

Mono- and di-bridged heterobimetallic systems from group 5 hydride phosphido and hydride phosphino metalloligands. Crystal structure of $Cp_2Ta(H)(\mu-H)(\mu-PMe_2)Cr(CO)_4$

Olivier Lavastre, Gilles Bonnet, Gilles Boni, Marek M. Kubicki, Claude Moïse*

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (Unité de recherche associée au C.N.R.S.-UMR 5632), Université de Bourgogne, Faculté des Sciences, 6 Boulevard Gabriel, 21000 Dijon, France

Received 23 December 1996; received in revised form 14 March 1997

Abstract

The trihydrides Cp_2MH_3 ($M = Nb, Ta$) react with chlorophosphines PR_2Cl ($R = Me, Ph$) affording phosphonium salts $[Cp_2MH_2(PR_2H)]^+ Cl^-$ (**2** (a, b) **2'** (a, b)). Depending on the metal (Nb or Ta) and on the nature of the phosphine substituent (Me or Ph), deprotonation of these salts leads to hydride phosphino $Cp_2MH(PR_2H)$ (**3** (a, b) **3'a**) or hydride phosphido $Cp_2TaH_2(PPh_2)$ (**4'**) metalloligands. These two kinds of complexes are able to bind $[M'(CO)_2]$ or $[M'(CO)_4]$ ($M' = Cr, Mo, W$) organometallic fragments to give mono- or di-bridged heterobimetallic systems. The crystallographic analysis of $Cp_2Ta(H)(\mu-H)(\mu-PMe_2)Cr(CO)_4$ (**7'aCr**) is reported and discussed. © 1997 Elsevier Science S.A.

Keywords: Niobium; Tantalum; Metalloligand; Phosphido bridge; Hydrido bridge; Heterobimetallic complexes

1. Introduction

Numerous synthetic strategies can be employed to prepare heterobimetallic systems [1]. Among them, the use of metalloligands is of great interest because various bimetallic combinations are promising through this synthetic way. For some years our group has been researching in this area with phosphido derivatives of group 5 and 6 transition metals and we have reported different types of phosphido bridged heteronuclear complexes [2,18–27]. Metallaphosphines are easily obtained by reacting d^2 monohydrides $Cp_2M(L)H$ ($M = Nb, Ta$; $L =$ two electron donor) or dihydrides Cp_2MH_2 ($M = Mo, W$) with chlorophosphines PR_2Cl . A chlorine nucleophilic displacement involving the basic metallic centre is assumed to occur in the initial step [3].

In keeping with our interest in phosphido derivatives, we turned our attention to the trihydrides Cp_2MH_3 ($M = Nb, Ta$), which are good precursors of highly reactive unsaturated intermediates $[Cp_2MH]$ and are therefore able to undergo coordination or insertion reac-

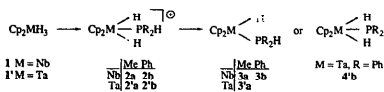
tions with phosphines. As we have mentioned earlier [4], and more recently Nikonov et al. [5,28], trihydrides Cp_2MH_3 give clean reactions with chlorophosphines PR_2Cl . The structure of reactional products (phosphino or phosphido complex) depends on the nature of M (Nb or Ta) and on that of phosphorous substituents. In this paper we wish to report on some studies concerning this isomerism phenomenon and on the nature of heterodinuclear complexes obtained from these two kinds of metalloligands.

2. Results and discussion

2.1. Synthesis

Trihydrides **1** and **1'** easily react with chlorophosphines PR_2Cl in toluene at room temperature affording complexes **2** and **2'** as white solids (Scheme 1). The central position of the PR_2H group is unambiguously established by 1H NMR spectra (Table 1) which exhibit an unique resonance for the two $M-H$ protons (doublet $^2J_{PH} \approx 75$ Hz). The cationic species **2** and **2'** can be related to previously described complexes [6] obtained

* Corresponding author. Tel.: 03 8039 6081. Fax: 03 8039 6076. E-mail: cmoise@u-bourgogne.fr.

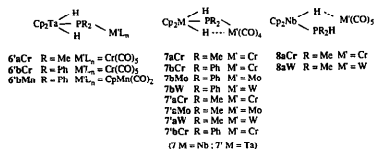


Scheme 1.

by protonation of monohydride derivatives $\text{Cp}_2\text{MH}(\text{PR}_3)$. In this case, the acidic treatment leads to a mixture of symmetric and asymmetric structures with the phosphorus ligand lying either in the central or in the lateral position in the plane bisecting that of $\text{Cp}/\text{Ta}/\text{Cp}$. Thus, the total regioselectivity of the formation of **2** and **2'** is worth noting. A direct insertion of chlorophosphines into the central M–H bond of Cp_2MH_3 can so be postulated in order to account for the formation of ionic complexes **2** and **2'** [5].

