[(\eta\text{-}C_6H_5R)Mo\{Ph_2PX{\cdots}C({\cdots}O)Ph\text{-}\kappa^2P,O\}_2]$ (R = H, Me; R′ = Ph, NPh_2, Me; X = N, C) represent, to the best of our knowledge, rare examples of early transition metal complexes, containing a chelating phosphinoenolate ligand.[22,23] Very recently, Edwards *et al.* reported the compound $[(\eta\text{-}C_5H_5)_2Ti\{OC(O)CH_2PPh_2\}_2]$, prepared by treatment of $[(\eta\text{-}C_5H_5)_2TiCl_2]$ with the anion $Ph_2PCH_2C(O)O^-$.[60] The titanocene and zirconocene complexes of a camphor-derived phosphino-enolate have also been

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† Dedicated to Prof. P. Royo on the occasion of his 65th birthday, with our warmest congratulations.

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described.[61] Further zirconocene phosphino-enolates derived from the α-ketophosphine $Ph_2PC(O)R$ (R = Me, Et) have been prepared by Floriani *et al.*[62,63]

Here, we report the first investigations into the coordination chemistry of P,O ligands, namely $Ph_2PCH_2C(O)NPh_2$ **1**, $Ph_2PCH_2C(O)Ph$ **2** and $Ph_2PNHC(O)Me$ **3**, with the half-metallocene complexes $[(\eta\text{-}C_5R_5)MCl_4]$ **4** (**a**: $R_5 = H_5$, M = Nb; **b**: $R_5 = H_5$, M = Ta; **c**: $R_5 = Me_5$, M = Ta; **d**: $R_5 = {}^iPrH_4$, M = W). The latter were chosen because they represent versatile precursors for new materials, the design of highly efficient catalysts for organic transformations and polymerization reactions[64–68] or for W≡W triply bonded complexes (**4d**),[69] which have a remarkably rich chemistry.[70] We will show that under similar reaction conditions, the P,O ligands **1**–**3** lead to complexes in which they adopt either a P-monodentate, an anionic P,O-chelating or, quite unexpectedly, a neutral O-monodentate coordination mode.

Results and discussion

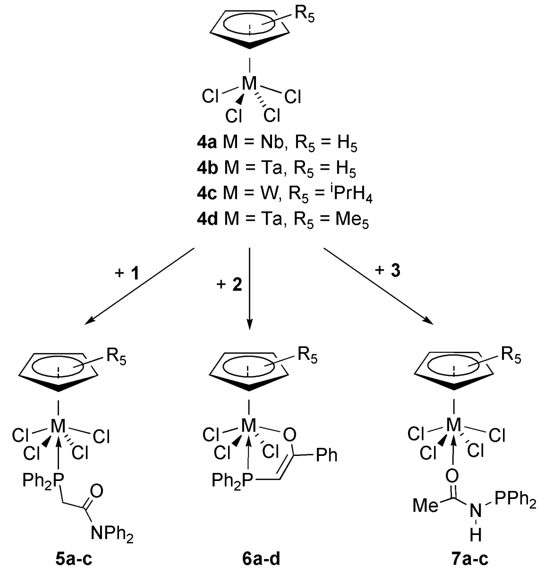
Half-sandwich complexes $[(\eta\text{-}C_5R_5)MCl_4]$ **4a**–**d** have Lewis acid character and form mono-adducts $[(\eta\text{-}C_5R_5)MCl_4(L)]$ with neutral ligands such as L = amines, phosphines or phosphites.[71] Early studies led to the conclusion that adducts of **4a**, $[(\eta\text{-}C_5H_5)NbCl_4(L)]$ where L = a tertiary phosphine or phosphite, were labile in contrast to their tantalum analogues.[72–74] The niobium adducts $[(\eta\text{-}C_5H_4Me)NbCl_4(L)]$ ($L = PMe_3$, PEt_3 or $P(OMe)_3$) slowly decompose in solution.[75] Recently, Poli *et al.* showed that adducts of **4a** with PMe_nPh_{3-n} (n = 3, 2 or 1) could be isolated provided that no excess of the phosphine, which may cause reduction side-products, was present.[76] The adducts of **4c**, $[(\eta\text{-}C_5H_4{}^iPr)WCl_4(L)]$ where $L = vinylPH_2$, $allylPH_2$ or PMe_3, are stable.[77,78]

Formation of P-monoadducts

Treatment of $[(\eta\text{-}C_5H_5)NbCl_4]$ **4a** with one mol. equiv. of **1** gave the P-monoadduct $[(\eta\text{-}C_5H_5)NbCl_4\{PPh_2CH_2C(O)NPh_2\}]$ **5a** as a brown solid. The proposed structure is supported by the presence, in the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2), of a very broad peak at *ca.* δ 33.1 ($w_{1/2} > 2500$ Hz), owing to the quadrupolar broadening due to Nb (spin 9/2), and by the occurrence of a $\nu_{C=O}$ vibration at 1658 cm^{-1} in the IR spectrum, which indicates non-coordination of the amide moiety (free ligand: 1657 cm^{-1}).[42] In the ^1H NMR spectrum (CD_2Cl_2), the $\eta\text{-}C_5H_5$ and PCH_2 protons are observed at δ 6.89 (singlet) and 3.88 (doublet, $^2J(P,H) = 7$ Hz), respectively. The absence of coupling between the ^{31}P nucleus and the Cp protons was also noted for $[(\eta\text{-}C_5H_5)NbCl_4(PMe_nPh_{3-n})]$ (n = 3, 2 or 1).[76] Complexes $[(\eta\text{-}C_5H_5)TaCl_4\{PPh_2CH_2C(O)NPh_2\}]$ **5b** and $[(\eta\text{-}C_5H_4{}^iPr)WCl_4\{PPh_2CH_2C(O)NPh_2\}]$ **5c** were prepared from **4b,c** and **1**. The spectroscopic data of the tantalum complex **5b** mirror those of **5a**. The paramagnetic tungsten complex **5c** was characterized by IR spectroscopy ($\nu_{C=O}$ 1662 cm^{-1}), mass spectroscopy (m/z: 793 [M − Cl]) and elemental analysis. Complexes **5a**–**c** were stable in solution for several hours and in the solid state for a few days, in the absence of oxygen. Contrary to the situation reported for the Mo complexes mentioned in the introduction,[20,22,23] there was no observed tendency for chelation for **1** in complexes **5a**–**c**.

