Bidentate metalloligands containing the phosphinocyclopentadienyl ligand. New heterobimetallic complexes and crystal structure of $(C_5Me_5)(C_5H_4PPh_2)Ta(CO)(\mu\text{-}PPh_2)Cr(CO)_4$

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Four new kinds of metalloligands $Cp^*(C_5H_4PPh_2)TaL_n$ [L_n = (H)$_3$, (H)(CO), (H)$_2$(PPh$_2$), (CO)(PPh$_2$)] **2**, **3**, **4b**, **5b** containing the diphenylphosphinocyclopentadienyl ligand have been prepared and characterized. The trihydride complex **2** was obtained by reduction of the dichloride compound $Cp^*(C_5H_4PPh_2)TaCl_2$ **1**. Treatment of **2** under a CO atmosphere at 140 °C in decane affords the monohydride complex **3**. Compounds **2** and **3** easily react with chlorophosphines leading to phosphido derivatives **4b** and **5b** respectively. All these metalloligands act as monodentate and/or chelating bidentate ligands. Their reactivity toward unsaturated organometallic fragments [M'(CO)$_5$] or [M'(CO)$_4$] (M' = Cr, W) has been studied. The X-ray crystal structure of $Cp^*(C_5H_4PPh_2)Ta(CO)(\mu\text{-}PPh_2)Cr(CO)_4$ **10Cr** is reported.

The study of heterobimetallic complexes is of great interest in the main fields of the application of organometallic chemistry, namely catalysis.[1] Part of the increasing interest in this research is the hope that such heterobimetallic structures might exhibit unusual catalytic activity due to a cooperative reactivity between electron-deficient and electron-rich metals.[2]

Bridging ligands have been widely developed to maintain the two metal sites in a close proximity and to prevent breaking of the bimetallic framework. Among these linking ligands, the heterodifunctional diphenylphosphinocyclopentadienyl has received significant attention in the last few years and numerous examples of its ability to join two different metallic centers have been reported.[3]

In the course of our work on binuclear complexes, we have already reported various hydrido and/or phosphido bridged systems. A series of bimetallic polyhydrides[4] and of μ-hydrido μ-phosphido cyclic structures[5] has been obtained which prove hydrido and phosphido bridges to be efficient in tying two metal centers.

In this paper, we report on the combination of the coordinating ability of a diphenylphosphinocyclopentadienyl ligand and that of a terminal phosphido or a hydrido functionality in the synthesis of new bimetallic tantalum–chromium and tantalum–tungsten complexes. The synthesis of the bidentate metalloligands proceeds in two main steps: firstly the diphenylphosphinocyclopentadienyl ligand is involved in the preparation of a Cp-phosphino functionalised tantalocene dichloride. Then, the hydrido or phosphino coordination site is introduced on the tantalum center by chemical transformations. The X-ray crystal structure of a tantalum–chromium compound is reported.

Results and discussion

The synthesis of complex **1** $Cp^*(C_5H_4PPh_2)TaCl_2$ is adapted from Bercaw's method[6] as outlined in Scheme 1.

Complex **1** is isolated in good yield (95%) as a green solid soluble in halogenated solvents. It displays the eight-line ESR
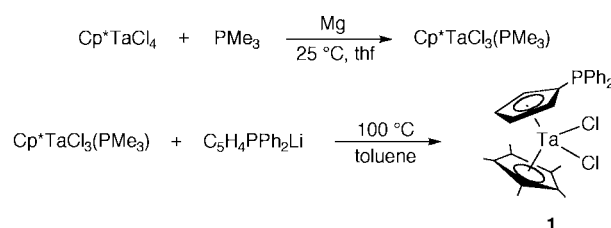
Scheme 1

spectrum characteristic of bis(cyclopentadienyl) tantalum(IV) derivatives.[7] Treatment of **1** with NaAl(H)$_2$(OCH$_2$CH$_2$OMe)$_2$ in toluene over a period of three hours affords a red solution which, on hydrolysis, gives the trihydride metallocene **2**. Heating of **2** in decane under an atmosphere of carbon monoxide leads to the purple carbonyl derivative **3** (Scheme 2).
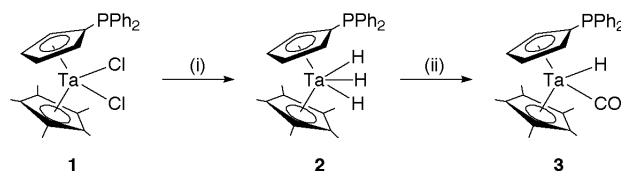

Scheme 2 (i) NaAl(H)$_2$(OCH$_2$CH$_2$OMe)$_2$, toluene; (ii) CO, decane, 130 °C.

The ^{1}H NMR spectrum of **2** exhibits, in the region of the metal hydrides, a doublet of triplets and a doublet of doublets [J(H–H) = 11.2 Hz, J(P–H) = 1.9 Hz; J(H–H) = 11.2 Hz, J(P–H) = 5.9 Hz] corresponding to the central and lateral hydrides respectively. Noteworthy for the monohydride complex **3** is the doublet resonance at δ −5.9 [J(P–H) = 5.8 Hz] as well as the ν_{CO} absorption at 1882 cm^{-1}.

