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Terminal and bridged diphenyl phosphido complexes derived from niobocene and Group 6 metal carbonyls (Cr, Mo, W). Structures of $Cp_2Nb(L)(\mu-PPh_2)Cr(CO)_5,S (L=CO, S=CH_3COCH_3;$ $L=P(OMe)_3, S=C_6H_5CH_3)$

Pascal Oudet, Danièle Perrey, Gilles Bonnet, Claude Moïse *, Marek M. Kubicki *

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (Unité de recherche associée au CNRS 1685), Faculté des Sciences, 6 Bd Gabriel, 21000 Dijon, France

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Abstract

New terminal monophosphido complexes derived from bent niobocene $Cp_2Nb(L)PPh_2$ (L=P(OMe)₃, PMe₂H) have been prepared by a procedure described earlier for $Cp_2Nb(CO)PPh_2$. These metallophosphines have been used to bind the M(CO)₅ (M=Cr, Mo, W) fragments. The expected dimetallic monobridged complexes of the type $Cp_2Nb(L)$ (μ -PPh_2)M(CO)₅ (L=CO, P(OMe)_3, PMe_2H; M=Cr, Mo, W) are formed. When L=CO the dibridged compounds $Cp_2Nb(\mu$ -PPh₂) (μ -CO)M(CO)₄ (M=Cr, W) are also obtained. All new mono- and dimetallic complexes have been characterized by ¹H and ³¹P NMR and IR spectroscopies. X-ray diffraction studies of solvated $Cp_2Nb(CO)$ (μ -PPh_2)Cr(CO)₅ and $Cp_2Nb(P(OMe)_3)$ (μ -PPh_2)Cr(CO)₅ indicate that the metallic centers in both complexes are tethered by a single bridge. The large Nb–P–Cr angles (125.94(8) and 129.11(5)°, respectively) and the long Nb–Cr distances (4.653(1) and 4.7575(9) Å, respectively) clearly show the absence of metal-metal interaction.

Keywords: Crystal structures; Group 6 transition metal complexes; Niobium complexes; Carbonyl complexes; Phosphido complexes

1. Introduction

The chemistry of terminal phosphido transition-metal complexes derived from bent metallocenes has been developed in the last decade [1-4]. The study of their capability to coordinate transition-metal fragments has allowed the isolation of phosphido-bridged dimetallic systems with interesting bondings and structures [5,6]. Only three crystal structures of monophosphido-bridged complexes derived from bent metallocenes without a metal-metal bond and without other bridges have been published [7-9]. In a recent paper [10], we reported on the synthesis of dimetallic systems Nb/Fe made by reactions of niobophosphines $Cp_2Nb(CO)PR_2$ (R = Ph, Me) with $Fe_2(CO)_9$. In this last case, the reaction provided a mixture of two complexes: the monobridged $(\mu$ -PR₂) compounds without a metal-metal interaction and the dibridged ones (μ -PR₂, μ -CO) with a metal-metal bond. The formation of this dibridged molecule was possible owing to the presence of the strong π -acceptor carbonyl ligand bound to the niobium atom in the parent metallophosphine Cp₂Nb(CO)PR₂. In this paper, we describe the syntheses of two new terminal phosphido niobium compounds Cp₂Nb(L)PPh₂ (L = P(OMe)₃, PMe₂H). All metallophosphines Cp₂Nb(L)PPh₂ (L = CO, P(OMe)₃, PMe₂H) were used to bind the Group 6 metal carbonyl fragments. The influence of the ligand L (P(OMe)₃ versus CO) on the metric parameters of monobridged dimetallic complexes is discussed on the basis of X-ray structures of Cp₂Nb(CO)(μ -PPh₂)Cr(CO)₅,CH₃COCH₃ and Cp₂Nb-(P(OMe)₃)(μ -PPh₂)Cr(CO)₅,CeH₅CH₃.

2. Experimental

All reactions were carried out under an argon atmosphere with use of standard Schlenk techniques. The solvents and eluents were distilled under argon from sodium and benzophenone immediately before use. Column chromatographies were prepared under argon and with silica gel (70–230 mesh). Elemental (C, H) analyses were performed by the 'Service Central d'Analyse du CNRS' (Gif sur Yvette). IR

^{*} Corresponding authors.

spectra were recorded with a Nicolet 205 spectrophotometer; NMR ¹H and ³¹P spectra were recorded on a Bruker WM 400 spectrometer; chemical shifts are given in ppm relative to Me₄Si (¹H) or (external) H₃PO₄ (³¹P). The starting monohydride complex Cp₂Nb(CO)H was prepared by the published procedure [11]. The metallophosphine Cp₂Nb(CO)PPh₂ (1a) was synthesized by the reported method [10]. The commercial chlorophosphine PPh₂Cl and phosphite P(OMe)₃ (STREM) and carbonyl derivatives M(CO)₆ (M=Cr, Mo, W) (JANSSEN) were used as received. M(CO)₅THF was prepared by the method indicated in the literature [12,13].

2.1. Preparation of $Cp_2Nb(P(OMe)_3)H$

This complex was prepared by an extension of the published methods [14]. NMR (δ , ppm): ¹H (C₆D₆): 4.52 (d, ³J(PH) = 2.0 Hz, Cp), 3.35 (d, ³J(PH) = 11 Hz, OMe), -7.45 (d, ²J(PH) = 30 Hz, (Nb-)H); ³¹P{¹H} (C₆D₆): 229. This complex is extremely air sensitive.