Formation of P,O-enolate complexes

Surprisingly, attempts to form the P-monodentate analogues of **5a**–**c** from $[(\eta\text{-}C_5H_5)NbCl_4]$ **4a** and the β-ketophosphine $Ph_2PCH_2C(O)Ph$ **2** failed. Instead, the reaction followed a different pathway, which resulted in the formation of a deep red solution from which HCl fumes emanated (the acidic nature of the gas was confirmed with pH-paper). After work up, brick-red $[(\eta\text{-}C_5H_5)\overline{NbCl_3\{PPh_2CH\cdots C(\cdots O}){Ph}\}]$ **6a** was isolated (Scheme 1). The ^1H NMR spectrum of **6a** contains a sharp singlet at δ 6.95 (Cp) and a doublet at δ 6.25 [$J(P,H) = 3.5$ Hz], which is ascribed to the enolate proton. There were also signals arising from the aromatic hydrogens. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) shows a very broad hump at *ca.* δ 36.5, as a result of the P–Nb coupling ($w_{1/2} > 2500$ Hz). In the IR spectrum, a $\nu_{C\cdots C} + \nu_{C\cdots O}$ vibration is observed at 1547 cm^{-1} (*vs* 1670 cm^{-1} for the $\nu_{C=O}$ vibration of uncoordinated **2**).[35] This value lies within the range of those already reported for the same phosphino-enolate moiety in other metal complexes.[35,37–39,41,43–46,49] The proposed structure of **6a** was confirmed by X-ray diffraction (*vide infra*). Note that **6a** was also obtained as the sole product when an excess of the ketophosphine ligand was used (2 to 4 mol. equiv.), no side-reaction being observed.



Scheme 1 *Reaction conditions*: Room temperature; solvent: M = Nb: DME; M = Ta: CH_2Cl_2; M = W: THF (**1**), toluene (**2**) or CH_2Cl_2/toluene 1:1 (**3**).

Spontaneous elimination of HCl was also observed when **2** was reacted with **4b**–**d**, thus leading to the formation of the phosphino-enolate derivatives **6b**–**d**, respectively (Scheme 1). The spectroscopic data of the tantalum complex **6b** mirror those of **6a**. In the case of the Cp* complex **6d**, the $^{31}P\{^1H\}$ resonance occurs at slightly higher field (δ 31.3), whereas, in the ^1H NMR spectrum, the enolate and $\eta\text{-}C_5Me_5$ protons are observed at δ 6.08 [$J(P,H) = 3.6$ Hz] and 2.38 (singlet), respectively. The paramagnetic complex **6c** was characterized by IR spectroscopy ($\nu_{C\cdots C} + \nu_{C\cdots O}$ 1542 cm^{-1}), mass spectroscopy (m/z: 701 [M]) and elemental analysis. It was isolated as a burgundy solid, whereas phosphine adducts of the type $[(\eta\text{-}C_5H_4{}^iPr)WCl_4(PR_3)]$ range from yellow ochre to brown.[77,78] The X-ray structures of the tantalum complexes **6b,d** have been determined (*vide infra*).

To the best of our knowledge, such a spontaneous and facile HCl elimination in the absence of base has not been described for transition metal complexes containing **2** or any similar ligands. Yet, thermal activation or treatment with I_2 of Ru clusters of the type $[Ru_3(CO)_{12-n}L_n]$ (L = **2**, n = 1–3) have led to phosphino-enolate Ru complexes,[43,44] whereas a Rh(III) phosphino-enolate complex has been obtained by deprotonation of a co-ordinated ketophosphine **2** by an excess of this ligand present in the reaction mixture, the latter being a slow process (*ca.* 1 week).[48] Although the mechanism of the formation of **6** has not been established, we suggest, on the basis of the formation of complexes **5**, that P-coordination of **2** at the metal centre occurs first. This would result in an enhanced acidity of the PCH_2 protons and thus favour HCl elimination. This is consistent with our recent observation of an H/D exchange involving the methylene protons of **2** in the Mo(II) complexes $[(\eta\text{-}C_6H_5R)Mo(\eta\text{-}C_3H_5)\{Ph_2PCH_2C(O)Ph\}][PF_6]$ (R = H, Me).[23] The dehydrochlorination may also be facilitated by intra- and/or inter molecular H···Cl interactions involving the methylene protons, a bonding situation which has been encountered in the crystal structure of the Mo(II) complex $[(\eta\text{-}C_6H_5Me)Mo(\eta\text{-}C_3H_5)Cl\{Ph_2PCH_2C(O)Ph\}]$.[23]

The complexes **6** exhibit remarkable stability both in solution and in the solid state. In the latter case they can be kept for weeks in the air. Note that when **6** was treated with an excess of PMe_3, no opening or complete displacement of the P,O chelate was observed. The straightforward formation of these phosphino-enolate complexes, under the same reaction conditions as those used for the preparation of **5a–c**, emphasizes a marked difference of behaviour between the β -keto-phosphine **2** and its β-amido counterpart **1**. This is related to the more acidic character of the CH_2 protons in **2**, owing to the different electronic influence of its Ph substituent *vs.* the NPh_2 group in **1**.

