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Monohydrido-bridged carbonyl complexes of early transition metals, containing the η^5-$C_5H_5Nb(CO)_3$ moiety

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Abstract

$[(Ph_2P)_2N][CpNb(CO)_3H]$ has been made and shown to react with {M}THF (M = CpV/Nb$(CO)_3$, Cr/Mo/W$(CO)_5$ and $C_5H_4RMn(CO)_2$ (R = H, Me)) to yield the dinuclear, hydride-bridged complexes $[(Ph_2P)_2N][CpNb(CO)_3(\mu\text{-}H)\{M\}]$. Spectroscopic characteristics are consistent with a bent Nb–H–M linkage (closed three-centre bond). In some cases ({M} = Cr/W$(CO)_5$, CpMn$(CO)_2$), the homo-dinuclear complexes $[\{M\}_2\text{-}\mu\text{-}H]^-$ are also formed.

Introduction

Hydride transfer and hydride exchange between transition metal hydrides and carbonyls has been subject of extensive research in the context of catalysed hydrogenations of substrates such as CO [1,2], CO_2 [3], ketones, and aldehydes [4]. In these reactions, dinuclear, hydrido-bridged compounds (e.g. $Cp_2Nb(CO)\text{-}\mu\text{-}H\{M'\}$ ({M'} = $Fe(CO)_4$ [1,2], $CpV(CO)_3$ [5]) or $[(CO)_5W\text{-}\mu\text{-}HFe(CO)_4]^-$ [6]) and formyl complexes such as $[Fe(CO)_4CHO]^-$ [6] or Rh(octaethylporphyrine)CHO [7] have been observed as products, by-products, or intermediates. Our own studies on the reactions between $[CpM(CO)_3H]^-$ (M = V, **1**; M = Nb, **2**) and group 14 organyls, e.g. R_3SnCl [8,9] have shown that the R_3Sn fragment replaces the hydride in the metal complex. In an extension of this investigation of the reaction patterns of carbonylhydrido complexes of transition metals, we have synthesized the homo- and hetero-dinuclear monohydrido-bridged salts of the anions $[CpNb(CO)_3\text{-}\mu\text{-}H\{M\}]^-$ (Cp = η^5-C_5H_5) by reaction of **2** with solvent-stabilized 16-electron group 5 to group 7 carbonyls.

Results and discussion

Preparation and reaction pattern

The hydridoniobium anion **2** is conveniently synthesized by the reduction of $CpNb(CO)_4$ in a suitable solvent [10,11]. The primary product is the anion

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$[CpNb(CO)_3]^{2-}$ (**3**), which, if the reduction is carried out with sodium in liquid ammonia, can be isolated and characterized as the caesium salt [11]. In THF with sodium amalgam as the reductant, **3** is rapidly converted into $[CpNb(CO)_3H]^-$, isolated earlier as its $[Et_4N]^+$ salt [10], which is only sparingly soluble in THF. $[P_2N]$-**2** ($[P_2N] = [(Ph_2P)_2N]^+$), which is much more soluble in THF and hence a better starting material for consecutive reactions, is formed upon addition of $[P_2N]Cl$ to **2**, along with a yet unidentified carbonylniobium complex (see Experimental section). The spectroscopic characteristics of $[P_2N]$-**2** (ν(CO) 1896m and 1785vs,br cm^{-1} in THF; $\delta(^1H_5C_5)$ 5.18 ppm in THF-d_8, $\delta(^1H^-)$ −5.6vbr ppm; $\delta(^{93}Nb)$ −1802 ppm) are consistent with those reported for $[Et_4N]$-**2** [10,11].

The dinuclear, hydrido-bridged complexes $[CpNb(CO)_3\mu\text{-}H\{M\}]^-$ ($\{M\}$ = $CpV(CO)_3$: **4a**; $CpNb(CO)_3$: **4b**; $M'(CO)_5$, M' = Cr: **5a**, Mo: **5b**, W: **5c**; $C_5H_4RMn(CO)_2$, R = H: **6a**, CH_3: **6b**) were produced in a reaction in the dark between **2** and {M}THF generated by UV irradiation of {M}CO in THF at room temperature or, in the case of **4a**, at 200 K, since $CpV(CO)_3THF$ decomposes at temperatures above ca. 240 K to form $Cp_2V_2(CO)_5$ and $CpV(CO)_4$ [12,13]. There are two competing reaction paths (eq. 1 and 2):

$$\mathbf{2} + \{M\}THF \rightarrow [CpNb(CO)_3\mu\text{-}H\{M\}]^- + THF \tag{1}$$

$$\begin{gathered}\mathbf{2} + \{M\}THF \rightarrow CpNb(CO)_3THF + [\{M\}H]^- \\ [\{M\}H]^- + \{M\}THF \rightarrow [\{M\}_2\mu\text{-}H]^-\end{gathered} \tag{2}$$

The reaction represented by eq. 1 can be regarded as a nucleophilic attack of the σ donor **2** on the 16-electron fragment {M}, similar to that discussed for the formation of $Cp_2M''(CO)\mu\text{-}H\{M\}$ (M'' = Nb, Ta) from $Cp_2M''(CO)H$ and {M}CO or {M}THF [5]. This is the sole path in the reaction leading to **4a** (and probably also **4b**) and is the predominant path in the reactions leading to the complexes **5** and **6**, if the reaction temperature is kept at 195 K and {M}THF is slowly added to an excess of **2**.