2.2. Preparation of $[Cp_2Nb(PMe_2H)PPh_2H]^+, Cl^-$

To a toluene solution (20 ml) of Cp₂Nb(PMe₂H)H (0.5 g, 1.75 mmol) was added PPh₂Cl (0.38 g, 1.75 mmol). An orange precipitate was instantaneously formed. After 30 min of stirring it was filtered, washed with pentane and dried under vacuum yielding 0.8 g (90%) of orange powder. NMR (δ , ppm): ¹H (D₂O): 7.40–7.20 (m, Ph), 6.80 (d, ¹J(PH) = 345 Hz; (PPh₂)H), 4.93 (t, ³J(PH) = 2.0 Hz, Cp), 4.72 (dh, ¹J(PH) = 335 Hz, ²J(PH) = 7 Hz, (PMe₂)H), 1.29 (dd, ²J(PH) = 7 Hz, ³J(MeH) = 9 Hz, CH₃); ³¹P{¹H} (D₂O): 47.5 (PPh₂H), -7.4 (PMe₂H). This complex is extremely air sensitive.

2.3. Preparation of $[Cp_2Nb(P(OMe)_3)PPh_2H]^+, Cl^-$

This salt was prepared by a procedure similar to that for $[Cp_2Nb(PMe_2Ph)PPh_2H]^+,Cl^-$ but from $Cp_2Nb-(P(OMe)_3)H(0.5 g, 1.44 mmol)$ and $PPh_2Cl(0.32 g, 1.44 mmol)$ (orange powder, yield 0.73 g, 90%). NMR (δ , ppm): ¹H (CD_3COCD_3): 7.45–7.30 (m, Ph), 7.24 (d, ¹J(PH) = 359 Hz, (PPh_2)H), 5.27 (t, ³J(PH) = 2 Hz, Cp), 3.82 (d, ³J(PH) = 11 Hz, OCH_3); ³¹P{¹H} (CD_3COCD_3): 46.9 (PPh_2H), 192.4 (P(OMe)_3). This complex is highly air sensitive.

2.4. Preparation of $Cp_2Nb(PMe_2H)PPh_2$ (1b)

A solution of KOH (0.6 g) in water (15 ml) was added to a 20 ml toluene suspension of the salt [Cp₂Nb-(PMe₂H)PPh₂H]⁺,Cl⁻ (0.5 g, 1.21 mmol). The mixture was stirred for 30 min. The organic layer was separated and evaporated yielding a red-black powder of **1b** (yield 0.40 g, 70%). This complex is air sensitive. *Anal.* Calc. for C₂₄H₂₇P₂Nb: C, 61.29; H, 5.79. Found: C, 59.81; H, 5.88%.

2.5. Preparation of $Cp_2Nb(P(OMe)_3)PPh_2$ (1c)

A solution of KOH (0.6 g) in water (15 ml) was added to a toluene suspension of the salt $[Cp_2Nb(P(OMe)_3)-PPh_2H]^+,Cl^-$ (0.5 g, 0.88 mmol). The mixture was stirred for 30 min. The organic layer was separated and evaporated yielding a red powder of 1c (yield 0.33 g, 70%). This complex is air sensitive. *Anal.* Calc. for $C_{25}H_{29}O_3P_2Nb$: C, 56.40; H, 5.49. Found: C, 55.79; H, 5.59%.

2.6. Reactions of $Cp_2Nb(CO)PPh_2$ (1a) with metal carbonyls

In a typical operation, a 20% excess of Cr(CO)₅(THF) in THF was added at room temperature to a 10 ml THF solution of 0.3 g (0.69 mmol) of 1a and the mixture was stirred for 1 h. During this time the solution turned from orange to redbrown. The solvent was removed in vacuo and the resulting solid was washed with pentane $(2 \times 10 \text{ ml})$, extracted with toluene (15 ml) and chromatographed. Elution with toluene led to $Cp_2Nb(CO)(\mu$ -PPh₂)Cr(CO)₅ (**2aCr**). Recrystallization from CH₃COCH₃ gave reddish-brown solvated crystals of 2aCr in 70% yield (0.3 g). The dibridged complex $Cp_2Nb(\mu-PPh_2)(\mu-CO)Cr(CO)_4$ (**3aCr**) was eluted with toluene/THF (1/1). Recrystallization from CH₃COCH₃ gave a red powder of **3aCr** in 25% yield (0.1 g). A similar procedure applied to $M(CO)_{5}(THF)$ (M = Mo, W) gave the monobridged complexes 2aMo, 2aW (70% yield) and the dibridged one 3aW (25% yield). Anal. Calc. for C₂₈H₂₀O₆PNbW (**2aW**): C, 44.24; H, 2.65; P, 4.07. Found: C, 44.20; H, 2.75; P, 4.02%. Anal. Calc. for C27H20O5PNbW (**3aW**): C, 44.29; H, 2.75; P, 4.23. Found: C, 44.33; H, 2.75; P, 4.02%.

2.7. Reactions of 1b and 1c with metal carbonyls

The complexes 2b(Cr,Mo,W) and 2c(Cr,Mo,W) were synthesized by analogous procedures to those for 2a(Cr,Mo,W) and were obtained in similar yields (70%). Recrystallization from C₆H₅CH₃ gave orange solvated crystals of 2bCr. Anal. Calc. for C₃₀H₂₉O₈P₂NbMo (2bMo): C, 46.90; H, 3.80. Found: C, 46.20; H, 3.75%. Anal. Calc. for C₂₉H₂₇O₅P₂NbCr (2cCr): C, 52.58; H, 4.11. Found: C, 51.98; H, 4.07%.