Deprotonation of salts **2** gives exclusively niobophosphino complexes **3** independently of the nature of substituents borne by the phosphorus atom. There is a difference of chemical behaviour of tantalum salts **2'**: the phenyl derivative **2'b** gives rise upon deprotonation to a dihydride phosphido complex **4'b** whereas the methyl salt **2'a** leads to the hydride phosphino complex **3'a**.

The above observations indicate that the cationic compounds **2** or **2'** contain two competing acidic sites: one at the metal and other at the phosphorus atom. Thus, the deprotonation pathway depends on the relative strengths of these two acidic centres. A more detailed study of this behaviour will be published in a forthcoming paper. In order to check the presence of a tautomeric equilibrium between the phosphino and phosphido isomers, variable temperature ^1H and ^{31}P NMR studies have been carried out on hydrido-phos-



Scheme 2.

phino complex **3b**. No noticeable amount of the corresponding dihydrido-phosphido tautomer was detected. A similar trend has been reported by Malisch for molybdenum compounds [7] while Baker mentions an easy NMR observation of phosphino-phosphido equilibrium for related tungsten system [8].

Both phosphino **3(a,b)** and **3'a** and phosphido **4'b** compounds are able to act as metalloligands. Their reactions with metal tetracarbonyls $\text{M}'(\text{CO})_4\text{L}_2$ ($\text{M}' = \text{Cr}$; $\text{L}_2 = \text{NBD}$; $\text{M}' = \text{Mo}$, W ; $\text{L} = \text{piperidine}$) lead to the μ -phosphido μ -hydrido di-bridged complexes **7** and **7'**. Similar results are observed when the reactions are carried out with pentacarbonyls $\text{M}'(\text{CO})_5(\text{THF})$ (Scheme 2).

However, small amounts of monobridged complexes **6'aCr** and **6'bCr** are isolated in addition to complexes **7'aCr** and **7'bCr** when the tantalum derivatives **3'a** and **4'b** are allowed to react with $[\text{Cr}(\text{CO})_5]$. Therefore, this suggests that the initial products of the reaction between the metalloligands and the $[\text{M}'(\text{CO})_5]$ fragments are in fact the μ -phosphido complexes **6** or **6'**. The formation of a second (hydride) bridge leading to the μ -phosphido μ -hydrido derivatives **7** or **7'** results from an easy loss of one CO ligand at the M' site in mono-bridged structures **6** or **6'**. A tantalum manganese dinuclear

Table 1
 ^1H and ^{31}P NMR and IR ($\nu(\text{CO})$) data for **2(a, b)**, **2'(a, b)**, **3(a, b)**, **3'a**, **4'b**

Complex	^1H (ppm)		H	^{31}P (^1H) (ppm)
	Cp	Me or Ph		
2a^a	5.64 (s)	1.52 (dd) (6.4; 10.8)	5.28 (dhp) (6.4; 365) –2.50 (d) (78.5)	–35 (s) (D ₂ O)
2b^a	5.80 (d) (1.6)	7.91–7.11	7.74 (d) (396) –1.68 (d) (76)	14.9
2'a^a	5.84 (s)	1.77 (dd) (11; 4)	5.30 (dm) (370) –1.16 (d) (74)	–55 (s)
2'b^a	5.81 (d) (1)	7.82–7.52 (m)	8.18 (dt) (4; 400) –0.55 (dd) (4; 72)	–6 (s)
3a^b	4.47 (d) (2.6)	1.01 (dd) (6; 8)	4.60 (dh) (6; 304) –7.93 (d) (30)	–5 (s)
3b^b	4.44 (d) (2.0)	7.70–7.01 (m)	6.74 (d) (321) –7.37 (d) (25.6)	60.0 (s)
3'a^b	4.35 (d) (2.7)	1.15 (dd) (6; 8)	4.95 (dh) (6; 313) –9.35 (d) (20)	–43 (s)
4'b^b	4.67 (s)	7.81–7.15 (m)	0.02 (d) (57)	–47 (s)

^aCD₃COCD₃.