The reaction of the trihydride **2** with PPh$_2$Cl in toluene results in the rapid insertion of the chlorophosphine into the central Ta–H bond affording quantitatively the ionic com-

plex $[Cp^*(C_5H_4PPh_2)Ta(H)_2(PPh_2H)]^+Cl^-$ **4a** as depicted in Scheme 3.[5,8] Complex **4a** is very sparingly soluble in hydro-
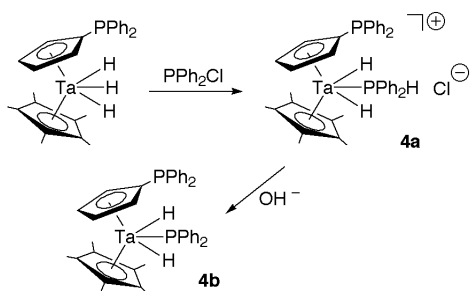
Scheme 3

carbon and aromatic solvents. However, it is sufficiently soluble in acetone to allow NMR spectra to be recorded. The ^{1}H NMR spectrum exhibits a unique resonance for the two Ta–H protons (doublet of doublets of doublets) indicative of the central position of the PPh$_2$H group. The hydrogen signal of the P–H bond is displayed as a doublet of triplets at δ 7.8 [J(H–H) = 4.9 Hz, J(P–H) = 393 Hz]. Notably, no exchange process with the phosphorus of the cyclopentadienyl ring is detected. This trend confirms previous observations on the enhanced basicity of a metal-bonded phosphido group with respect to a classical organic phosphine.[9] The salt **4a** is quantitatively deprotonated by sodium hydroxide leading to the corresponding dihydride phosphido complex $Cp^*(C_5H_4PPh_2)Ta(H)_2(PPh_2)$ **4b**. The formation of the phosphido derivative **4b** rather than the phosphino one suggests that the P–H bond is a more acidic site than the Ta–H bond.

According to a procedure previously described, the carbonyl monohydride $Cp^*(C_5H_4PPh_2)TaH(CO)$ **3** quickly reacts with chlorodiphenylphosphine.[10] In a first step, the metallophosphonium salt $[Cp^*(C_5H_4PPh_2)Ta(CO)(PPh_2H)]^+Cl^-$ **5a** is formed, probably by a nucleophilic substitution at the phosphorus atom followed by H$^+$ transfer onto the basic phosphorus center; deprotonation of this salt is achieved by hydroxide anion and leads to the corresponding neutral phosphido derivative $Cp^*(C_5H_4PPh_2)Ta(CO)(PPh_2)$ **5b** (Scheme 4).
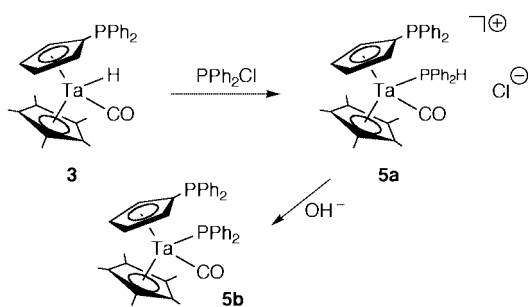
Scheme 4

The four previous kinds of metalloligand derivatives (**2**, **3**, **4b**, **5b**) are able to act as monodentate and/or chelating bidentate ligands. The trihydride complex $Cp^*(C_5H_4PPh_2)Ta(H)_3$ **2** may bond to other metal fragments in different ways, through phosphorus or through both hydrogen and phosphorus. In order to check its coordinating abilities, complex **2** was reacted with the tungsten pentacarbonyl fragment [W(CO)$_5$]. The reaction proceeds at room temperature over a period of 20 min, affording $Cp^*(C_5H_4PPh_2)Ta(H)_3W(CO)_5$ **6** (Scheme 5). The structure of this complex was determined by a combination of elemental analysis, IR and NMR spectral data. The ^{31}P NMR spectrum shows a deshielded resonance [δ = 16.1; J(W–P) = 256 Hz] with respect to that observed for the starting

material **2** indicating the presence of a tungsten coordinated phosphorus. The IR spectrum in thf solution shows the expected three ν_{CO} bands for the monosubstituted octahedral W(CO)$_5$ moiety.