2.8. X-ray structure determination of 2aCr and 2bCr

The reddish-brown crystals of **2aCr** suitable for X-ray measurements were grown from acetone solution, and the deep orange ones of **2bCr** from toluene. Both compounds crystallize with the solvent molecules. All X-ray measurements were carried out on an Enraf-Nonius CAD4 diffractometer. The unit cells of **2aCr** and of **2bCr** were determined and refined from 25 randomly selected reflections obtained by using the CAD4 routines [15]. The crystal data and data collection parameters for both complexes are summarized in

Table 1 Crystallographic data for $2aCr, CH_3COCH_3$ and $2bCr, C_6H_5CH_3$

	2aCr,CH ₃ COCH ₃	2bCr ,C ₆ H ₅ CH ₃
Molecular formula	C ₃₀ H ₂₆ O ₇ PNbCr	C ₃₇ H ₃₇ O ₈ P ₂ NbCr
Formula weight (g)	686.42	816.55
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Cell dimensions		
a (Å)	7.936(7)	17.226(2)
b (Å)	10.010(7)	10.268(2)
c (Å)	15.153(8)	19.337(2)
β (°)	105.51(2)	94.48(1)
$V(Å^3)$	2933.4	3409.8
Z	4	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.554	1.591
F(000)	1392	1672
Radiation, λ (Å)	Μο Κα, 0.71073	Μο Κα, 0.71073
Scan type	ω -2 θ	ω-2θ
Scan speed (° min ⁻¹)	1.8-16.5	1.3-8.3
Scan width $\Delta \omega$ (°)	$1.2 + 0.34 \tan \theta$	$0.7 + 0.34 \tan \theta$
Reflections measured	h: -19, 19; k: 0, 12; l: 0, 21	h: 0, 19; k: 0, 12; l: -22, 22
θ Range (°)	1–25	2-25
Linear absorption, μ (cm ⁻¹)	8.329	7.759
No. reflections measured	3262	6424
Decay (%)	- 16 (linear correction)	-3.3 (linear correction)
Absorption correction	none	PSI SCAN
abs _{min} -abs _{max}		0.8868-0.9995
Cut off for observed data	$I \ge 3\sigma(I)$	$I \ge 3\sigma(I)$
No. unique observed data (NO)	1915	4356
No. variables (NV)	240	408
R(F)	0.037	0.040
Rw(F)	0.039	0.042
Weight, $1/\sigma(F_0)^2 = [\sigma(I)^2 + (pF_0^2)^2]^{-1/2}, p$	0.03	0.04
GOF	2.358	1.942
ρ_{\max} (e Å ⁻³)	0.150	0.708

Table 1. The Enraf-Nonius SDP library [15] was used for data reductions, as well as for the solution and refinement of the structures of 2aCr and 2bCr. Neutral-atom scattering factors and anomalous dispersion corrections were those of Cromer and Waber [16]. The structures were solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. For the structure of **2aCr**, the metals, phosphorus and the carbonyls were treated in an anisotropic model; other atoms in this structure were given as isotropic. The solvent molecule (acetone) for 2aCr was easily detected on a difference Fourier map. The molecule of toluene in 2bCr lies in a disordered position around the 0.5, 1.0, 0.5 symmetry center. All nonhydrogen atoms in the organometallic molecule of 2bCr were refined with anisotropic tempereature factors. The carbon atoms of the disordered toluene molecule were treated in an isotropic model. The hydrogen atoms in both structures were placed in calculated positions (except those of the solvent molecules) riding on the carbon atoms bearing them and included in the final calculations with B_{iso} fixed at the values equal to 1.3 B_{eq} for the corresponding carbon atoms. Final

positional parameters of the non-hydrogen atoms for 2aCr and 2bCr are given in Tables 2 and 3, respectively.

3. Results and discussion

Molecular complexes $Cp_2Nb(L)PPh_2$ (L=CO (1a), P(OMe)₃ (1b), PMe₂H (1c)) were synthesized according to Eq. (1).

$$Cp_{2}Nb \begin{pmatrix} H \\ L \end{pmatrix}^{PPh_{2}Cl} toluene \end{pmatrix}$$

$$\left[Cp_{2}Nb \begin{pmatrix} PPh_{2}H \\ L \end{pmatrix}\right]^{+}, Cl = KOH \\ toluene \end{pmatrix} Cp_{2}Nb \begin{pmatrix} PPh_{2} \\ L \end{pmatrix}$$

$$Ia (L = CO) \\ Ib (L = P(OMe)_{3}) \\ Ic (L = PMe_{2}H) \end{pmatrix}$$

$$(1)$$

The preparation of complex 1a (L = CO) has been already described [10] and we applied this synthetic route to prepare