^bC₆D₆; J values in Hz in parentheses.

complex **6'bMn** is obtained starting from **4'b** and $\text{CpMn}(\text{CO})_2(\text{THF})$. No transformation of **6'bMn** to the corresponding di-bridged structure could be achieved by photochemical process. Similar results have been already observed for molybdenocene–cymantrene system [2].

The structures of the complexes **7** and **7'** are established by their NMR spectroscopic data (Table 2). Two distinct ^1H resonances close to -1 and -11 ppm are observed for metallic hydrides; that at -1 ppm corresponds to the terminal hydride while the upfield signal clearly characterizes the bridging hydrido ligand. Furthermore, the strongly deshielded ^{31}P resonances are indicative of a significant decreasing of the M–P–M' angle [9], as a consequence of the μ -phosphido μ -hydrido di-bridged nature of the central four-membered ring. An illustrative example is given by comparing ^{31}P chemical shifts for monobridged **6'aCr** and di-bridged **7'aCr** complexes, which show signals at $\delta = -86$ and $+55$ ppm, respectively ($\Delta\delta = 141$ ppm). However, such a low field shift of ca. 140 ppm does not indicate the presence of direct metal–metal interaction. When a metal–metal bond is present, as it has been stated for Nb/Fe or Nb/Cr μ -phosphido μ -carbonyl complexes [21,26], the low field shift of ^{31}P resonance accompanying the formation of the second bridge reaches some 230 ppm.

Another kind of mono-bridged bimetallic complex is afforded by the dimethylphosphino metalloligand **3a**.

When opposed to $[\text{M}'(\text{CO})_2]_3\mathbf{3a}$ gives rise, together with **7aCr** or **7aW**, to the μ -hydrido complexes **8aCr** or **8aW**, which are isolated as green products after column chromatography. The bridging nature of hydride ligands is clearly evidenced by their ^1H high-field signals [10] located at -21.4 and -18.4 ppm, respectively. The P–H protons of the PMe_2H group resonate as doublets of septuplets at 5.1 and 5.2 ppm (Table 2).

2.2. Structure of $\text{Cp}_2\text{Ta}(\text{H})(\mu\text{-H})(\mu\text{-PMe}_2)(\text{Cr}(\text{CO})_2)(\text{7'aCr})$

The crystal structure of **7'aCr** is built of discrete organobimetallic molecules (Fig. 1). The usual deformed octahedral geometry is observed for chromium atom and that of pentacoordinated tantalum may be considered as a very distorted trigonal bipyramidal structure with the pseudotrigonal fragment Cp_2TaP (CP is the geometrical centre of a C_5 ring) and with the axial hydrides forming a Ht–Ta–Hb angle of $122(4)^\circ$. Selected interatomic distances and angles are gathered in Table 3.

The Ta–Cr separation of $3.293(1)$ Å is non-bonding. It is much longer (even if one takes into account the different sizes of organometallic fragments) than the Nb–Fe distance of $2.884(2)$ Å observed in dinuclear $\text{Nb}^{\text{III}} \mu$ -phosphido μ -carbonyl $\text{Cp}_2\text{Nb}(\mu\text{-PPH}_2)(\mu\text{-CO})\text{Fe}(\text{CO})_3$ complex in which the metal–metal bond is present [21].

Table 2
 ^1H and ^{31}P NMR and IR ($\nu(\text{CO})$) data for bimetallic complexes