Formation of O-monoadducts

The reaction of **4a–c** with the acetamido-phosphine $Ph_2PNHC(O)Me$ **3** led to the new complexes **7a–c** in which the P,O ligand is O-monocoordinated and this is an unsual coordination mode for such a P,O ligand (Scheme 1). This proposed stucture is supported by the $\nu_{C=O}$ vibration at 1646 cm^{-1} (**7a,b**) or 1651 cm^{-1} (**7c**), to be compared to 1715 cm^{-1} for the free ligand.[79] The fact that the P atom does not coordinate to the metal centre is suggested by the $^{31}P\{^1H\}$ NMR resonances of **7a** (δ 33.1) and **7b** (δ 40.6), which occur in the same region as that of **3** (δ 31.1). These values suggest that the electronic properties of the phosphorus centre are slightly more affected by O-coordination of the ligand in the case of M = Ta (**7b**) than in the case of M = Nb (**7a**). Furthermore, the slightly broadened ^{31}P singlet ($w_{1/2}$ = 65 Hz) observed for **7a** contrasts with the very broad signals ($w_{1/2}$ > 2500 Hz) observed for **5a** and **6a**, in which the P atoms are coordinated to Nb. The ^1H NMR spectra of **7a,b** show all the expected signals, including those of the NH protons at *ca.* δ 9 (free ligand: δ 6.15).[79] Complexes **7** are stable for a few days in the solid state, in the absence of air and moisture. They represent rare examples of transition metal derivatives in which a neutral functionalized phosphine is coordinated to the metal *via* the alternative donor atom instead of the P atom. Precedents include N- and O-adducts of MnI_2 of 2-(diphenylphosphino)pyridine and **2**, respectively.[80] In the case of phosphino-enolate zirconocene and titanocene complexes, O-monocoordination of the anionic P,O ligands results from the formation of a covalent M–O bond.[61–63] Previous investigations on the coordination properties of **3** concerned the synthesis of neutral and cationic Pd,[79] Mo[22] and Rh complexes,[81] for which O-monocoordination was never encountered. Comparative studies showed that **3** is a better P,O-chelate than the keto- and amidophosphines **1** and **2**, respectively.[79]

Crystal structures of 6a,b,d

Crystal data and data collection parameters are given in Table 1. There are two crystallographically different but very similar molecules in the asymmetric unit of **6b** whose selected bond lengths and angles are given in Table 2 together with those of complexes **6a,d**. ORTEP views of **6a**, **6b** and **6d** are pictured in Fig. 1, 2 and 3, respectively. If one considers the Cp centroid of the cyclopentadienyl ligands as an apex of the metal coordination polyhedron, then the three complexes exhibit a distorted pseudooctahedral geometry, with the three chlorine atoms and the oxygen atom lying in the equatorial plane and the P atom *trans* to the cyclopentadienyl ring.[82] The Cp_{cent}–M–P(1) angles range from 175.76° (**6a**) to 178.48° (**6d**) and are slightly more obtuse than those found in the ylide complex $[(\eta\text{-}C_5Me_5)TaCl_4(CH_2{=}PMePh_2)]$ (173°)[83] or in $[(\eta\text{-}C_5H_5)NbCl_4(PMePh_2)]$ (174.6°),[76] the only phosphine adduct of $[(\eta\text{-}C_5H_5)NbCl_4]$ that has been structurally characterized to date. The chlorine and oxygen atoms are bent away from the cyclopentadienyl ring towards the P ligand. The molecular structures show M–Cl [2.3873(9)–2.446(1) Å] bond lengths, Cp_{cent}–M–Cl [103.35–105.28°] and Cl–M–Cl [87.08(4)–90.31(3)° *cis*; 150.95(3)–152.37(8)° *trans*] bond angles which are consistent with those reported for related structures.[76,83–85] The M–O(1) bond lengths are similar to those found in other transition metal complexes with the same phosphino-enolate ligand[35–39,41,43–46,49] or in $[(\eta\text{-}C_5Me_5)TaCl_3\{OC(SiMe_3)NNCPh_2\}]$ [1.98(1) Å].[85] In the case of $[(\eta\text{-}C_5Me_5)TaCl_3\{PPh_2CH{\cdots}C({\cdots}O)Ph\}]$ **6d** [2.024(2) Å] it is slightly longer than in the other complexes **6a,b** [1.977(2)–1.983(3) Å]. The M–P(1) bond lengths of *ca.* 2.66 Å are shorter than those found in $[(\eta\text{-}C_5H_4Me)TaCl_4\{PH_2(C_6H_2{}^iPr_3)\}]$

Table 1 Selected crystallographic data for complexes **6a,b,d**

	6a	**6b**	**6d**
Formula	$C_{25}H_{21}Cl_3OPNb\cdot0.5C_7H_8$	$C_{25}H_{21}Cl_3OPTa$	$C_{30}H_{31}Cl_3OPTa$
FW	613.75	655.72	725.86
Colour	Red	Yellow	Yellow
Crystal system	Monoclinic	Triclinic	Trigonal
Space group	$P21/c$	$P\bar{1}$	$R\bar{3}$
T/K	150(2)	150(2)	150(2)
a/Å	7.876(1)	8.4611(1)	42.5519(5)
b/Å	26.392(1)	16.6441(3)	42.5519(5)
c/Å	12.650(1)	16.8443(3)	8.7407(5)
α/°	90	92.6314(8)	90
β/°	97.01(1)	99.3326(9)	90
γ/°	90	94.1166(11)	120
V/Å^3	2609.8	2330.7	13 706.1
Z	4	4	18
μ/mm^{-1}	0.851	5.145	3.945
Unique reflections	5001	10 582	6943
Reflections	4100 with $I > 3\sigma(I)$	8244 with $I > 2\sigma(I)$	5794 with $I > 3\sigma(I)$
R	0.0515	0.0314	0.0281
R_w	0.0543	0.0366	0.0298

Table 2 Selected bond lengths (Å) and angles (°) for **6a**, **6b** (2 molecules) and **6d**; $\mathrm{Cp_{cent}}$ refers to the computed cyclopentadienyl ring centroids

	6a	**6b** (molecule 1)	**6b** (molecule 2)	**6d**
M–P1	2.667(1)	2.670(1)	2.674(1)	2.6596(9)
$\mathrm{Cp_{cent}}$–M	2.132	2.127	2.142	2.168
M–Cl1	2.4186(9)	2.415(1)	2.410(1)	2.4209(8)
M–Cl2	2.4057(9)	2.4131(11)	2.402(1)	2.3873(9)
M–Cl3	2.446(1)	2.422(1)	2.413(1)	2.3934(8)
M–O1	1.977(2)	1.983(3)	1.982(3)	2.023(2)
P1–C1	1.779(4)	1.779(5)	1.792(4)	1.773(3)
C1–C2	1.345(5)	1.352(6)	1.342(6)	1.349(5)
C2–O1	1.346(4)	1.349(5)	1.352(3)	1.342(4)
$\mathrm{Cp_{cent}}$–M–P1	175.76	175.80	177.40	178.48
$\mathrm{Cp_{cent}}$–M–Cl1	104.02	103.59	105.28	104.39
$\mathrm{Cp_{cent}}$–M–Cl2	104.24	104.05	104.60	103.99
$\mathrm{Cp_{cent}}$–M–Cl3	103.44	104.02	103.35	103.81
$\mathrm{Cp_{cent}}$–M–O1	101.83	103.17	101.78	103.82
Cl1–M–Cl2	88.92(3)	88.25(4)	87.41(4)	89.49(3)
Cl1–M–Cl3	152.37(3)	151.26(3)	152.35(4)	150.95(3)
Cl1–M–O1	87.60(8)	85.21(9)	85.50(9)	82.04(7)
Cl2–M–Cl3	87.26(3)	87.08(4)	87.16(4)	90.31(3)
Cl2–M–O1	153.80(8)	153.56(8)	152.76(9)	152.12(7)
Cl3–M–O1	83.921(8)	86.47(9)	87.04(9)	84.70(7)
P1–M–O1	73.97(7)	74.10(8)	74.23(8)	74.83(7)
P1–C1–C2	115.4(3)	115.3(3)	114.7(3)	116.0(3)
C1–C2–O1	121.3(3)	121.5(4)	122.3(4)	122.6(3)
C2–O1–M	131.8(2)	131.6(2)	131.2(3)	129.2(2)