 Table 2

 Positional parameters and their e.s.d.s for 2aCr,CH₃COCH₃

Atom	<i>x</i>	у	z	B (Å ²)
Nb	0.65760(3)	0.44940(6)	0.19806(5)	2.23(2)
Cr	0.69230(6)	0.0611(1)	0.07488(9)	2.87(4)
Р	0.7399(1)	0.2287(2)	0.1814(1)	2.13(6)
01	0.5088(3)	0.2792(6)	0.2348(4)	5.6(2)
02	0.6490(4)	-0.1727(6)	-0.0272(4)	6.1(2)
03	0.5943(3)	0.2157(6)	-0.0607(4)	5.0(2)
04	0.8423(3)	0.1306(7)	0.0150(4)	5.5(2)
05	0.7865(4)	-0.1387(5)	0.1899(4)	5.1(2)
O6	0.5261(3)	0.0224(8)	0.1131(4)	7.9(2)
C1	0.5632(4)	0.3359(7)	0.2208(5)	3.4(3)
C2	0.6655(5)	-0.0812(7)	0.0113(6)	4.4(3)
C3	0.6317(4)	0.1640(7)	-0.0065(5)	3.4(2)
C4	0.7883(4)	0.1038(7)	0.0409(5)	2.9(2)
C5	0.7529(4)	-0.0610(7)	0.1478(5)	3.5(3)
C6	0.5900(5)	0.0381(9)	0.1016(6)	4.6(3)
CII	0.7805(4)	0.4618(7)	0.3042(5)	3.2(1)*
C12	0.7659(4)	0.5876(7)	0.2747(5)	3.1(2)*
C13	0.6867(4)	0.6304(8)	0.2840(5)	3.7(2)*
C14	0.6527(5)	0.5301(8)	0.3186(6)	4.3(2)*
C15	0.7108(4)	0.4220(7)	0.3301(5)	3.5(2)*
C16	0.6652(5)	0.5811(7)	0.0897(5)	3.9(2)*
C17	0.6487(4)	0.4515(8)	0.0650(5)	3.7(2)*
C18	0.5686(4)	0.4131(7)	0.0750(5)	3.4(2)*
C19	0.5365(5)	0.5232(7)	0.1065(5)	3.9(2)*
C20	0.5957(5)	0.6252(8)	0.1154(5)	4.0(2)*
C21	0.8512(4)	0.2664(6)	0.1822(5)	2.2(1)*
C22	0.9140(4)	0.1705(7)	0.2000(5)	2.9(1)*
C23	0.9973(4)	0.2000(7)	0.1978(5)	3.6(2)*
C24	1.0171(5)	0.3219(8)	0.1775(6)	4.1(2)*
C25	0.9554(4)	0.4176(8)	0.1574(5)	3.8(2)*
C26	0.8732(4)	0.3886(7)	0.1616(5)	2.8(1)*
C27	0.7538(4)	0.1386(7)	0.2717(5)	2.7(1)*
C28	0.8276(4)	0.1424(7)	0.3305(5)	3.7(2)*
C29	0.8330(6)	0.0758(9)	0.3991(6)	5.7(2)*
C30	0.7655(5)	0.0061(9)	0.4089(6)	5.8(2)*
C31	0.6929(5)	0.0005(8)	0.3515(6)	4.8(2)*
C32	0.6852(5)	0.0679(8)	0.2847(6)	4.2(2)*
031	0.8631(5)	0.7011(8)	0.0711(5)	8.5(2)*
C31	0.9045(5)	0.7794(9)	0.0469(6)	5.7(2)*
C32	0.9727(6)	0.857(1)	0.0965(6)	7.0(3)*
C33	0.8809(7)	0.812(1)	-0.0367(7)	9.3(4)*
CP1	0.7192	0.5264	0.3023	
CP2	0.6029	0.5188	0.0903	

CP1 and CP2 are the gravity centers of C11-C15 and C16-C20 rings. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos \gamma)B(1,2)+ac(\cos \beta)B(1,3)+bc(\cos \alpha)B(2,3)].$

similar complexes with other ligands L (1b and 1c). The ¹H NMR data for 1b and 1c confirm the presence of two Nb-P bonds since the cyclopentadienyl ligands resonate as triplets.

The reaction of metallophosphines 1(a,b,c) with $M(CO)_5$ THF (M=Cr, Mo, W) afforded the expected binuclear monophosphido-bridged complexes 2(a,b,c)-(Cr,Mo,W) (Eq. (2)). In the case of the mononuclear complex 1a (L=CO), the reaction led to a mixture of mono- and dibridged phosphido compounds 2a and 3a which are easily separated by chromatography. The dibridged complexes 3a

were formed in lower yields than the corresponding monobridged compounds 2a(Cr,W). When M = Mo no formation of dibridged compound was detected.



All new compounds were characterized by ${}^{1}H$ and ${}^{31}P$ NMR and IR spectroscopies (Table 4).

The phosphido-bridged heterobimetallic compounds 2 exhibit the typical pattern of the $M(CO)_5$ fragment. When L = CO(2a) the IR spectra show an additional $\nu(CO)$ band near 1940 cm^{-1} which is only 20 cm^{-1} higher than the corresponding band in the parent niobophosphine $Cp_2Nb(CO)PPh_2$ (1a) ($\nu(CO) = 1919 \text{ cm}^{-1}$). This band is strongly shifted to lower frequencies in 3 (1745 (3aCr) and 1733 (**3aW**) cm⁻¹) indicating the presence of a bridging carbonyl ligand. Similar wavenumber values have been reported for dibridged molecules $Cp_2Nb(\mu-PR_2)(\mu-PR_2)$ CO)Fe(CO)₃ (e.g. R = Ph, $\nu(\mu$ -CO) = 1751 cm⁻¹) [10] suggesting a similar nature of the bridging carbonyl ligand in complexes 3 and in the Nb/Fe systems. The most important feature concerning the $\nu(CO)$ frequencies recorded for bimetallic complexes 2 is a red shift ($\Delta \nu \approx 20-40 \text{ cm}^{-1}$) with respect to the values observed in related LM(CO), molecules [17] (e.g. $L = PPh_3$, M = Cr, $\nu(CO) = 2065$, 1980, 1940 cm^{-1}). This indicates that diphenylmetallophosphines are better electron donors than PPh₃.