Complex	^1H (ppm, CD_3COCD_3)			^{31}P (^1H)(ppm, CD_3COCD_3)	IR (cm^{-1} , THF)
	Cp	Me or Ph	H		
6'aCr	5.60 (s)	1.64 (d) (5.9)	0.66 (d) (58.0)	-86.2 (s)	2037 m, 1912 vs, 1896 s
6'bCr	5.48 (s)	7.93–7.06 (m)	1.38 (d) (57.0)	-19.0 (s)	2046 m, 1920 vs, 1897 s
6'bMn^a	4.71 (s)	8.08–7.06 (m)	0.91 (d) (55.5)	27.1 (s)	1908 s, 1838 s
	3.94 (d) (1.7)				
7bCr	5.45 (d) (0.7)	1.87 (d) (8.1)	-2.06 (dd) (7.0; 28.3) -11.92 (d) (33.9)	83.5 (broad)	1987 m, 1892 s, 1864 vs
7bCr	5.32 (d) (0.7)	8.31–7.18 (m)	-0.69 (dd) (7.7; 18.0) -12.38 (dd) (7.7; 31.3)	138.6 (broad)	1992 w, 1897 s, 1875 s, 1862 s
7bMo	5.34 (d) (0.7)	8.31–7.27 (m)	-0.68 (dd) (8.4; 23.2) -10.24 (dd) (8.4; 23.2)	108.8 (broad)	2003 w, 1895 s, 1884 s, 1859 s
7bW	5.39 (d) (0.7)	8.32–7.31 (m)	-1.27 (dd) (8.1; 16.9) -10.42 (d) (25)	99.8 (broad)	1999 w, 1890 s, 1875 s, 1855 s
7'aCr	5.48 (s)	1.90 (d) (8.9)	-1.18 (dd) (8.6; 32.5) -12.73 (dd) (8.6; 30.5)	55.5 (s)	1985 w, 1886 s, 1861 s, 1854 s
7'aMo	5.53 (s)	1.86 (d) (6.9)	-0.90 (dd) (8.8; 32.5) -10.80 (dd) (8.8; 22.6)	17.5 (s)	1998 w, 1890 s, 1874 s, 1855 s
7'aW	5.58 (s)	1.93 (d) (8.9)	-1.52 (dd) (8.8; 32.5) -11.24 (dd) (8.8; 17.7)	2.1 (s) $J_{\text{PW}} = 234$ Hz	1994 w, 1883 s, 1864 s, 1851 s
7'bCr	5.31 (s)	7.29–8.19 (m)	0.35 (dd) (9.1; 24.0) -13.29 (dd) (9.1; 27.2)	112.7 (s)	1990 w, 1892 s, 1872 s, 1855 s
8aCr	4.98 (d) (2.4)	1.54 (dd) (6.2; 8.7)	5.12 (dh) (6.2; 318) -21.41	-6.1 (broad)	2046 w, 1916 vs, 1897 s
8aW	5.03 (s)	1.56 (dd) (6.4; 8.4)	5.20 (dh) (6.1; 321) -18.36	-6.1 (broad)	2053 w, 1913 vs, 1891 s

^a(C_6D_6); J values in Hz in parentheses.

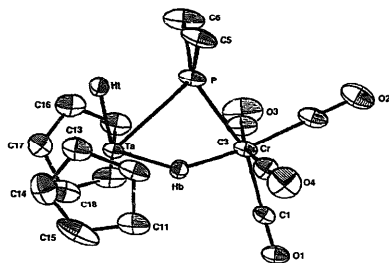


Fig. 1. ORTEP drawing of **7aCr** (50% probability level).

The Ta–P bond length of 2.587(2) Å corresponds well to that found by Nikonof et al. in the structure of mononuclear metallophosphine $\text{Cp}_2\text{TaH}_2\text{PPh}_2$ (2.595(3) Å) [28] and to those observed in metallocenes of Nb^{III} and Ta^{III} bearing the P^{V} based PMe_2S ligand (~2.58 Å) [11]. The Ta–P distance in di-bridged structure of **7aCr** is however significantly longer than the $\text{Nb}^{\text{III}}\text{–P}$ one in metal–metal bonded complexes $\text{Cp}_2\text{Nb}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Fe}(\text{CO})_3$ (2.49 Å) [21] and $\text{Cp}_2\text{Nb}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Cr}(\text{CO})_2(\text{PMe}_2\text{H})$ (2.53 Å) [26]. On the other hand, it is shorter than the Ta^{III} or $\text{Nb}^{\text{III}}\text{–P}$ bond lengths observed in monophosphido bridged bimetallics $\text{Cp}^*\text{Ta}(\text{CO})(\mu\text{-PMe}_2)\text{W}(\text{CO})_2(\text{PAMP})$ (2.68 Å) [27] and $\text{Cp}_2\text{Nb}(\text{L})(\mu\text{-PPh}_2)\text{Cr}(\text{CO})_3$ (2.68 Å) [26]. Moreover, the Ta–P bond length is much shorter than the Nb–P separation of 2.635(2) Å found for the structurally analogous di-bridged Nb^{V} complex $\text{Cp}_2\text{Nb}(\text{H})(\mu\text{-H})(\mu\text{-PPh}_2)\text{W}(\text{CO})_4$ [12]. All these observations indicate that the actual metal (Ta or Nb of metallocene fragment) — phosphorus bond length depends on many factors, like the formal charge of M (Ta or Nb), the size of M' (group 6 metal) and the mono- or di-bridged nature of bimetallic systems: the influence of phosphorus substituent (Me vs. Ph) seems to be less significant.