[2.710 Å][86] or in $[(\eta\text{-}C_5H_5)NbCl_4(PMePh_2)]$ [2.7844(9) Å][76] and similar to those reported for $[Nb(O)Cl_3(PMe_3)_3]$ [2.640(3) Å].[87] The other bond lengths and angles of the phosphino-enolate and cyclopentadienyl ligands are within the expected range.

Conclusion

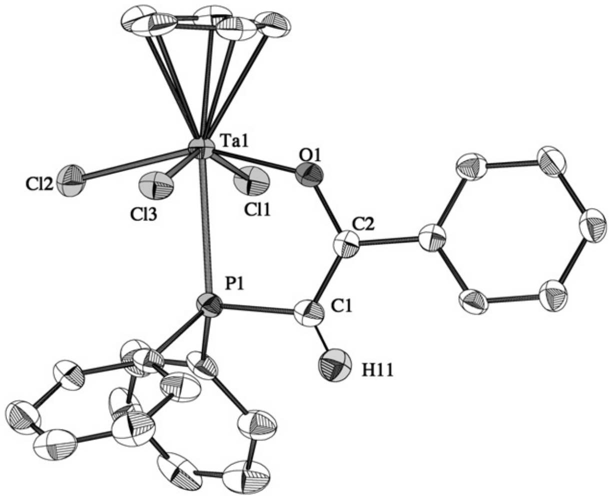


Fig. 2 Molecular structure of **6b**. Only one of the two independent molecules of the unit cell is shown. Hydrogen atoms, except H(11), are omitted for clarity.

We have described here the first investigations on the chemistry of half-sandwich complexes of the type $[(\eta\text{-}C_5R_5)MCl_4]$ (M = Nb, Ta or W) with β-carbonylphosphines. Depending on the nature of the P,O ligand three different coordination modes have been observed. With $Ph_2PCH_2C(O)NPh_2$ **1** P-monoadducts were obtained, whereas $Ph_2PNHC(O)Me$ **3** led to O-monoadducts, which is an unsual coordination mode for P,O ligands. The reactions with the β-ketophosphine $Ph_2PCH_2C(O)Ph$ **2** followed another pathway. In this case, no phosphine adduct was isolated, instead HCl elimination readily occurred giving the corresponding phosphino-enolate complexes. To the best of our knowledge, such a facile formation of transition metal phosphino-enolate complexes, in the absence of a base, has not been reported previously. The crystal structures of the Nb and Ta complexes **6a**,**b**,**d** have been determined. The striking difference between **1** and **3** in bonding cannot be of steric origin since P-coordination of **3** would have led to a very similar steric situation at the metal centre. Therefore, the bonding difference must be of electronic origin, which has not been quantified at the moment and deserves further investigations.

Experimental

Reagents and physical measurements

All manipulations of air- and/or moisture sensitive materials were performed under an inert atmosphere of argon using standard Schlenk line techniques, or in an inert atmosphere dry box containing dinitrogen. Solvents were dried over the appropriate drying agent and distilled under nitrogen.

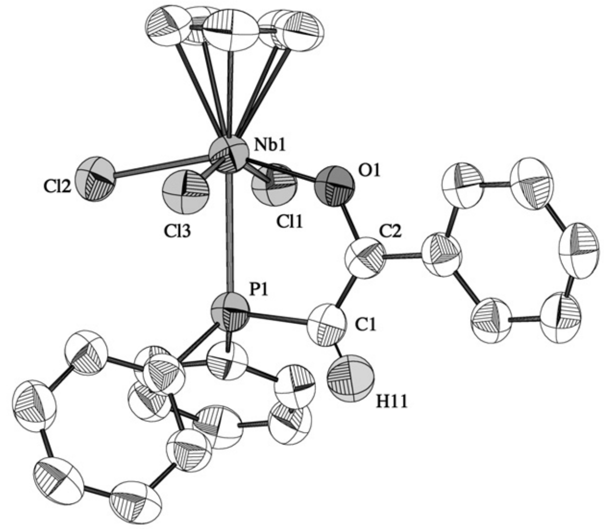


Fig. 1 Molecular structure of **6a**. Hydrogen atoms, except H(11), and the solvent molecule (toluene) are omitted for clarity.

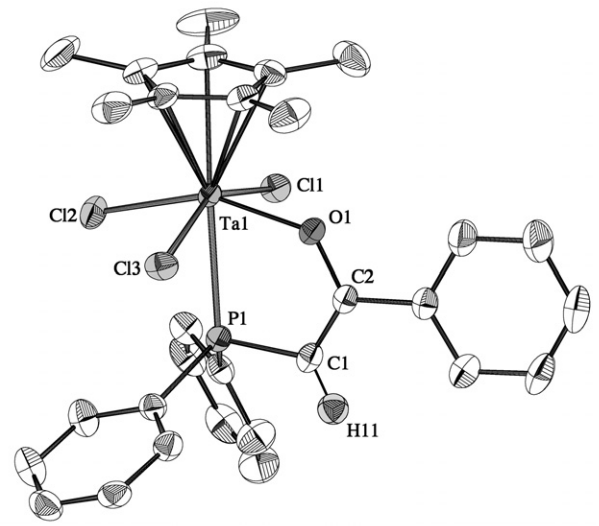


Fig. 3 Molecular structure of **6d**. Hydrogen atoms, except H(11), are omitted for clarity.