The complexes 1 belong to the family of terminal monophosphido derivatives of bent niobocene. According to the model of Lauher and Hoffman for bent metallocenes [18], the orbital $1a_1$ (in $C_{2\nu}$ symmetry) which is occupied by the metallic electron lone pair (Nb^{III}, d²) can interact with the in-plane $\pi^*(CO)$ symmetry adapted MO in complex 1a. We have confirmed the existence of such a π -backbonding by EHMO calculations in Nb/Fe systems [10]. The strength of this π -backbonding should decrease as a function of π -acceptor abilities of the ligands $(CO > P(OMe)_3 > PMe_2H)$. Thus, the electron densities retained on the Cp₂Nb fragment should depend on the nature of ligands L and decrease in the order $PMe_2H > P(OMe)_3 > CO$ as observed (Table 4). The same trends are observed for the dimetallic complexes 2(a,b,c)M. For a given ligand L the nature of the metal M has no significant influence on the ¹H chemical shifts of the Cp rings.

For all monobridged complexes 2, the bridging phosphorus atom resonates as a broad signal (due to the interactions with the quadrupolar $(I=9/2)^{93}$ Nb nucleus) in the range of

Table 3 Positional parameters and their e.s.d.s for $2bCr, C_8H_5CH_3$

Atom	x	у	z	<i>B</i> (Å ²)
Nb	0.23150(2)	0.21752(4)	0.78068(2)	3.564(8)
Cr	0.15076(4)	-0.15523(8)	0.90240(4)	3.93(2)
P1	0.25299(6)	-0.0045(1)	0.85322(6)	2.90(2)
P2	0.17588(7)	0.0949(1)	0.67760(7)	3.94(3)
CP1	0.1718	- 0.0904	0.8186	
CP2	0.1196	0.0169	0.7032	
01	0.0515(3)	-0.3486(5)	0.9692(2)	8.8(1)
02	0.1981(3)	-0.0732(5)	1.0503(2)	7.1(1)
O3	0.2711(2)	-0.3686(4)	0.9054(2)	6.2(1)
04	0.0080(2)	0.0155(5)	0.9047(3)	10.8(2)
05	0.0854(2)	-0.2745(4)	0.7675(2)	7.1(1)
06	0.1176(2)	-0.0201(3)	0.6913(2)	4.75(8)
07	0.1193(2)	0.1692(4)	0.6202(2)	5.98(9)
08	0.2407(2)	0.0360(4)	0.6323(2)	5.13(8)
Cl	0.0887(3)	-0.2738(6)	0.9431(3)	5.8(1)
C2	0.1825(3)	-0.0994(5)	0.9934(3)	4.8(1)
C3	0.2281(3)	-0.2841(5)	0.9042(3)	4.3(1)
C4	0.0644(3)	-0.0411(6)	0.9020(3)	6.5(1)
C5	0.1117(3)	-0.2223(5)	0.8161(3)	5.0(1)
C6	0.0541(4)	-0.0680(7)	0.6455(3)	8.0(2)
C7	0.1435(4)	0.2807(6)	0.5834(3)	7.5(2)
C8	0.2247(4)	-0.0338(8)	0.5691(3)	82(2)
CII	0.1745(4)	0 3570(6)	0.8641(3)	6.2(2)
C12	0.1544(4)	0.3570(0)	0.7978(4)	8.0(2)
C13	0.1086(3)	0.1055(0) 0.3154(6)	0.7601(3)	6.8(1)
C14	0.1006(3)	0.2052(6)	0.8044(3)	49(1)
C15	0.1000(3)	0.2354(5)	0.8680(3)	4.5(1)
C16	0.3172(4)	0.2337(6)	0.7464(4)	79(2)
C17	0.3169(3)	0.2819(6)	0.6981(3)	62(1)
C18	0.3497(3)	0.1724(5)	0.7340(3)	47(1)
C19	0.3703(3)	0.2117(6)	0.8028(3)	52(1)
C20	0.3494(3)	0.3399(6)	0.8020(3)	7.0(2)
C21	0.3181(3)	0.0282(5)	0.9324(2)	3.6(1)
C22	0.3602(3)	-0.0696(6)	0.9524(2)	4.7(1)
C23	0.4071(3)	-0.0455(7)	10292(3)	64(2)
C24	0.4100(3)	0.0822(8)	0.0562(3)	71(2)
C25	0.3688(3)	0.0022(0)	1.0222(3)	63(1)
C26	0.3000(3)	0.1526(5)	0.9612(3)	4.6(1)
C27	0.3254(3)	-0.1020(3)	0.9012(3) 0.8036(2)	3.25(9)
C28	0.2824(3)	-0.1840(4)	0.3050(2) 0.7404(2)	4.0(1)
C20	0.2024(3)	-0.2611(5)	0.7494(2) 0.7000(3)	4.0(1)
C30	0.3209(3)	-0.2011(5)	0.7030(3)	5.0(1)
C31	0.4001(3)	= 0.2007(0) = 0.1934(6)	0.7220(3) 0.7745(3)	5.5(1)
C32	0.3077(3)	-0.1153(5)	0.8152(3)	$\frac{3.3(1)}{4.4(1)}$
C41	0.3572(3)	0.1155(5)	0.0132(3)	4.4(1) 6.0*
C42	0.491	1.003	0.475	6.0*
C42	0.491	0.030	0.555	6.0*
C43	0.480	1 000	0.507	6.0*
C45	0.480	0.080	0.008	0.0*
C45	0.334	0.000	0.570	0.0.

CP1 and CP2 are the gravity centers of C11-C15 and C16-C20 atoms, respectively. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)].$

-13.8 to +20.8 ppm. It is consistent with the lack of a metalmetal interaction [19,20] and with the presence of large Nb-P-M angles [5]. However, this resonance is dramatically shifted downfield in dibridged molecules **3aCr** (168.5 ppm) and **3aW** (136 ppm). These downfield resonances reveal the existence of a metal-metal bond in complexes 3. The structure of 3 should be similar to that described for dibridged complexes $Cp_2Nb(\mu-PR_2)(\mu-CO)Fe(CO)_3$ [10] where the presence of a donor-acceptor metal-metal bond and of a semibridging carbonyl group has been suggested. An expected upfield shift of ³¹P resonances (μ -PPh₂) is observed on going from Cr to W [21].