When exposed to $M'(CO)_4L_2$ fragments ($M' = Cr, L_2 = nbd$; $M' = W, L = MeCN$), the trihydride complex **2** behaves as a bidentate ligand through the hydrogen and phosphorus atoms, leading to the substitution of L$_2$ ligands with formation of cyclic compounds $Cp^*(C_5H_4PPh_2)Ta(H)_2(\mu-H)M'(CO)_4$ **7**(Cr,W). Very characteristic of these structures is the bridging central hydride resonance which exhibits a high-field signal.[5] As for complex **6**, the deshielded ^{31}P resonance is indicative of the coordinated phosphorus. The IR spectra of **7**(Cr,W) show the typical four band pattern of the cis-$M'(CO)_4$ fragments.
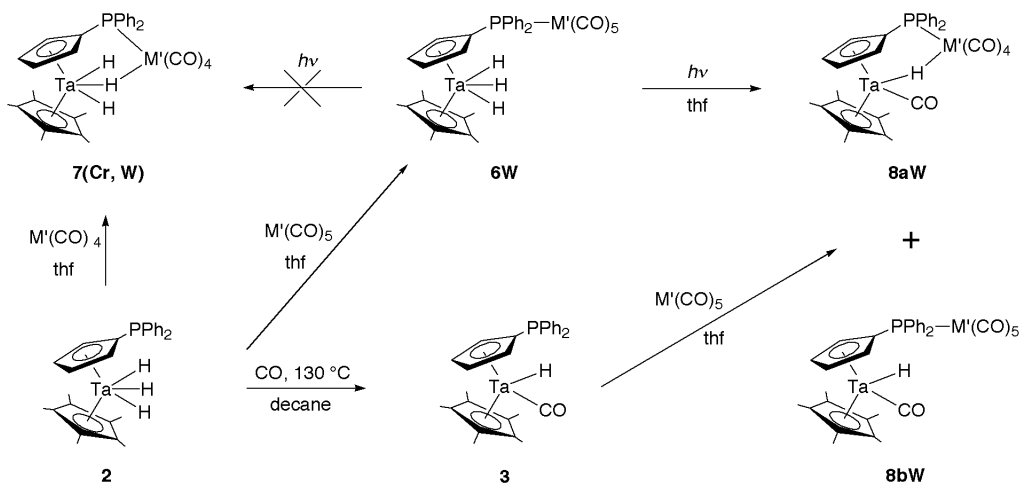
A photochemical process was carried out in order to convert complex **6W** to the cyclic compound **7W**. Surprisingly this attempt did not lead to the expected complex since the reaction product is the tantalum(III) derivative Cp^*-$(C_5H_4PPh_2)Ta(CO)(\mu-H)W(CO)_4$ **8aW** which results from the migration of a carbon monoxide fragment to the Ta center. The structure of this complex is proposed on the basis of IR, ^{1}H and ^{31}P NMR data. The ^{1}H NMR spectrum of **8aW** shows a unique shielded hydride resonance at δ −15.0 [J(H–W) = 40 Hz] characteristic of a hydrido bridge. The tungsten coordinated phosphorus is evidenced by the ^{31}P NMR singlet resonance at δ 8.2 [J(P–W) = 226 Hz]. The IR spectrum of **8aW** exhibits five CO absorptions: four attributed to the cis disubstituted [W(CO)$_4$] fragment and one for the tantalum coordinated carbonyl.

In a similar way, the reactivity of **3** was investigated. When opposed to [W(CO)$_5$], the monohydride **3** leads to a mixture of the phosphido linked complex **8bW** and the cyclic structure **8aW**. The formation of the hydrido bridge in **8aW** results from an easy loss of one CO ligand at the tungsten site.
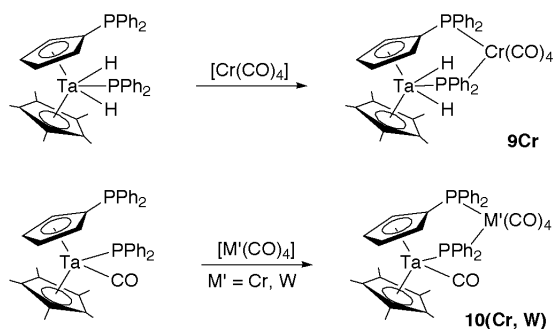
Unfortunately, complexes **8aW** and **8bW** are not separable from their mixture either by crystallisation or by column chromatography. However, when monohydride **3** is reacted with the [W(CO)$_4$] moiety, the cyclic structure **8aW** is obtained as the sole product.

The metalloligands **4b** and **5b** combine the coordinating abilities of a metallophosphine with those of an organic phosphine. Toward [$M'(CO)_4$] moieties, they behave as chelating ligands affording two types of Ta(V) **9Cr** or Ta(III) **10**(Cr,W) heterobimetallic systems (Scheme 6).