Deuterated solvents were dried over the appropriate drying agent and vacuum distilled prior to use. The compounds $[(\eta\text{-}C_5H_5)NbCl_4]$,[75] $[(\eta\text{-}C_5H_5)TaCl_4]$,[75] $[(\eta\text{-}C_5Me_5)TaCl_4]$,[88] $[(\eta\text{-}C_5H_4{}^iPr)WCl_4]$,[89] $Ph_2PCH_2C(O)Ph$,[35] $Ph_2PCH_2C(O)NPh_2$[42] and $Ph_2PNHC(O)Me$[79] were prepared according to previously published methods. NMR spectra were recorded on a Varian Mercury 300 (^1H, ^{13}C, and ^{31}P at 300.17, 75.48 and 121.51 MHz, respectively) spectrometer. They were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances and measured relative to tetramethylsilane (^1H and ^{13}C; δ 0 ppm). ^{31}P NMR was referenced externally to 85% H_3PO_4 (δ 0 ppm). Elemental analyses were provided by the microanalytical department, Inorganic Chemistry Laboratory, University of Oxford or by the Service de Microanalyses, Université Louis Pasteur, Strasbourg. Infra-red spectra were recorded on a Perkin Elmer 1600 Series FTIR or a Bruker IFS66 FTIR spectrometer. Mass spectra were recorded at the Inorganic Chemistry Laboratory, on a Macromass LC Tof spectrometer.

Synthesis

$[(\eta\text{-}C_5H_5)NbCl_4\{PPh_2CH_2C(O)NPh_2\}]$ 5a. Solid $[(\eta\text{-}C_5H_5)NbCl_4]$ (0.200 g, 0.66 mmol) and $Ph_2PCH_2C(O)NPh_2$ (0.261 g, 0.66 mmol) were placed in a Schlenk flask and DME (10 mL) was added. The solution was stirred for 3 h. The volatiles were then removed under reduced pressure and the residue washed with Et_2O (10 mL) and pentane (10 mL). Complex **5a** was obtained as a pale brown air-sensitive solid (0.417 g, yield 90%). ^1H NMR (CD_2Cl_2, 300.18 MHz): δ 3.89 (d, 2H, $^2J_{PH} = 7$ Hz, PCH_2); 6.90–7.79 (m, 25H, Cp and aromatics). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 33.1 (vbr, $w_{1/2} > 2500$ Hz). IR (CH_2Cl_2): 1658 cm^{-1} ($\nu_{C=O}$). Anal. calc. for $C_{31}H_{27}Cl_4NNbOP$: C, 53.55; H, 3.91; N, 2.01. Found: C, 53.81; H, 4.06; N, 1.95%.

$[(\eta\text{-}C_5H_5)TaCl_4\{PPh_2CH_2C(O)NPh_2\}]$ 5b. This compound was prepared in a similar manner to **5a** from $[(\eta\text{-}C_5H_5)TaCl_4]$ (0.150 g, 0.38 mmol) and $Ph_2PCH_2C(O)NPh_2$ (0.152 g, 0.38 mmol) in CH_2Cl_2 (10 mL). Complex **5b** was obtained as a yellow solid (0.257 g, 85%). ^1H NMR (CD_2Cl_2, 300.18 MHz): δ 3.69 (d, 2H, $^2J_{PH} = 5.5$ Hz, PCH_2); 6.77 (s, 5H, Cp); 6.95–7.97 (m, 20H, aromatics). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 27.9. IR (CH_2Cl_2): 1658 cm^{-1} ($\nu_{C=O}$). Anal. calc. for $C_{31}H_{27}Cl_4NOPTa$: C, 47.54; H, 3.47; N, 1.79. Found: C, 47.69; H, 3.38; N, 1.92%.

$[(\eta\text{-}C_5H_4{}^iPr)WCl_4\{PPh_2CH_2C(O)NPh_2\}]$ 5c. This compound was prepared in a similar manner to **5a** from $[(\eta\text{-}C_5H_4{}^iPr)WCl_4]$ (0.600 g, 1.386 mmol) and $Ph_2PCH_2C(O)NPh_2$ (0.548 g, 1.386 mmol) in THF (30 mL). Complex **5c** was obtained as a green-brown solid (0.845 g, 74%). IR (KBr): 1662 cm^{-1} ($\nu_{C=O}$). MS *m*/*z*: 793 ($M^+ - Cl$ showing the expected isotopic pattern), 758 ($M^+ - 2Cl$). Anal. calc. for $C_{34}H_{33}Cl_4OPW$: C, 49.30; H, 4.02; N, 1.69. Found: C, 48.87; H, 4.27; N, 1.53%.

$[(\eta\text{-}C_5H_5)\overline{NbCl_3\{PPh_2CH\overset{\cdots}{-}C(\overset{\cdots}{-}O})Ph\}]$ 6a. Solid $[(\eta\text{-}C_5H_5)NbCl_4]$ (0.400 g, 1.33 mmol) and $Ph_2PCH_2C(O)Ph$ (0.405 g, 1.33 mmol) were placed in a Schlenk flask and DME (30 mL) was added at ambient temperature. Rapidly, the solution turned deep red, and HCl emanated from it. The mixture was then stirred for 2 h and the volatiles were removed under reduced pressure. The red-brown residue was washed with Et_2O (2 × 20 mL) and pentane (2 × 20 mL) and dried *in vacuo* affording **6a** as a red-brown solid (0.704 g, yield 93%). ^1H NMR (CD_2Cl_2, 300.18 MHz): δ 6.25 (d, 1H, $^2J_{PH} = 3.5$ Hz, PCH); 6.95 (s, 5H, Cp); 7.24–7.88 (m, 15H, aromatics). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 36.5 (vbr, $w_{1/2} > 2500$ Hz). IR (Nujol): 1547 cm^{-1} ($\nu_{C\overset{\cdots}{-}C} + \nu_{C\overset{\cdots}{-}O}$). Anal. calc. for $C_{25}H_{21}Cl_3NbOP$: C, 52.90; H, 3.72. Found: C, 53.21; H, 3.82%.

X-Ray quality single crystals were grown by slow diffusion of Et_2O into a toluene solution of **6a**.