At room temperature, route 2 becomes more important. In this reaction, which leads to the well known homodinuclear anions $[\{M'\}_2\text{-}\mu\text{-}H]^-$ (**7a**, **7b**, **7c**) and the new dimanganese anions $[\{C_5H_4RMn(CO)_2\}_2\mu\text{-}H]^-$ (**8a**, **8b**), the primary step is a hydride transfer to the substrate with simultaneous formation of the (solvent-stabilized) fragment $\{CpNb(CO)_3\}$. Support for this mechanism comes from the reaction pattern which has been observed for $[CpV(CO)_3H]^-$ (**1**; eq. 3–6 [12,14,15]), and which can be fully interpreted in terms of formation of a reactive 16-electron intermediate $\{CpV(CO)_3\}$:

$$\mathbf{1} + RX \rightarrow [\{CpV(CO)_3\}_2\mu\text{-}H]^- + [CpV(CO)_3X]^- + RH \tag{3}$$

$$\mathbf{1} + TsOH \rightarrow [\{CpV(CO)_3\}_2\mu\text{-}H]^- + TsO^- + H_2 \tag{4}$$

$$\mathbf{1} + CPh_3^+ \rightarrow [\{CpV(CO)_3\}_2\mu\text{-}H]^- + CHPh_3 \tag{5}$$

$$\mathbf{1} + Fe(CO)_5 \rightarrow [Fe(CO)_4H]^- + CpV(CO)_4 \tag{6}$$

The reaction between **1** and $Cr(CO)_6$ yields a mixture of $CpV(CO)_4$, $[Cr(CO)_5H]^-$, and **7a** [15]; no hydrido-bridged, hetero-dinuclear compound containing the $\{CpV(CO)_3\}$ moiety has been reported, and this agrees with our observation that the V complex is considerably less stable than the corresponding Nb species **5a**, which is formed readily (see eq. 1).

Table 1

CO stretching frequencies in THF

Complex	ν(CO)(cm^{-1})			
[CpV(CO)$_3$H]$^-$ [a] (**1**)	1889m	1775vs		
[CpNb(CO)$_3$H]$^-$ [b] (**2**)	1896m	1785vs		
[{CpV(CO)$_3$}$_2$-μ-H]]$^-$ [c] (**4c**)	1857	1817		
[CpNb(CO)$_3$-μ-H{M}]$^-$ [b]:				
{M} = CpV(CO)$_3$ (**4a**)	1950sh	1921s	1845vs	1812s
CpNb(CO)$_3$ (**4b**)	1950m	1921s	1841vs	1815s
Cr(CO)$_5$ (**5a**)	2055w	1915vs	1872m	1830s
Mo(CO)$_5$ (**5b**)	2062w	1825vs	1875m	1825s
W(CO)$_5$ (**5c**)	2062w	1812vs	1870m	1828s
CpMn(CO)$_2$ (**6a**)	1885m	1872s	1820vs [d]	
C$_5$H$_4$MeMn(CO)$_2$ (**6b**)	1882m	1869s	1820vs [d]	
[{M}$_2$-μ-H]$^-$:				
{M} = Cr(CO)$_5$ (**7a** [b])	2037w	1932vs	1873s	
Mo(CO)$_5$ [e] (**7b**)	2035w	1920vs	1860s	
W(CO)$_5$ [b] (**7c**)	2045w	1930vs	1873s	
CpMn(CO)$_2$ (**8a**)	1872s	1822s		
C$_5$H$_4$MeMn(CO)$_2$ (**8b**)	1869s	1820s		

[a] Ref. 26, counter-ion is [Et$_4$N]$^+$. [b] Counter-ion is [P$_2$N]$^+$. [c] Refs. 12 and 14. [d] Broad band with shoulders. [e] Ref. 27, counter-ion is [Et$_4$N]$^+$.

Characterization and structure

Spectroscopic data (ν(CO) and δ(^{1}H)) for the complexes **2** to **8** are summarized in Tables 1 and 2. For comparison, data for related complexes taken from the literature are included.