The formation of of **9Cr** and **10**(Cr,W) is ascertained by the noticeable deshielding found for the ^{31}P resonances with respect to that observed in the parent metallodiphosphines. Furthermore, in the two chromium derivatives **9Cr** and **10Cr**, the low field signals fall in the same range (δ 59.7 and 65.5 respectively) and therefore can be attributed to the phosphorus nuclei of the CpPPh$_2$ ligand. In **9Cr** and **10W**, the weak J(P–P) value (10 Hz) is indicative of a cis configuration for the two phosphorus nuclei.[11] As expected, the two ^{31}P resonances of **10W** are surrounded by the [183]W satellites [J(P–W) = 249 Hz and J(P–W) = 151 Hz]. No coupling effect between the two phosphorus atoms is detected in **10Cr**. The crystal structure of the bimetallic complex **10Cr** is shown in Fig. 1. The compound crystallized with two chloroform solvate molecules. Selected bond lengths and bond angles are reported in Table 1. The structure consists of two fragments: a tantalocene moiety linked to a chromium-carbonyl unit by two phosphorus atoms leading to a five membered chelate ring. The same structural features were reported for the Re, Rh diphosphido bridged complex $(PPh_3)(C_5H_4PPh_2)Re(NO)(\mu-PPh_2)Rh(nbd)$.[12] In both cases the five membered ring adopts a similar distorted "envelope" conformation[13] the tantalum atom and the $ipso$-cyclopentadienyl carbon C(1) lying 0.207 Å and 0.664 Å below the P(1)–Cr–P(2) plane. The structural parameters of the tantalocene moiety are similar to those reported for several
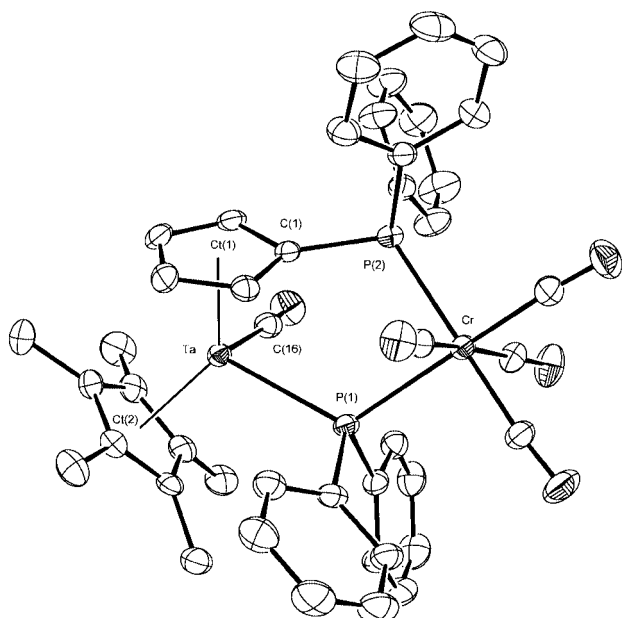
Scheme 5

Scheme 6

Cr–C(17)	1.843(4)	Ta–Ct(1)	2.06
Cr–C(18)	1.887(4)	Ta–Ct(2)	2.10
Cr–C(19)	1.838(5)	Ta–C(16)	2.025(4)
Cr–C(20)	1.885(5)	Ta–P(1)	2.6695(11)
Cr–P(2)	2.3671(12)	P(2)–C(1)	1.807(4)
Cr–P(1)	2.5288(14)		
C(16)–Ta–P(1)	90.65(12)	C(18)–Cr–P(1)	87.92(12)
Ct(1)–Ta–Ct(2)	135.1	C(18)–Cr–P(2)	88.00(13)
Ct(1)–Ta–C(16)	103.1	C(18)–Cr–C(19)	88.5(2)
Ct(2)–Ta–C(16)	101.5	C(18)–Cr–C(20)	172.2(2)
Ct(1)–Ta–P(1)	104.4	C(19)–Cr–P(1)	176.1(2)
Ct(2)–Ta–P(1)	112.4	C(19)–Cr–P(2)	93.51(14)
P(1)–Cr–P(2)	87.95(4)	C(19)–Cr–C(20)	87.4(2)
C(17)–Cr–P(1)	92.79(14)	C(20)–Cr–P(1)	95.97(14)
C(17)–Cr–P(2)	177.87(14)	C(20)–Cr–P(2)	98.82(14)
C(17)–Cr–C(18)	90.0(2)	Cr(1)–P(1)–Ta	119.68(4)
C(17)–Cr–C(19)	85.6(2)	C(1)–P(2)–Cr	113.13(12)
C(17)–Cr–C(20)	83.1(2)		

length is 2.367(1) Å and compares to those usually observed for PCr(CO)$_n$ groups.[15] In contrast, the P(1)–Cr distance is remarkably long: 2.5288(14) Å. This distance is close to the sum of the covalent radii of Cr (1.48 Å)[16] and P (1.10 Å).[17] Such long distances (>2.50 Å) have already been reported for some crystal structures involving a M–P–Cr(CO)$_n$ bridge.[18]

Experimental

General

Nuclear magnetic resonance spectra were recorded on a Bruker AC 200 instrument at 200 MHz for ^{1}H and 81 MHz for ^{31}P. The chemical shifts are reported in ppm relative to SiMe$_4$ (^{1}H) and external H$_3$PO$_4$ (^{31}P-{^{1}H}). Infrared spectra were obtained with a Nicolet 250 spectrometer, with the sample in a solution of thf. Elemental analyses were performed on an EA 1108 CHNS-O FISONS Instruments apparatus.

All reactions were carried out under an atmosphere of argon using standard Schlenk line techniques and conventional glass vessels. The solvents were dried over suitable reagents and freshly distilled under argon before use. Li(C$_5$H$_4$PPh$_2$),[19] Cp*TaCl$_4$,[6] Cr(CO)$_4$(nbd),[20] W(CO)$_4$(MeCN)$_2$[21] and M′(CO)$_5$-(thf)[22] (M′ = Cr, W) were prepared according to literature methods.