Considering the metallophosphines 1 as free ligands, the lowfield coordination shifts ($\Delta = \delta(\text{complex}) - \delta(\text{free} \text{ligand})$) of ³¹P resonances are rather weak ($\Delta \approx 15 \text{ ppm}$) and are roughly 40 ppm smaller than those observed for $M(\text{CO})_5(\text{PPh}_3)$ complexes (M = Cr, Mo, W) [17]. This may be related to a weakening of the (Nb)P–M bond which is probably due to the steric requirements of both the metallocene and the metal carbonyl moieties.

In order to check the steric influences of ligands on the geometrical parameters, and in particular on those involving the flexible phosphido bridge, we carried out the single-crystal X-ray analyses of $Cp_2Nb(CO)(\mu-PPh_2)Cr(CO)_5$ (**2aCr**) and $Cp_2Nb(P(OMe)_3)(\mu-PPh_2)Cr(CO)_5$ (**2bCr**). These complexes belong to the very limited number of monobridged μ -phosphido dinuclear complexes derived from bent metallocenes without a metal-metal bond and without other bridges.

The ORTEP drawings of dinuclear compounds **2aCr** and **2bCr** are shown in Figs. 1 and 2, respectively, and selected interatomic distances and angles are given in Table 5. Geometrical parameters in both structures are roughly similar. Both molecules exhibit the typical geometries of bent metallocenes and of pentacarbonyls of Group 6 metals which are singly bridged by a diphenylphosphido group. The Nb-Cr separations of 4.653(1) and 4.7575(9) Å in **2aCr** and **2bCr**, respectively, are clearly non-bonding.

The distances Nb–P1 (2.674(2) Å in **2aCr** and 2.687(1) Å in **2bCr**) are longer than the Nb–P bond lengths observed in terminal phosphido Nb^{III} Cp₂Nb(CO)(PⁱPrPh) (Nb- $P \approx 2.63 \text{ Å}$ [22] and in the seven-coordinated Nb^I complex $[Nb^{I}{COSi({}^{i}Pr)_{3}}(CO)(dmpe)_{2}] (Nb-P \approx 2.57 \text{ \AA}) [23].$ It has been stated that metal-phosphorus bonds are longer when the phosphorus based ligand is a pyramidal phosphide than in the cases where it is a phosphine. It has been attributed to the operation of avoided overlap between the adjacent metal and ligand electron lone pairs (transition metal gauche effect) [22,24]. Thus, the Nb-P1 bond lengths in the structures of 2aCr and 2bCr, where the phosphorus lone pair is involved in the bonding to the chromium atom, should be shorter than in the terminal phosphido complex $Cp_2Nb(CO)(P^iPrPh)$ [23]. However, the observed distances are longer. It may be due to the steric repulsions between the Cp₂Nb moiety of the starting phosphido complexes and Cr(CO), fragments coordinated to the PPh₂ ligand. The Nb-P1 bond is slightly longer in 2bCr (2.687(1) Å) than in 2aCr (2.674(2) Å) and the P–Nb–L angle in **2bCr** $(91.01(5)^{\circ})$ is larger than in **2aCr** $(89.0(2)^{\circ})$. This observation corresponds to a steric influence induced by the