The Cr–P bond length in (2.284(3) Å) is rather short and may be compared to that found for Nb–Cr bonded structure of $\text{Cp}_2\text{Nb}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Cr}(\text{CO})_3(\text{PMe}_2\text{H})$

(2.31 Å) [26]. It is much shorter than in monophosphido bridged complexes (2.55–2.58 Å) [12] and than in the pentacarbonyl chromium ones $\text{Cr}(\text{CO})_5\text{L}$ (L = PPh_3 , 2.422 Å), L = $\text{P}(\text{O}i\text{Pr})_3$, 2.309 Å [13]). Such a short Cr–P bond length seems to be due to the presence of four-membered ring in $\text{Cp}_2\text{Ta}(\text{H})(\mu\text{-H})(\mu\text{-PMe}_2)\text{Cr}(\text{CO})$, (**7aCr**).

The Ta–P–Cr angle (84.8(1)°) reflects well the presence of di-bridged structure with Ta/P/Cr/H ring ($\text{Nb–P–W} = 83.7(1)^\circ$ in the structure of Nb/W [12]) but does not indicate the metal–metal interaction. The values of 75.4° (1) [21] and 77.1° (4) [26] were observed in di-bridged μ -phosphido, μ -carbonyl structures with metal–metal bond.

3. Experimental section

3.1. X-ray structure determination of **7aCr**

An irregularly shaped orange crystal of **7aCr** grown from toluene solution was used for unit cell determination and data collection, carried out at 296K on an Enraf-Nonius CAD4 diffractometer. The pertinent crystallographic data are given in Table 4. The routine

Table 4	
Crystallographic data for $\text{Cp}_2\text{Ta}(\text{H})(\mu\text{-H})(\mu\text{-PMe}_2)\text{Cr}(\text{CO})_4$ 7aCr	
Molecular formula	$\text{C}_{16}\text{H}_{18}\text{O}_2\text{PCrTa}$
Formula weight, g	538.24
Crystal system	monoclinic
Space group	$\text{P}2_1/\text{n}$ (No. 14)
Cell dimensions:	
<i>a</i> , Å	8.318(1)
<i>b</i> , Å	12.953(2)
<i>c</i> , Å	16.877(2)
β , deg	90.76(1)
<i>V</i> , Å ³	1818.2
<i>Z</i>	4
ρ_{calc} , g·cm ⁻³	1.966
<i>F</i> (000)	1032
Radiation, Å	$\lambda(\text{Mo K}\alpha)$ 0.71073
<i>T</i> , °C	18
Scan type	$\omega - 2\theta$
Scan speed, deg·min ⁻¹	1.1–5.6
Scan width, deg.	$\Delta\omega = 0.8 + 0.347\tan\theta$
θ Range, deg.	2–25
Linear abs., μ , cm ⁻¹	66.296
No. of reflections measured.	3590
Decay, %	–9.9, corrected
Cut off for obsd. data	$I \geq 3\sigma(I)$
No. of unique obsd.data (NO)	2355
No. of variables (NV)	216
Absorption correction (DIFABS)	
Min–max transmission	0.8240–1.4601
<i>R</i> (<i>F</i>)	0.033
<i>w</i> (<i>F</i>)	0.035
Weighting scheme	$1/\sigma(F_o)^2$
	$[\sigma(I)]^2 + (0.04F_o^2)^2$ ^{1/2}
G.O.F.	4.964

Table 3
Selected interatomic distances (Å) and angles (deg) for $\text{Cp}_2\text{Ta}(\text{H})(\mu\text{-H})(\mu\text{-PMe}_2)\text{Cr}(\text{CO})_4$ **7aCr**

Distance	Angle	
Ta–P	2.587(2)	P–Ta–HT 61(4)
Ta–HT	1.60(9)	P–Ta–HB 64(3)
Ta–HB	1.83(8)	HT–Ta–HB 122(4)
Ta–CP1	2.08	CP1–Ta–CP2 134.4
Ta–CP2	2.08	P–Cr–HB 73(3)
Cr–P	2.284(3)	Ta–P–Cr 84.85(8)
Cr–HB	1.71(9)	C5–P–C6 97.8(5)
Ta–Cr	3.293(1)	Ta–HB–Cr 137(5)

Table 5
Positional parameters and their e.s.d. for $Cp_2Ta(H)(\mu-H)(\mu-PMe_2)Cr(CO)_4$, 7aCr