Syntheses

Cp*(C$_5$H$_4$PPh$_2$)TaCl$_2$ 1. Compound **1** was synthesized according to Bercaw's method reported for Cp*CpTaCl$_2$[6] with minor modifications. 4.58 g (10 mmol) of Cp*TaCl$_4$ was

Fig. 1 ORTEP[24] view of Cp*(C$_5$H$_4$$\overline{PPh_2)Ta(CO)(\mu\text{-}PPh_2)}$Cr(CO)$_4$ **10Cr**. The chloroform solvate molecules are omitted for clarity.

monophosphido bridged derivatives, i.e. Cp′CpTa(CO)(μ-PMe$_2$)W(CO)$_4$L (L = (o-anisyl)methylphenylphosphine), Cp$_2$-Ta(CO)(μ,η^1:η^1-PMe$_2$S)W(CO)$_5$ and Cp*CpTa(CO)(μ-PPh-OMe)Cr(CO)$_5$.[14] The main differences observed between the mono bridged complex Cp*CpTa(CO)(μ-PPhOMe)Cr(CO)$_5$ and **10Cr** result from the cyclic nature of the bridge in **10Cr**, thus the Ta–P(1)–Cr angle is smaller in **10Cr** than in the mono bridged compound (119.68(4)° vs. 127.1(1)°) leading to a smaller Ta···Cr distance in **10Cr** than in the mono bridged complex (4.495 Å for **10Cr** vs. 4.646 Å). The P(2)–Cr bond

reduced with 0.5 equiv. of Mg in thf in the presence of 1 equiv. of PMe$_3$. Removal of the solvent afforded a red residue. This crude product was treated with 2.49 g (10 mmol) Li(C$_5$H$_4$PPh$_2$) in toluene at 100 °C. After 12 h of stirring, extraction and crystallization in acetone afforded 6.04 g (95%) of the green paramagnetic product **1** (Found: C, 50.69; H, 4.52. C$_{27}$H$_{29}$-Cl$_2$PTa requires C, 50.96; H, 4.59%). The ESR spectrum in toluene showed an eight-line spectrum: g_{iso} = 1.9306; $A_{Ta, iso}$ = 122.18 G.

Cp*(C$_5$H$_4$PPh$_2$)Ta(H)$_3$ 2. 3.18 g of **1** (5 mmol) was reduced by 5 cm^3 of NaAlH$_2$(OCH$_2$CH$_2$OMe)$_2$ (2 M in toluene, 10 mmol) in 50 cm^3 of toluene at 0 °C. After 3 h of stirring, the brown-red solution was hydrolyzed slowly by 10 cm^3 of degassed water. The organic layer was decanted and extracted. Evaporation of the solvent, followed by washing with pentane gave 1.48 g (52%) of complex **2** (Found: C, 56.86; H, 5.71. C$_{27}$H$_{32}$PTa requires C, 57.05; H, 5.67%). NMR (CD$_3$COCD$_3$): ^{1}H, δ 7.47–7.15 (m, Ph), 5.19 (t, J = 2.4 Hz, C$_5$H$_4$), 4.56 (q, J = 2.4 Hz [J_{H-H} = J_{P-H}], C$_5$H$_4$), 1.99 (s, Me), −0.54 (dt, J = 1.9, 11.2 Hz, H), −1.77 (dd, J = 5.9, 11.2 Hz, H); ^{31}P-{^{1}H}, δ −11.4 (s).

Cp*(C$_5$H$_4$PPh$_2$)Ta(H)(CO) 3. 2 g of **2** was stirred in 30 cm^3 of decane at 140 °C under a carbon monoxide atmosphere for 3 h. The solvent was then removed under reduced pressure and the residue was dried *in vacuo*. Crystallization from pentane yielded 1.25 g (60%) of the green compound **3** (Found: C, 56.27; H, 5.02. C$_{28}$H$_{30}$POTa requires C, 56.57; H, 5.09%). FT IR (thf, cm^{-1}): 1882s (ν_{CO}). NMR (CD$_3$COCD$_3$): ^{1}H, δ 7.63–7.19 (m, Ph), 5.25 (m, C$_5$H$_4$), 4.80 (m, C$_5$H$_4$), 4.20 (m, C$_5$H$_4$), 4.00 (m, C$_5$H$_4$), 1.88 (s, Me), −5.94 (d, J = 5.8 Hz, H); ^{31}P-{^{1}H}, δ −12.5 (s).

[Cp*(C$_5$H$_4$PPh$_2$)Ta(H)$_2$(PPh$_2$H)]$^+$Cl$^-$ 4a. To a toluene solution (30 cm^3) of **2** (1 g, 1.76 mmol) was added PPh$_2$Cl (0.39 g, 1.76 mmol). A precipitate was immediately formed. After 30 min of stirring, it was filtered off, washed with pentane, and dried under vacuum affording 0.83 g (80%) of a white powder (Found: C, 58.96; H, 5.58. C$_{39}$H$_{42}$P$_2$ClTa requires C, 59.36; H, 5.36%). NMR (CD$_3$COCD$_3$): ^{1}H, δ 8.24–7.11 (m, Ph), 7.85 (td, J = 4.9, 393 Hz, PPh$_2$H), 5.90 (m, C$_5$H$_4$), 4.67 (m, C$_5$H$_4$), 2.04 (s, Me), 0.30 (ddd, J = 5.1, 5.9 Hz, J = 72 Hz, Ta–H); ^{31}P-{^{1}H}, δ 2.2 (s), −16.2 (s).