$[(\eta\text{-}C_5H_5)\overline{TaCl_3\{PPh_2CH\overset{\cdots}{-}C(\overset{\cdots}{-}O}) Ph\}]$ 6b. Solid $[(\eta\text{-}C_5H_5)TaCl_4]$ (0.400 g, 1.03 mmol) and $Ph_2PCH_2C(O)Ph$ (0.313 g, 1.03 mmol) were placed in a Schlenk flask and CH_2Cl_2 (20 mL) was added at room temperature. The mixture was stirred for 3 h, during which its colour changed from yellow to orange. The volatiles were then removed under reduced pressure. The dark yellow residue was extracted with toluene (15 mL) at 60 °C. The resulting clear yellow solution was evaporated under reduced pressure affording **6b** as a yellow powder (0.563 g, yield 83%). ^1H NMR ($CDCl_3$, 300.18 MHz): δ 6.34 (d, 1H, $^2J_{PH} = 3.0$ Hz, PCH); 6.72 (s, 5H, Cp); 7.20–7.91 (m, 15H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 37.2. IR (Nujol): 1552 cm^{-1} ($\nu_{C\overset{\cdots}{-}C} + \nu_{C\overset{\cdots}{-}O}$). Anal. calc. for $C_{25}H_{21}Cl_3OPTa$: C, 45.79; H, 3.63. Found: C, 46.01; H, 3.46%.

X-Ray quality single crystals were grown by slow diffusion of petroleum ether (bp 40–60 °C) into a $CDCl_3$ solution of **6b**.

$[(\eta\text{-}C_5H_4{}^iPr)\overline{WCl_3\{PPh_2CH\overset{\cdots}{-}C(\overset{\cdots}{-}O})Ph\}]$ 6c. Solid $[(\eta\text{-}C_5H_4{}^iPr)WCl_4]$ (0.600 g, 1.38 mmol) and $Ph_2PCH_2C(O)Ph$ (0.420 g, 1.38 mmol) were placed in a Schlenk flask and toluene (15 mL) was added at room temperature. The mixture was stirred overnight, affording a claret solution. The volatiles were then removed under reduced pressure and the residue was washed with Et_2O (15mL) and pentane (2 × 10 mL). It afforded **6c** as a purple solid, which was dried *in vacuo* (0.786 g, yield 81%). IR: 1539 cm^{-1} (Nujol), 1542 cm^{-1} (KBr) ($\nu_{C\overset{\cdots}{-}C} + \nu_{C\overset{\cdots}{-}O}$). MS *m*/*z*: 701 ($M^+$, showing the expected isotopic pattern), 666 ($M^+ - Cl$). Anal. calc. for $C_{28}H_{27}Cl_3OPW$: C, 48.00; H, 3.88. Found: C, 47.83; H, 3.72%.

$[(\eta\text{-}C_5Me_5)\overline{TaCl_3\{PPh_2CH\overset{\cdots}{-}C(\overset{\cdots}{-}O})Ph\}]$ 6d. This complex was prepared in a similar manner to **6b** from $[(\eta\text{-}C_5Me_5)TaCl_4]$ (0.400 g, 0.873 mmol) and $Ph_2PCH_2C(O)Ph$ (0.266 g, 0.873 mmol). It was obtained as a yellow solid (0.544 g, yield 86%). ^1H NMR ($CDCl_3$, 300.18 MHz): δ 2.38 (s, 15H, Me); 6.08 (d, 1H, $^2J_{PH} = 3.6$ Hz, PCH); 6.90–7.90 (m, 15H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 36.5 (vbr, $w_{1/2} > 2500$ Hz). IR (Nujol): 1552 cm^{-1} ($\nu_{C\overset{\cdots}{-}C} + \nu_{C\overset{\cdots}{-}O}$). Anal. calc. for $C_{30}H_{31}Cl_3OPTa$: C, 49.64; H, 4.30. Found: C, 49.87; H, 4.18%.

X-Ray quality single crystals were grown by slow diffusion of Et_2O into a $CDCl_3$ solution of **6d**.

$[(\eta\text{-}C_5H_5)NbCl_4\{O{=}C(Me)NHPPh_2\}]$ 7a. This complex was prepared in a similar manner to **5a** from $[(\eta\text{-}C_5H_5)NbCl_4]$ (0.500 g, 1.67 mmol) and $Ph_2PNHC(O)Me$ (0.354 g, 1.67 mmol) in DME (20 mL). It was obtained as an orange-pink solid (0.751 g, yield 88%). ^1H NMR (CD_2Cl_2, 300.18 MHz): δ 2.16 (s, 3H, Me); 7.18 (s, 5H, Cp); 7.22–7.95 (m, 10H, aromatics); 9.64 (br s, 1H, NH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 33.1 ($w_{1/2} = 65$ Hz). IR (CH_2Cl_2): 1646 cm^{-1} ($\nu_{C=O}$). Anal. calc. for $C_{19}H_{19}Cl_4NNbOP$: C, 42.02; H, 3.53; N, 2.58. Found: C, 42.26; H, 3.81; N, 2.61%.

$[(\eta\text{-}C_5H_5)TaCl_4\{O{=}C(Me)NHPPh_2\}]$ 7b. This complex was prepared in a similar manner to **5b** from $[(\eta\text{-}C_5H_5)TaCl_4]$ (0.150 g, 0.38 mmol) and $Ph_2PNHC(O)Me$ (0.080 g, 0.38 mmol) in CH_2Cl_2 (10 mL). It was obtained as a yellow-brown solid (0.185 g, yield 80%). ^1H NMR ($CDCl_3$, 300.18 MHz): δ 2.61 (s, 3H, Me); 6.91 (s, 5H, Cp); 6.80–8.02 (m, 10H, aromatics); 8.85 (br s, 1H, NH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 40.6. IR ($CDCl_3$): 1646 cm^{-1} ($\nu_{C=O}$). Anal. calc. for $C_{19}H_{19}Cl_4NOPTa$: C, 36.16; H, 3.03; N, 2.22. Found: C, 36.28; H, 3.05; N, 2.26%.