Atom	x	y	z	B (\AA^2)
TA	0.39882(5)	0.22948(3)	0.39876(2)	3.740(8)
CR	0.4967(2)	0.1773(1)	0.21462(8)	4.00(3)
P	0.5340(3)	0.0781(2)	0.3252(2)	4.27(6)
HT	0.48(1)	0.137(7)	0.449(5)	4(2)*
HB	0.45(1)	0.251(7)	0.296(5)	4(2)*
CP1	0.1509	0.2102	0.4062	
CP2	0.5632	0.3335	0.4472	
O1	0.4195(9)	0.3610(5)	0.1109(4)	6.4(2)
O2	0.616(1)	0.0367(7)	0.0874(5)	10.9(3)
O3	0.838(1)	0.2465(9)	0.2182(6)	12.5(3)
O4	0.185(1)	0.0749(7)	0.1713(5)	9.3(2)
C1	0.448(1)	0.2907(7)	0.1505(5)	4.4(2)
C2	0.568(1)	0.0916(8)	0.1372(6)	6.7(3)
C3	0.705(1)	0.2210(9)	0.2188(6)	6.7(3)
C4	0.302(1)	0.1144(8)	0.1912(5)	5.5(3)
C5	0.437(1)	-0.0456(7)	0.3396(7)	6.7(3)
C6	0.733(1)	0.043(1)	0.2629(8)	9.1(4)
C11	0.135(1)	0.2397(9)	0.3400(6)	6.4(3)
C12	0.159(1)	0.1383(8)	0.3645(6)	5.0(2)
C13	0.169(1)	0.1369(9)	0.4469(6)	6.5(3)
C14	0.154(2)	0.237(1)	0.4716(7)	9.9(4)
C15	0.138(1)	0.300(1)	0.4083(8)	9.4(4)
C16	0.624(2)	0.266(1)	0.4840(7)	9.9(4)
C17	0.505(2)	0.3270(9)	0.5972(7)	9.4(4)
C18	0.460(2)	0.3979(9)	0.4492(7)	10.7(4)
C19	0.559(1)	0.3809(8)	0.3886(7)	9.3(3)
C20	0.668(1)	0.2960(9)	0.4074(7)	7.7(3)

CP1 and CP2 are geometrical centers of C5 rings. Starred hydrogen atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + ab(\cos \beta) \cdot B(1,2) + ac(\cos \beta) \cdot B(1,3) + bc(\cos \alpha) \cdot B(2,3)]$.

treatment of the measured data was done by use of the CAD4-SDP library [14] with neutral-atom scattering factors taken from the usual sources [15]. The structure was solved by Patterson and subsequent difference Fourier syntheses. After isotropic refinement of the model on non-averaged data an absorption correction DIFABS [16] was applied. All non-hydrogen atoms were then refined with anisotropic temperature factors. The hydrogen atoms of cyclopentadienyl ligands and of the methyl groups of dimethylphosphido bridge were placed in calculated positions in a riding model. Final difference Fourier map showed two peaks in positions which might be reasonably assigned to the terminal and bridging hydrides. Refinement of their positions was successful. Final residuals are given in Table 4 and the atomic coordinates of non-hydrogen atoms in Table 5.

3.2. Syntheses of the new complexes

All reactions were carried out under an argon atmosphere with use of standard Schlenk techniques. The solvents and eluents were dried and distilled under

argon from sodium and benzophenone immediately before use. Column chromatography was performed under argon and with silica gel (70–230 mesh). Cp_2MH_3 ($M = Nb, Ta$), $M'(CO)_2(THF)$ ($M' = Cr, Mo, W$), $Cr(CO)_4NBD$, $M'(CO)_4(\text{piperidine})_2$ ($M' = Mo, W$) were prepared according to literature procedures [17]. PMe_2Cl , PPH_2Cl (Strem) have been used as received.

Elemental analyses (C, H) were performed by the Service d'Analyse de l'Université de Bourgogne (Dijon, France). Infrared spectra were recorded on a Nicolet 205 IR-FT. 1H and ^{31}P NMR spectra were recorded on Bruker AC 200 spectrometer; chemical shifts are given in ppm relative to Me_4Si (1H) or (external) H_3PO_4 (^{31}P).