Cp*(C$_5$H$_4$PPh$_2$)Ta(H)$_2$(PPh$_2$) 4b. A saturated aqueous solution of KOH (10 cm^3) was added to the dried salt [Cp*(C$_5$H$_4$PPh$_2$)Ta(H)$_2$(PPh$_2$H)]$^+$Cl$^-$ **4a** (1 g, 1.27 mmol). The mixture was stirred for 30 min. The product was extracted with 2 × 15 cm^3 of toluene, and the organic layer was separated and evaporated giving 0.57 g (60%) of the white product **4b** (Found: C, 61.98; H, 5.22. C$_{39}$H$_{41}$P$_2$Ta requires C, 62.24; H, 5.49%). NMR (CD$_3$COCD$_3$): ^{1}H, δ 7.63–6.86 (m, Ph), 5.33 (t, J = 2.46 Hz, C$_5$H$_4$), 4.51 (m, C$_5$H$_4$), 1.89 (s, Me), 0.63 (dd, J = 5.9, 61 Hz, Ta–H); ^{31}P-{^{1}H}, δ −12.0 (s), −16.4 (s).

[Cp*(C$_5$H$_4$PPh$_2$)Ta(CO)(PPh$_2$H)]$^+$Cl$^-$ 5a. To a toluene solution (30 cm^3) of **3** (1 g, 1.68 mmol) was added 1 equiv. of PPh$_2$Cl. The white precipitate was filtered, washed with toluene (10 cm^3) and pentane (2 × 10 cm^3), and dried *in vacuo* to yield 1.16 g (85%) of **5a** (Found: C, 59.13; H, 4.64. C$_{40}$H$_{40}$P$_2$OClTa requires C, 58.94; H, 4.95%). FT IR (thf, cm^{-1}): 1894 s (ν_{CO}). NMR (CD$_3$COCD$_3$): ^{1}H, δ 8.22–7.05 (m, Ph), 7.77 (d, J = 378 Hz, PPh$_2$H), 6.48 (m, C$_5$H$_4$), 5.28 (m, C$_5$H$_4$), 4.99 (m, C$_5$H$_4$), 3.24 (m, C$_5$H$_4$), 1.9s (s, Me); ^{31}P-{^{1}H}, δ 11.2 (s), −13.4 (s).

Cp*(C$_5$H$_4$PPh$_2$)Ta(CO)(PPh$_2$) 5b. To the dried salt **5a** (1 g, 1.23 mmol) was added a saturated aqueous solution of KOH (10 cm^3) followed by 15 cm^3 of toluene. The green organic layer was separated and the aqueous layer was extracted with 15 cm^3

of toluene. The solvent was removed and the green product was dried *in vacuo* to yield 0.62 g of **5b** (65%) (Found: C, 61.47; H, 5.12. C$_{40}$H$_{39}$P$_2$OTa requires C, 61.70; H, 5.05%). FT IR (thf, cm^{-1}): 1910s (ν_{CO}). NMR (CD$_3$COCD$_3$): ^{1}H, δ 8.20–8.05 (m, Ph), 7.56–6.77 (m, Ph), 5.35 (m, C$_5$H$_4$), 5.23 (m, C$_5$H$_4$), 4.21 (m, C$_5$H$_4$), 2.91 (m, C$_5$H$_4$), 1.87 (s, Me); ^{31}P-{^{1}H}, δ −5.6 (s), −12.3 (s).

Cp*(C$_5$H$_4$P̄Ph$_2$)Ta(H)$_3$W̄(CO)$_5$ 6. To a thf solution (20 cm^3) of Cp*(C$_5$H$_4$PPh$_2$)Ta(H)$_3$ **2** (0.57 g, 1 mmol) was added an excess (20%) of W(CO)$_5$(thf). The mixture was stirred for 20 min at room temperature (the reaction was monitored by IR spectroscopy). The solvent was removed under vacuum, and the crude reaction product was crystallized from acetone affording 0.66 g (75%) of **6** (Found: C, 43.11; H, 3.66. C$_{32}$H$_{32}$O$_5$PTaW requires C, 43.07; H, 3.61%). FT IR (thf, cm^{-1}): 2070m, 1940vs, 1895s (ν_{CO}). NMR (CD$_3$COCD$_3$): ^{1}H, δ 8.00–7.28 (m, Ph), 5.23 (m, C$_5$H$_4$), 5.08 (m, C$_5$H$_4$), 1.95 (s, Me), −0.46 (td, 5.9, 9.8 Hz, H), −1.91 (dd, 4.9, 9.8 Hz, H); ^{31}P-{^{1}H}, δ 16.07 [s, J(W–P) = 256 Hz].