$[(\eta\text{-}C_5H_4{}^iPr)WCl_4\{O{=}C(Me)NHPPh_2\}]$ 7c. This complex was prepared in a similar manner to **5c** from $[(\eta\text{-}C_5H_4{}^iPr)WCl_4]$ (1.000 g, 2.30 mmol) and $Ph_2PNHC(O)Me$ (0.490 g, 2.30 mmol) in a 1:1 CH_2Cl_2–toluene mixture (30 mL). It was obtained as a green-brown solid (1.212 g, yield 81%). IR (Nujol): 1651 cm^{-1} ($\nu_{C=O}$). MS m/z: 641 ($M^+ - Cl$, showing the expected isotopic pattern), 606 ($M^+ - 2Cl$). Anal. calc. for $C_{22}H_{25}Cl_4NOPW$: C, 39.08; H, 3.73; N, 2.07. Found: C, 38.70; H, 3.78; N, 2.03%.

Crystallography

Data were collected on an Enraf-Nonius DIP2000 Image Plate diffractometer (**6a**) and on an Enraf-Nonius KappaCCD diffractometer (**6b**,**d**) (graphite-monochromated MoK_α radiation $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package[90] running on a Silicon Graphics Indy computer. The structures were solved using the direct-methods program SIR-92.[91] Subsequent full-matrix least-squares refinements were carried out using the SHELXL-93[92] (**6a**) or the CRYSTALS[93] programs. The structure of **6b** consists of two "pseudo-dimers" representing two slightly different mononuclear complexes, referred to as molecules 1 and 2 in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Selected crystal data and refinement details are given in Table 1.

CCDC reference numbers 190864–190866.

See http://www.rsc.org/suppdata/nj/b2/b202983a/ for crystallographic data in CIF or other electronic format.

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References

1 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27 and references cited therein.
2 E. Lindner, S. Pautz and M. Haustein, *Coord. Chem. Rev.*, 1996, **155**, 145.
3 C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233 and references cited therein.
4 P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680.
5 R. W. Wegman, A. G. Abatjoglou and A. M. Harrison, *J. Chem. Soc., Chem. Commun.*, 1987, 1891.
6 G. J. P. Britovsek, W. Keim, S. Mecking, D. Sainz and T. Wagner, *J. Chem. Soc., Chem. Commun.*, 1993, 1632.
7 E. Lindner, Q. Wang, H. A. Mayer, A. Bader, H. Kühbauch and P. Wegner, *Organometallics*, 1993, **12**, 3291.
8 M. Alvarez, N. Lugan and R. Mathieu, *J. Organomet. Chem.*, 1994, **468**, 249.
9 C. Abu-Gnim and I. Amer, *J. Chem. Soc., Chem. Commun.*, 1994, 115.
10 H. Yang, M. Alvarez, N. Lugan and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 1995, 1721.
11 G. J. P. Britovsek, K. J. Cavell and W. Keim, *J. Mol. Catal.*, 1996, **110**, 77.
12 S. Mecking and W. Keim, *Organometallics*, 1996, **15**, 2650.
13 H. Yang, M. Alvarez-Gressier, N. Lugan and R. Mathieu, *Organometallics*, 1997, **16**, 1401.
14 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**.
15 J. I. Dulebohn, S. C. Haefner, K. A. Berglund and K. R. Dunbar, *Chem. Mater.*, 1992, **4**, 506.
16 K. R. Dunbar, *Comments Inorg. Chem.*, 1992, **13**, 313.
17 H. Werner, M. Schulz and B. Windmüller, *Organometallics*, 1995, **14**, 3659.
18 E. Lindner, B. Keppleler, H. A. Mayer, K. Gierling, R. Fawzi and M. Steinmann, *J. Organomet. Chem.*, 1996, **526**, 175.
19 H. Werner, J. Bank, B. Windmüller, O. Gevert and W. Wolfsberger, *Helv. Chim. Acta*, 2001, **84**, 3163.
20 J.-M. Camus, D. Morales, J. Andrieu, P. Richard, R. Poli, P. Braunstein and F. Naud, *J. Chem. Soc., Dalton Trans.*, 2000, 2577.
21 C. D. Andrews, A. D. Burrows, J. M. Lynam, M. F. Mahon and M. T. Palmer, *New J. Chem.*, 2001, **25**, 824.
22 N. G. Jones, M. L. H. Green, I. Vei, X. Morise and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, 2002, 1487.
23 N. G. Jones, M. L. H. Green, I. C. Vei, L. H. Rees, S. I. Pascu, D. Watkin, A. Cowley, X. Morise and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, 2002, in the press.
24 J. A. Canich, F. A. Cotton and S. A. Duraj, *Inorg. Chim. Acta*, 1989, **41**, 156.
25 S. Gambarotta, M. Pasquali, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1981, **20**, 1173.
26 F. E. Kuhn, A. D. Lopes, A. M. Santos, E. Herdtweck, J. J. Haider, C. C. Romao and A. G. Santos, *J. Mol. Catal. A: Chem.*, 2000, **151**, 147.
27 D. J. McCabe, E. N. Duesler and R. T. Paine, *Inorg. Chem.*, 1987, **26**, 2300.
28 V. S. Sergienko, N. A. Ovchinnikova, M. A. Porai-Koshits and M. A. Glushkova, *Koord. Khim.*, 1986, **12**, 1650.
29 D. G. L. Holt, L. F. Larkworthy, D. C. Povey, G. W. Smith and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1990, 3229.
30 F. A. Cotton and G. W. Rice, *Inorg. Chem.*, 1978, **17**, 2004.
31 P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 3675.
32 L. R. Falvello, M. M. Garcia, I. Lazaro, R. Navarro and E. P. Urriolabeitia, *New J. Chem.*, 1999, 227.
33 R. Navarro and E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.*, 1999, 4111.
34 W. Keim, A. Behr, B. Gruber, B. Hoffmann, F. H. Kowaldt, U. Kürschner, B. Limbäcker and F. P. Sistig, *Organometallics*, 1986, **5**, 2356 and references cited therein.
35 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.
36 F. Balegroune, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1988, **27**, 3320.
37 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1988, **27**, 2279.
38 P. Braunstein, D. Matt, D. Nobel, F. Balegroune, S.-E. Bouaoud, D. Grandjean and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1988, 353.
39 P. Braunstein, T. M. Gomes-Carneiro, D. Matt, F. Balegroune and D. Grandjean, *Organometallics*, 1989, **8**, 1737.
40 W. Keim, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235.
41 P. Berno, P. Braunstein, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1991, **30**, 1407.
42 J. Andrieu, P. Braunstein and A. D. Burrows, *J. Chem. Res. (S)*, 1993, 380.
43 P. Braunstein, S. Coco-Cea, M. I. Bruce, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1992, 2539.
44 P. Braunstein, S. Coco-Cea, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1992, **423**, C38.
45 P. Braunstein, L. Douce, F. Balegroune, D. Grandjean, D. Bayeul, Y. Dusausoy and P. Zanello, *New J. Chem.*, 1992, **16**, 925.
46 P. Braunstein, D. J. Kelly, A. Tiripicchio and F. Ugozzoli, *Inorg. Chem.*, 1993, **32**, 4845.
47 P. Braunstein, Y. Chauvin, J. Nähring, Y. Dusausoy, D. Bayeul, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc., Dalton Trans.*, 1995, 851.
48 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1995, 863.
49 P. Braunstein, Y. Chauvin, J. Fischer, H. Olivier, C. Strohmann and D. V. Toronto, *New J. Chem.*, 2000, **24**, 437.
50 P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1994, 2203.
51 J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.*, 1998, **22**, 467.
52 K. A. O. Starzewski and J. Witte, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 63.
53 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 299.