3.2.1. Synthesis of $Cp_2M(H)(PR_2H)^+Cl^-$ ($M = Nb, Ta$; $R = Me, Ph$): General procedure

To a solution (20 ml) of Cp_2MH_3 ($M = Nb, Ta$) (0.5 g) was added PR_2Cl (1 eq). A solid immediately precipitated. After 30 min of stirring the precipitate was filtered, washed with pentane and dried under vacuum, affording grey or beige powder (yield 65–75%).

$Cp_2Nb(H)(PMe_2H)^+Cl^-$ (2a). Anal. Found: C, 43.92; H, 5.72. $C_{12}H_{19}ClNbP$ calc.: C, 44.68; H, 5.94%.

$Cp_2Nb(H)(PPH_2H)^+Cl^-$ (2b). Anal. Found: C, 59.95; H, 4.85. $C_{22}H_{23}ClNbP$ calc.: C, 59.15; H, 5.19%.

$Cp_2Ta(H)(PMe_2H)^+Cl^-$ (2'a). Anal. Found: C, 34.82; H, 4.25. $C_{12}H_{19}ClPTa$ calc.: C, 35.10; H, 4.66%.

$Cp_2Ta(H)(PPH_2H)^+Cl^-$ (2'b). Anal. Found: C, 48.82; H, 4.12. $C_{22}H_{23}ClPTa$ calc.: C, 49.41; H, 4.33%.

3.2.2. Synthesis of $Cp_2M(H)(PR_2H)$ ($M = Nb, R = Me$ or Ph ; $M = Ta, R = Me$) and $Cp_2Ta(H)(PPH_2)$: General procedure

An aqueous solution of KOH was added to the dried salts $Cp_2M(H)(PR_2H)^+Cl^-$. The mixture was stirred for 15 min. The product was extracted with 2×15 ml of toluene, and the organic layer was separated and evaporated yielding an orange red solid (80–90%).

$Cp_2Nb(H)(PMe_2H)$ (3a). Anal. Found: C, 50.76; H, 6.05. $C_{12}H_{19}NbP$ calc.: C, 50.37; H, 6.34%.

$Cp_2Nb(H)(PPH_2H)$ (3b). Anal. Found: C, 64.62; H, 5.53. $C_{22}H_{23}NbP$ calc.: C, 64.40; H, 5.40%.

$Cp_2Ta(H)(PMe_2H)$ (3'a). Anal. Found: C, 38.90; H, 4.62. $C_{12}H_{19}PTa$ calc.: C, 38.52; H, 4.85%.

$Cp_2Ta(H)(PPH_2H)$ (4'b). Anal. Found: C, 52.73; H, 4.30. $C_{22}H_{23}PTa$ calc.: C, 53.02; H, 4.45%.

3.2.3. Synthesis of $Cp_2Ta(H)(\mu-PR_2)M'L_n$ ($R = Me, M'L_n = Cr(CO)_3$; $R = Ph, M'L_n = Cr(CO)_3$, $CpMn(CO)_2$): General procedure

To a THF solution (30 ml) of $Cp_2Ta(H)(PMe_2H)$ (0.37 g, 1 mmol) or $Cp_2Ta(H)(PPH_2)$ (0.50 g, 1 mmol) was added an excess (20%) of $Cr(CO)_3(THF)$ or $CpMn(CO)_2(THF)$. The mixture was stirred for 1 h at

room temperature (the reaction was monitored by IR spectroscopy). The solvent was removed under vacuum and the crude reaction product was chromatographed on silica gel with toluene as eluant. The yellow bimetallic complexes were obtained with a 55–60% yield.

$Cp_2Ta(H)_2(\mu-PMe_2)Cr(CO)_5$ (**6'aCr**). Anal. Found: C, 36.23; H, 3.27. $C_{17}H_{18}CrO_5Pt_a$ calc.: C, 36.06; H, 3.20%.

$Cp_2Ta(H)_2(\mu-PPh_2)Cr(CO)_5$ (**6'bCr**). Anal. Found: C, 46.48; H, 3.12. $C_{27}H_{22}CrO_5Pt_a$ calc.: C, 46.97; H, 3.21%.

$Cp_2Ta(H)_2(\mu-PPh_2)Mn(CO)_5$ (**6'bMn**). Anal. Found: C, 51.88; H, 4.21. $C_{29}H_{27}MnO_5Pt_a$ calc.: C, 51.65; H, 4.04%.