Cp*(C$_5$H$_4$P̄Ph$_2$)Ta(H)$_2$(μ-H)M̄′(CO)$_4$ (M′ = Cr, W) 7(Cr, W). Cr(CO)$_4$(nbd) or [W(CO)$_4$(MeCN)$_2$] was added to a thf solution (30 cm^3) of **2** (0.3 g, 0.53 mmol). The orange solution was stirred for 2 h at 50 °C. The solvent was removed under reduced pressure and the resulting residue washed with pentane (10 cm^3) and dried *in vacuo*. The solid was crystallized from acetone affording the product **7** (70–74%).

Cp*(C$_5$H$_4$P̄Ph$_2$)Ta(H)$_2$(μ-H)Cr(CO)$_4$ 7Cr. (Found: C, 50.83; H, 4.46. C$_{31}$H$_{32}$O$_4$PTaCr requires C, 50.83; H, 4.40%). FT IR (thf, cm^{-1}): 2006s, 1898s, 1844s (ν_{CO}). NMR (CD$_3$COCD$_3$): ^{1}H, δ 8.00–7.77 (m, Ph), 7.54–7.32 (m, Ph), 5.78 (m, C$_5$H$_4$), 5.02 (m, C$_5$H$_4$), 2.21 (s, Me), 0.03 (d, J = 11.8 Hz, H), −15.35 (t, J = 11.8 Hz, H); ^{31}P-{^{1}H}, δ 55.06.

Cp*(C$_5$H$_4$P̄Ph$_2$)Ta(H)$_2$(μ-H)W̄(CO)$_4$ 7W. (Found: C, 42.80; H, 3.91. C$_{31}$H$_{32}$O$_4$PTaW requires C, 43.08; H, 3.73%). FT IR (thf, cm^{-1}): 2011s, 1937s, 1894s, 1847s (ν_{CO}). NMR (CD$_3$COCD$_3$): ^{1}H, δ 8.00–7.78 (m, Ph), 7.61–7.33 (m, Ph), 5.86 (m, C$_5$H$_4$), 5.09 (m, C$_5$H$_4$), 2.21 (s, Me), 0.03 (d, J = 12 Hz, H), −12.56 (td, J = 12, 5 Hz, H); ^{31}P-{^{1}H}, 11.43.

Cp*(C$_5$H$_4$P̄Ph$_2$)Ta(CO)(μ-H)W̄(CO)$_4$ 8aW. *Procedure A*. A thf solution (100 cm^3) of Cp*(C$_5$H$_4$P̄Ph$_2$)Ta(H)$_3$W̄(CO)$_5$ **6** (0.50 g, 0.56 mmol) was irradiated with a HANAU TQ 150 lamp for 3 h at room temperature. The solvent was evaporated to give a green powder. The crude product was chromatographed over a silica gel (70–230 mesh) column (toluene eluant) affording 0.30 g (60%) of **8aW**. *Procedure B*. To a thf solution of Cp*(C$_5$H$_4$-PPh$_2$)Ta(H)(CO) **3** (0.25 g, 0.42 mmol) was added 1 equiv. of W(CO)$_4$(MeCN)$_2$. The mixture was stirred for 2 h at 40 °C and the reaction was monitored by IR spectroscopy. The solvent was removed and the crude product was crystallised from acetone leading to an analytically pure sample of **8aW** (57%). *Procedure C*. To a thf solution of Cp*(C$_5$H$_4$PPh$_2$)Ta(H)(CO) **3** (0.25 g, 0.42 mmol) was added an excess (20%) of W(CO)$_5$(thf). The mixture was stirred for 2 h at room temperature and the reaction was monitored by IR spectroscopy. The solvent was removed *in vacuo* and the crude reaction product was chromatographed over a silica gel column (70–230 mesh). Impurities were first eliminated by eluting with toluene–pentane (90:10). Further elution with toluene gave a large band corresponding to a mixture of **8aW** and **8bW** (42:58).

Cp*(C$_5$H$_4$P̄Ph$_2$)Ta(CO)(μ-H)W̄(CO)$_4$ 8aW. (Found: C, 42.73; H, 3.40. C$_{32}$H$_{30}$O$_5$PTaW requires C, 43.14; H, 3.40%). FT IR (thf, cm^{-1}): 2007s, l919s, 1889s, 1883s, 1847s (ν_{CO}). NMR (CD$_3$COCD$_3$): ^{1}H, δ 8.04–7.34 (m, Ph), 5.36 (m, C$_5$H$_4$), 4.99 (m, C$_5$H$_4$), 4.82 (m, C$_5$H$_4$), 2.13 (s, Me), −15.05 [s, J(H–W) = 40 Hz, H]; ^{31}P-{^{1}H}, δ 8.22 [J(W–P) = 226 Hz].

Table 2 Crystal data and structure refinement for **10Cr**

Formula	$C_{44}H_{39}O_5P_2CrTa \cdot 2CHCl_3$
M	1181.38
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.095(2)
b/Å	11.395(2)
c/Å	20.220(2)
α/°	79.86(3)
β/°	80.42(3)
γ/°	72.31(3)
V/Å³	2380.0(6)
Z	2
μ/mm⁻¹	2.974
RC = Reflections Collected	10879
IRC = Independent RC	9653 [$R_{\text{int}} = 0.0141$]
IRCGT = IRC and [$I > 2\sigma(I)$]	8407
R for IRCGT	$R1^a = 0.0318$, $wR2^b = 0.0800$
R for IRC	$R1^a = 0.0451$, $wR2^b = 0.0855$

^{a} $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 2.03P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$.