54 J. Bank, P. Steinert, P. Windmüller, W. Wolfsberger and H. Werner, *J. Chem. Soc., Dalton Trans.*, 1996, 1153.

55 P. Crochet and B. Demerseman, *Organometallics*, 1995, **14**, 2173.

56 J. Vicente, M.-T. Chicote, M. A. Beswick and M. C. Ramirez-de-Arellano, *Inorg. Chem.*, 1996, **35**, 6592.

57 P. Crochet, B. Demerseman, M. I. Vallejo, M. P. Gamasa, J. Gimeno, J. Borge and S. Garcia-Granda, *Organometallics*, 1997, **16**, 5406.

58 L. R. Falvello, S. Fernandez, R. Navarro, I. Pascual and E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.*, 1997, 763.

59 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio and F. Ugozzoli, *Organometallics*, 1996, **15**, 5551.

60 D. A. Edwards, M. F. Mahon and T. J. Paget, *Polyhedron*, 2000, **19**, 757.

61 C. Mattheis, P. Braunstein and A. Fischer, *J. Chem. Soc., Dalton Trans.*, 2001, 800.

62 P. Veya, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1991, **10**, 2991.

63 P. Veya, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1994, **13**, 208.

64 K. Mashima, Y. Nakayama and A. Nakamura, *Adv. Polym. Sci.*, 1997, **133**, 1.

65 A. Togni and R. L. Halterman, *Metallocenes, Synthesis, Reactivity, Application*, vol. 1 and 2, Wiley-VCH, Weinheim, Germany, 1998.

66 J. M. Decker, S. J. Geib and T. Y. Meyer, *Organometallics*, 1999, **18**, 4417.

67 K. Mashima, Y. Matsuo, S. Nakamura and K. Tani, *J. Organomet. Chem.*, 2000, **593–594**, 69.

68 K. Mashima, Y. Matsuo and K. Tani, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 960.and references cited therein.

69 M. L. H. Green, P. C. McGowan and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1995, 1207.

70 M. L. H. Green and P. Mountford, *Chem. Rev.*, 1994, **94**, 29.

71 R. Poli, *Chem. Rev.*, 1991, **91**, 509 and references cited therein.

72 R. J. Burt and J. G. Leigh, *J. Organomet. Chem.*, 1978, **148**, C19.

73 R. J. Burt, J. G. Leigh and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1981, 793.

74 R. D. Sanner, S. T. Caster and W. J. Bruton, *J. Organomet. Chem.*, 1982, **240**, 157.

75 M. J. Bunker, A. DeCian, M. L. H. Green, J. J. E. Moreau and N. Siganporia, *J. Chem. Soc., Dalton Trans.*, 1980, 2155.

76 J. C. Fettinger, D. W. Keogh and R. Poli, *Inorg. Chem.*, 1995, **34**, 2343.

77 X. Morise, M. L. H. Green, P. C. McGowan and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1994, 871.

78 M. L. H. Green, X. Morise, A. H. Hamilton and A. N. Chernaga, *J. Organomet. Chem.*, 1995, **488**, 73.

79 P. Braunstein, C. Frison, X. Morise and R. D. Adams, *J. Chem. Soc., Dalton Trans.*, 2000, 2205.

80 P. Braunstein, D. J. Kelly, A. Tiripicchio and F. Ugozzoli, *Bull. Soc. Chim. Fr.*, 1995, **132**, 1083.

81 P. Braunstein, B. H. Heaton, C. Jacob, L. Manzi and X. Morise, to be published.

82 P. Kubácek, R. Hoffmann and Z. Havlas, *Organometallics*, 1982, **1**, 180.

83 R. Fandos, M. Gómez, P. Royo, S. Garcia-Blanco, S. Martinez-Carrera and J. Sanz-Aparicio, *Organometallics*, 1987, **6**, 1581.

84 M. V. Galakhov, M. Gómez, G. Jiménez, P. Royo, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, 1994, **14**, 1901.

85 J. Arnold, T. D. Tilley, A. L. Rheingold and S. J. Geib, *J. Chem. Soc., Chem. Commun.*, 1987, 793.

86 G. A. A. Hadi, K. Fromm, S. Blaurock, S. Jelonek and E. Hey-Hawkins, *Polyhedron*, 1997, **16**, 721.

87 V. Gibson, T. P. Kee, R. M. Sorrell, A. P. Bashell and M. McPartlin, *Polyhedron*, 1988, **7**, 2221.

88 W. A. Herrmann, W. Kalcher, H. Biersack, I. Bernal and M. Creswick, *Chem. Ber.*, 1981, **114**, 3558.

89 M. L. H. Green, J. D. Hubert and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3793.

90 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, in *Methods Enzymol.*, eds. C. W. Carter and R. M. Sweet, Academic Press, 1997, vol. 276, p. 357.

91 A Program Solution of Crystal Structure by Direct Methods: A. Almatore, G. Cascarano, C. Giavocazzo and A. Guargliardi, *J. Appl. Crystallogr.*, 1994, **27**, 435.

92 G. M. Sheldrick, SHELXL93, Program for Crystal Structure Refinement, 1993, Intitüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany.

93 D. J. Watkin, K. C. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, CRYSTALS issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.