3.2.4. Synthesis of $Cp_2M(H)(\mu-H)(\mu-PR_2)M'(CO)_5$ ($M = Nb, Ta$; $M' = Cr, Mo, W$; $R = Me, Ph$): General procedure

To a THF solution (30 ml) of $Cp_2M(H)(PR_2)_2$ (0.50 g) or $Cp_2Ta(H)_2(PPh_2)_2$ (0.50 g) was added one equivalent of $Cr(CO)_5(NBD)$ or $M'(CO)_5(\text{piperidine})_2$. The mixture was stirred for 1 h at 40°C (the reaction was monitored by IR spectroscopy). After cooling, the mixture was filtered and the solvent removed under vacuum. The crude reaction product was chromatographed on silica gel with toluene/THF (1/1) as eluant. The red–brown bimetallic complexes were obtained with a 65–70% yield.

$Cp_2Nb(H)(\mu-H)(\mu-PMe_2)Cr(CO)_5$ (**7aCr**). Anal. Found: C, 40.74; H, 3.90. $C_{16}H_{18}CrNbO_5P$ calc.: C, 42.69; H, 4.03%.

$Cp_2Nb(H)(\mu-H)(\mu-PPh_2)Cr(CO)_5$ (**7bCr**). Anal. Found: C, 53.66; H, 4.11. $C_{26}H_{22}CrNbO_5P$ calc.: C, 54.37; H, 3.86%.

$Cp_2Nb(H)(\mu-H)(\mu-PPh_2)Mo(CO)_5$ (**7bMo**). Anal. Found: C, 49.92; H, 3.75. $C_{26}H_{22}MoNbO_5P$ calc.: C, 50.51; H, 3.59%.

$Cp_2Nb(H)(\mu-H)(\mu-PPh_2)W(CO)_5$ (**7bW**). Anal. Found: C, 44.19; H, 3.45. $C_{26}H_{22}NbO_5PW$ calc.: C, 44.22; H, 3.14%.

$Cp_2Ta(H)(\mu-H)(\mu-PMe_2)Cr(CO)_5$ (**7'aCr**). Anal. Found: C, 35.03; H, 3.05. $C_{16}H_{18}CrTaO_5Pt_a$ calc.: C, 35.71; H, 3.37%.

$Cp_2Ta(H)(\mu-H)(\mu-PMe_2)Mo(CO)_5$ (**7'aMo**). Anal. Found: C, 32.24; H, 2.92. $C_{16}H_{18}MoTaO_5Pt_a$ calc.: C, 33.01; H, 3.12%.

$Cp_2Ta(H)(\mu-H)(\mu-PMe_2)W(CO)_5$ (**7'aW**). Anal. Found: C, 28.94; H, 2.65. $C_{16}H_{18}O_5Pt_aW$ calc.: C, 28.68; H, 2.71%.

$Cp_2Ta(H)(\mu-H)(\mu-PPh_2)Cr(CO)_5$ (**7'bCr**). Anal. Found: C, 47.25; H, 3.32. $C_{26}H_{22}CrTaO_5Pt_a$ calc.: C, 47.15; H, 3.35%.

3.2.5. Synthesis of $Cp_2Nb(PMe_2)H(\mu-H)M'(CO)_5$ ($M' = Cr, W$): General procedure

To a solution of $Cp_2Nb(H)(PMe_2)_2$ (0.29 g, 1 mmol) in 30 ml of THF was added an excess (20%) of

$M'(CO)_5(THF)$. The mixture was stirred for 1 h at room temperature and the reaction was monitored by IR spectroscopy. The solvent was removed in vacuum and the crude reaction product chromatographed on silica gel with toluene as eluant. The green bimetallic complexes were obtained with a 65–70% yield.

$Cp_2Nb(PMe_2)H(\mu-H)Cr(CO)_5$ (**8aCr**). Anal. Found: C, 42.89; H, 3.92. $C_{17}H_{18}CrNbO_5P$ calc.: C, 42.70; H, 3.79%.

$Cp_2Nb(PMe_2)H(\mu-H)W(CO)_5$ (**8aW**). Anal. Found: C, 33.38; H, 2.88. $C_{17}H_{18}NbO_5PW$ calc.: C, 33.47; H, 2.97%.

4. Supplementary material

Tables giving bond distances and angles, H atom coordinates, anisotropic thermal parameters and of the best planes (7 pages) are available. Ordering information is given on any current masthead page.

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- 4, $\mu = 25.13 \text{ cm}^{-1}$, $R = 0.030$. Selected distances (\AA) and angles (deg): Nb–V/ 3.4003(8), Nb–P 2.635(2), W–P 2.459(2), Nb–P–W 83.70(7).
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