$Cp^*(C_5H_4\overline{PPh_2})Ta(H)(CO)\overline{W(CO)_5}$ **8bW**. (Identified from the mixture of **8aW** and **8bW**.) FT IR (thf, cm⁻¹): 2071s, 1939s, 1913s, 1892s (ν_{CO}). NMR (CD₃COCD₃): ¹H, δ 7.76–6.76 (m, Ph), 4.96 (m, C_5H_4), 4.41 (m, C_5H_4), 4.00 (m, C_5H_4), 3.83 (m, C_5H_4), 1.65 (s, Me), −5.52 (d, $J = 14.8$ Hz, H); ³¹P-{¹H}, δ 11.83 [J(W–P) = 261 Hz].

Cp*(C₅H₄$\overline{PPh_2}$)Ta(H)₂(μ-PPh₂)Cr(CO)₄ 9Cr. The procedure described earlier for complex **7Cr** was performed but starting from (0.20 g, 0.26 mmol) Cp*(C₅H₄PPh₂)Ta(H)₂(PPh₂) and 1 equiv. of Cr(CO)₄(nbd). The crude product obtained after removal of solvent was recrystallised from acetone leading to 0.16 g of **9Cr** (65%) (Found: C, 56.01; H, 4.38. C₄₃H₄₁O₄P₂-TaCr requires C, 56.32; H, 4.51%). FT IR (thf, cm⁻¹): 1993s, 1908s, 1872s, 1858s (ν_{CO}). NMR (CDCl₃): ¹H, δ 8.22–7.96 (m, Ph), 7.57–7.02 (m, Ph), 6.26 (m, C_5H_4), 4.67 (m, C_5H_4), 2.47 (d, $J = 54$ Hz, H), 1.69 (s, Me); ³¹P-{¹H}, δ 59.7 (d, $J = 10$ Hz), −1.4 (d, $J = 10$ Hz).

Cp*(C₅H₄$\overline{PPh_2}$)Ta(CO)$\overline{(\mu\text{-}PPh_2)}$M′(CO)₄ (M′ = Cr, W) 10(Cr, W). The procedure described earlier for complex **7Cr** was performed but starting from 0.2 g (0.26 mmol) Cp*(C₅H₄-PPh₂)Ta(CO)(PPh₂) and 1 equiv. of Cr(CO)₄(nbd) or W(CO)₄-(MeCN)₂. The crude product was chromatographed over a silica gel (70–230 mesh) column (toluene eluant) affording a deep red powder (70-75%) of **10(Cr, W)**.

$Cp^*(C_5H_4\overline{PPh_2})Ta(CO)\overline{(\mu\text{-}PPh_2)}Cr(CO)_4$ **10Cr**. (Found: C, 55.54; H, 4.41. C₄₄H₃₉CrO₅P₂Ta requires C, 56.06; H, 4.17%). FT IR (thf, cm⁻¹): 1993s, 1906s, l900s, 1879s, 1854s (ν_{CO}). NMR (CDCl₃): ¹H, δ 7.96–7.67 (m, Ph), 7.60–6.96 (m, Ph), 5.66 (m, C_5H_4), 5.05 (m, C_5H_4), 4.19 (m, C_5H_4), 1.57 (s, Me); ³¹P-{¹H}, δ 65.5 (s), 18.8 (s).

$Cp^*(C_5H_4\overline{PPh_2})Ta(CO)\overline{(\mu\text{-}PPh_2)}W(CO)_4$ **10W**. (Found: C, 49.04; H, 3.76. C₄₄H₃₉O₅P₂TaW requires C, 49.18; H, 3.66%). FT IR (thf, cm⁻¹): 2003s, l909s, 1898s, 1880s, 1853s (ν_{CO}). NMR (CDCl₃): ¹H, δ 7.91–7.57 (m, Ph), 7.52–6.96 (m, Ph), 5.62 (m, C_5H_4), 5.09 (m, C_5H_4), 4.40 (m, C_5H_4), 1.58 (s, Me); ³¹P-{¹H}, δ 32.2 [d, $J = 10$, J(P–W) = 249 Hz], −9.0 [d, $J = 10$, J(P–W) = 151 Hz].

Crystal structure analysis

A crystal of **10Cr** (red; 0.30 × 0.25 × 0.20 mm³) was mounted on an Enraf Nonius CAD4 diffractometer. Experimental details are summarized in Table 2. The structure was solved *via* a Patterson search program[23] and refined (space group $P\bar{1}$)

with full-matrix least-squares methods[23] based on |F^2|. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the complex were included in their calculated positions and refined with a riding model. The rather large residual peak and hole in the final Fourier difference map are located close (<1 Å) to the Ta atom. Selected bond distances and angles are collected in Table 1.

CCDC reference number 186/1549.

See http://www.rsc.org/suppdata/dt/1999/2725/ for crystallographic files in .cif format.

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