Table 4 ¹H and ³¹P NMR and IR (ν (CO)) data for complexes 1, 2 and 3

Complex	¹ H (CD ₃ C	OCD ₃)		$^{31}P\{^{1}H\}$	IR (cm^{-1}, THF)	
	Ср		Others	(CD ₃ COCD ₃)		
1a 1b	5.08 (d) 4.90 (t)	${}^{3}J(HP) = 1.5 Hz$ ${}^{3}J(HP) = 2.0 Hz$	7.00–7.40 (m, Ph) 7.00–7.70 (m, Ph), 3.65 (d, OMe) ${}^{3}J(PMe) = 10.0$ Hz	-2.9 (br) 198.2 (br, P(OMe) ₃) -1.2(br, PPh ₂)	1919 vs ^a	
1c	4.78 (t)	$^{3}J(\mathrm{HP}) = 2.0 \mathrm{Hz}$	7.00–7.40 (m, Ph), 4.70 (dh, H) ${}^{3}J(HMe) = 6.2$ Hz, ${}^{1}J(HP) = 320$ Hz, 1.27 (dd, Me) ${}^{3}J(MeH) = 6.2$ Hz ${}^{2}J(MeP) = 8.0$ Hz	1.7 (br, PPh_2) - 3.5 (br, PMe_2H)		
2aCr	5.26 (d)	$^{3}J(\text{HP}) = 2.0 \text{ Hz}$	7.25–7.55 (m, Ph)	12.3 (br)	2046 w, 1943 s, 1921 s ^a , 1896 s	
2aMo	5.23 (d)	$^{3}J(\text{HP}) = 2.0 \text{ Hz}$	7.30–7.60 (m, Ph)	3.3 (br)	2065 w, 1947 s, 1930 s ^a , 1900 s	
2aW	5.25 (d)	$^{3}J(\text{HP}) = 2.0 \text{ Hz}$	7.30–7.60 (m, Ph)	-13.8 (br)	2058 w, 1943 s, 1921 s ^a , 1896 s	
2bCr	4.95 (t)	${}^{3}J(\text{HP}) = 2.0 \text{ Hz}$	7.00–7.70 (m, Ph), 3.74 (d, OMe), ${}^{3}J(PMe) = 10.2$ Hz,	201.0 (br, $P(OMe)_3$) 20.8(br, μ -PPh ₂)	2041 w, 1923 s, 1869 s	
2bMo	4.94 (t)	$^{3}J(HP) = 2.0 \text{ Hz}$	7.00–7.70 (m, Ph), 3.70 (d, OMe) ${}^{3}J(PMe) = 10.2 \text{ Hz}$	194.0 (br, $P(OMe)_3$) 13.5(br, μ -PPh ₂)	2057 w, 1919 s, 1894 s	
2DW	4.94 (t)	$^{3}J(HP) = 2.0 Hz$	$^{3}J(PMe) = 10.2 \text{ Hz}$ 7 10 7 60 (m Ph) 4 98 (dh H)	$5.4(br, \mu-PPh_2)$	2030 S, 1911 S, 1889 S	
2001	4.05 (t)	J(III) - 1.5 IIZ	${}^{3}J(HMe) = 6.0 \text{ Hz},$ ${}^{1}J(HP) = 316 \text{ Hz}$ 1.37 (dd, Me), ${}^{3}J(MeH) = 6.0 \text{ Hz},$ ${}^{2}J(MeP) = 8.8 \text{ Hz}$	-3.4 (br, PMe ₂ H)	20120,12200,12200	
2cMo	4.87 (t)	$^{3}J(\mathrm{HP}) = 2.0 \mathrm{Hz}$	7.10-7.60 (m, Ph), 4.76 (dh, H) ${}^{3}J(HMe) = 6.0$ Hz, ${}^{1}J(HP) = 316$ Hz, 1.36 (dd, Me) ${}^{3}J(MeH) = 6.0$ Hz, ${}^{2}J(MeP) = 8.6$ Hz	7.8 (br, μ-PPh ₂) 1.1 (br, PMe ₂ H)	2058 s, 1919 s, 1895 s	
2cCr	4.85 (t)	³ <i>J</i> (HP) = 1.5 Hz	7.10–7.60 (m, Ph), 4.98 (dh, H) ${}^{3}J(HMe) = 6.0 \text{ Hz},$ ${}^{1}J(HP) = 316 \text{ Hz}$ 1.37 (dd, Me) ${}^{3}J(MeH) = 6.0 \text{ Hz},$ ${}^{2}J(MeP) = 8.8 \text{ Hz}$	17.6 (br, μ -PPh ₂) - 3.4 (br, PMe ₂ H)	2042 s, 1920 s, 1891 s	
2cMo	4.87 (t)	$^{3}J(\mathrm{HP}) = 2.0 \mathrm{Hz}$	7.10-7.60 (m, Ph), 4.76 (dh, H) ${}^{3}J(HMe) = 6.0 \text{ Hz},$ ${}^{1}J(HP) = 316 \text{ Hz}$ 1.36 (dd, Me) ${}^{3}J(MeH) = 6.0 \text{ Hz},$ ${}^{2}J(MeP) = 8.6 \text{ Hz}$	7.8 (br, μ-PPh ₂) 1.1 (br, PMe ₂ H)	2058 s, 1919 s, 1895 s	
2cW	4.87 (t)	${}^{3}J(HP) = 2.0 Hz$	7.00-7.55 (m, Ph), 4.86 (dh, H) ${}^{3}J(HMe) = 6.0 \text{ Hz},$ ${}^{1}J(HP) = 316 \text{ Hz}$ 1.37 (dd, Me) ${}^{3}J(MeH) = 6.0 \text{ Hz},$ ${}^{2}J(MeP) = 8.8 \text{ Hz}$	2.5 (br, μ-PPh ₂) 2.2 (br, PMe ₂ H)	2054 s, 1919 s, 1890 s	
3aCr 3aW	5.13 (d) 5.17 (d)	${}^{3}J(HP) = 2.0 Hz$ ${}^{3}J(HP) = 2.0 Hz$	7.15–8.20 (m, Ph) 7.30–8.30 (m, Ph)	168.5 (br, μ -PPh ₂) 136 (br, μ -PPh ₂)	1997 w, 1921 s, 1893 s, 1745 m * 2014 w, 1927 s, 1899 s, 1733 m *	

^a ν (CO) of Nb–CO. br: broad signal.

bulkier $P(OMe)_3$ ligand in **2bCr** compared to the CO ligand in **2aCr**.

There is a dramatic elongation of the Cr-P1 bond in both structures (**2aCr**: Cr-P1 = 2.549(3) Å; **2bCr**: Cr-P1 = 2.581(1) Å) with respect to the values found in some chromium carbonyl complexes with phosphines; e.g.

 $Cr(CO)_5PPh_3$, Cr-P=2.422(1) Å; $Cr(CO)_5P(OPh)_3$, Cr-P=2.309(1) Å [25]. The bond lengths observed here lie between the values of 2.416 Å ($Cr(CO)_5(PCy)_3$) and 2.74 Å ($Cr(CO)_5(P^*Bu)_3$) calculated recently by molecular mechanics [26]. The authors suggested that in the last case of the very bulky phosphine (P^*Bu)₃, the repulsive interac-

Table 5



Fig. 1. Molecular structure of $Cp_2Nb(CO)(\mu$ -PPh₂)Cr(CO)₅,CH₃COCH₃ (**2aCr**,CH₃COCH₃).



Fig. 2. Molecular structure of $Cp_2Nb(P(OMe)_3)(\mu-PPh_2)Cr-(CO)_5,C_6H_5CH_3$ (2bCr,C₆H₅CH₃).

tions between the ligand and the $Cr(CO)_5$ fragment are extremely strong. Thus, the very long Cr-P bonds in the structures of **2aCr** and **2bCr** result from steric repulsions.

The Nb–P1–Cr angles of $125.9(1)^{\circ}$ (**2aCr**) and $129.11(5)^{\circ}$ (**2bCr**) are largely opened. It is a general property of monophosphido-bridged structures involving the bent metallocene unit. For example, this angle is equal to $124.86(2)^{\circ}$ in Cp₂Nb(CO)(μ -PMe₂)W(CO)₄(PMe₂Ph) [9], $125.5(1)^{\circ}$ in (C₅H₅)(C₅Me₅)Ta(CO)(μ -PMe₂)Mn(CO)₂Cp [8] and $124.47(7)^{\circ}$ in Cp₂Mo(H)(μ -PPh₂)Mn(CO)₂Cp [7]. The value found for **2bCr** is the largest one observed to date for a phosphido bridge. Carty et al. [5] have already suggested that owing to an extreme flexibility of phosphido bridges values of M–PR₂–M angles above the tetrahedral one are possible, especially when only a single μ -PR₂ bridge is present. The extent of this opening is outstanding.

Selected interatomic	distances	(Å)	and	bond	angles	(°)	for	2aCr,CH ₃ -
COCH ₃ and 2bCr,C ₆ H	H₅CH3							

2aCr,CH ₃ COCH ₃		2bCr ,C ₆ H ₅ CH ₃	
Cr-Nb	4.653(1)	Cr–Nb	4.7575(9)
Cr-P	2.549(2)	Cr-P(1)	2.582(1)
Cr-C(2)	1.834(8)	Cr-C(2)	1.890(5)
Cr-C(3)	1.873(8)	Cr-C(3)	1.877(5)
Cr-C(4)	1.888(9)	Cr-C(4)	1.892(6)
Cr-C(5)	1.896(8)	Cr-C(5)	1.880(5)
Cr-C(6)	1.88(1)	Cr-C(1)	1.837(6)
Nb-C(1)	2.058(8)	Nb-P(1)	2.687(1)
Nb-P	2.674(2)	Nb-P(2)	2.485(1)
Nb-CP(1)	2.061	Nb-CP(1)	2.058
Nb-CP(2)	2.062	Nb-CP(2)	2.059
Nb-P-Cr	125.94(8)	Nb-P(1)-Cr	129.11(5)
P-Nb-C(1)	89.0(2)	P(1)-Nb-P(2)	91.01(5)
P-Cr-C(2)	169.8(3)	P(1) - Cr - C(1)	172.6(2)
P-Cr-C(3)	103.0(3)	P(1)-Cr-C(2)	90.3(2)
P-Cr-C(4)	89.3(3)	P(1)-Cr-C(3)	85.7(2)
P-Cr-C(5)	84.4(3)	P(1)-Cr-C(4	100.8(2)
P-Cr-C(6)	89.8(3)	P(1)-Cr-C(5)	95.8(2)
Nb-C(1)-O1	176.2(7)	CP(1)-Nb-CP(2)	135.8
CP(1)-Nb- $CP(2)$	137.5		

CP(1) and CP(2) represent the gravity centers of C(11)–C(15) and C(16)–C(20) cyclopentadienyl rings in $2aCr,CH_3COCH_3$ as well as C(11)–C(15) and C(16)–C(20) in $2bCr,C_6H_5CH_3$.

Another interesting feature of the structures 2aCr and **2bCr** concerns the values of the dihedral angles (L)-Nb-P1-Cr equal to $68.4(1)^{\circ}$ (L=CO) and $71.1(0)^{\circ}$ $(L = P(OMe)_3)$, respectively. These values are some 5° smaller than the torsion angle C(CO)-Nb-P-LP (74°, LP is the phosphorus lone pair) found in the terminal phosphido complex Cp₂Nb(CO)PⁱPrPh [22]. This last complex is representative of the transition metal gauche effect [24] in bent metallocenes (metal d²) [13,22]. The small differences of these torsion angles in our dimetallic systems and in the parent metallophosphines indicate that the stereochemistry of the starting mononuclear phosphido compounds is little affected by complexation to the $M(CO)_5$ fragments. It is finally noteworthy that the bulky phenyl groups of the bridging ligands adopt an 'exo' orientation with respect to the ligands L (Nb-L; L = CO, $P(OMe)_3$), contrary to an 'endo' orientation of methyl groups of the μ -PMe₂ bridge in Cp₂Nb(CO)- $(\mu$ -PMe₂)W(CO)₄(PMe₂Ph) [9] and Cp₂Ta(CO)(μ - $PMe_2SW(CO)_5[27].$

4. Conclusions

As expected, the terminal phosphido complexes derived from bent niobocene $Cp_2Nb(L)PPh_2$ (L=CO, P(OMe)₃, PMe₂H) bind the metal carbonyl fragments M(CO)₅ (M=Cr, Mo, W) from M(CO)₅THF and form in all cases the corresponding monobridged dimetallic complexes $Cp_2Nb(L)(\mu$ -PPh₂)M(CO)₅ without metal-metal interaction. When L=CO, an additionnal complex Cp_2Nb - $(\mu$ -PPh₂) $(\mu$ -CO)M(CO)₄ with a metal-metal bond is formed when M=Cr and W, but not when M=Mo. The presence of a phosphine or of a phosphite ligand bound to the niobium atom hinders the formation of a second bridge.

5. Supplementary material

Tables of anisotropic thermal parameters and of hydrogen atom coordinates, and full tables of bond distances and angles, least-squares planes and F_o/F_c amplitudes may be obtained from author M.M.K.

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