[CpNb(CO)$_3\mu$-HV(CO)$_3$Cp]$^-$ (4a) and [{CpNb(CO)$_3$}$_2\mu$-H]$^-$ (4b)

The salts of anions **4** which decompose in solution within several days even at 240 K, separate as stable (when stored under N$_2$) grey-green powders when precipitated from their dark-green THF solutions with pentane. Their IR spectra in the CO stretching region exhibit four absorptions (Table 1, for **4b** see also Fig. 1,a). This contrasts with two ν(CO) bands reported for [{CpV(CO)$_3$}$_2$-μ-H]$^-$ (**4c**) [14,15] *, for which the structures I (C_{2h}) and II (D_{3d}) in Fig. 2 were proposed. These tentative formulations involving a linear V–H–V bridge are inconsistent, however, with more recent findings on comparable monohydrido-bridged, dinuclear carbonyl species such as Cp$_2$Nb(CO)-μ-H{M} [2,5,16,17] and [{W(CO)$_5$}$_2$-μ-H]$^-$ [18,19], for which the bent metal-hydride-metal linkage has been established, suggesting that this type of linkage is normally present in this type of compounds [19]. Therefore, III (local C_s symmetry) in Fig. 2 is a more likely structure for **4a** and **4b** (and possibly also for **4c**; cf. footnote), and is also much more consistent with the pattern of ν(CO) bands (Fig. 1).

The position of the hydride signals (**4a**: −19.7, **4b**: −17.1 ppm) is characteristic of bridging hydride [20]. The signals are typically broadened as a consequence of

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* Since **4c** is not very stable in solution, bands due to decomposition products are commonly present, among them the strong E mode of CpV(CO)$_4$ at 1920 cm^{-1} that coincides with one of the bands from **4a**. Additional unrecognised bands from **4c** may well have been present.

Table 2

^{1}H NMR data

Compound	Cp region $\delta(^1H)$ (ppm)	Hydride region $\delta(^1H)$ (ppm)	$W_{1/2}$ [a] (Hz)
1	–	−6.3 [b]	160(300) [b]
	4.57 [c]	−6.1 [c]	vbr [c]
2	5.38 [d]	−5.6 [d]	360(300) [d]
	5.18 [e]	–	–
4c [c]	4.67	–	–
$[CpNb(CO)_3\text{-}\mu\text{-}H\{M\}]^-$ [e]:			
4a	5.67, 5.20 [f]	−19.7	15(210)
4b	5.25	−17.1	40(310), 9(210)
5a	5.38	−18.17	18(300) [g]
5b	5.32	−14.55	37(300)
5c	5.41	−14.78 [h]	7(210)
6a	4.11, 5.21 [f,i]	−21.0	br
6b	3.99, 5.32 [f,i]	−21.2	br
$[Cp_2Nb(CO)\text{-}\mu\text{-}HNb(CO)_3Cp]$ [j]	5.34, 5.46	−19.8	br
$[Cp_2Nb(CO)\text{-}\mu\text{-}HV(CO)_3Cp]$ [j]	4.99, 5.34 [f]	−21.6	br
$[\{M\}_2\text{-}\mu\text{-}H]^-$ [e]			
7a		−19.44	
7b		−12.15	
7c		−12.47 [k]	
8a	4.11 [i]	−26.5	br
8b	3.99 [i]	−26.5	br
$[Cp_2Nb(CO)\text{-}\mu\text{-}HMn(CO)_2Cp]$ [j]	4.30, 5.28 [f]	−26.1	br

[a] Width at half-height (see also text for discussion), br = broad, vbr = very broad; temperature in parenthesis. [b] Counter-ion is $[Et_4N]^+$, in CD_3CN, ref. 26. [c] Counter-ion is $[P_2N]^+$, in THF-d_8, ref. 14. [d] Ref. 10 (counter-ion $[Et_4N]^+$, in CD_3CN). [e] This work (counter-ion $[P_2N]^+$, in THF-d_8). [f] The low-field (high-frequency) resonance corresponds to the $\{CpNb(CO)_3\}$ moiety. [g] See text for other temperatures and discussion. [h] $^1J(^1H-^{183}W)$ 39 Hz; cf. Fig. 3. [i] Due to partial decomposition, the signal at higher field (4.11 and 3.99 ppm, respectively), which belongs to the $[CpMn(CO)_2]$ moiety, cannot be assigned unambiguously to either **5** or **8**. [j] In acetone-d_6, ref. 10. [k] $^1J(^1H-^{183}W)$ 42 Hz; cf. Fig. 3.

interaction with the quadrupolar nuclei ^{51}V (nuclear spin $I = 7/2$, quadrupole moment $Q = -0.052 \times 10^{-28}$ m^2) and ^{93}Nb ($I = 9/2$, Q -0.2×10^{-28} m^2). The increase of viscosity (increase of the molecular correlation time) with decreasing temperature leads to increasingly effective relaxation decoupling of the two spin-coupled nuclei and thus to a narrowing of the resonances. The line widths at half-height, $W_{1/2}$, for compound **4b** are 62 Hz (333 K), 40 Hz (299 K) and 9 Hz (210 K) in THF-d_8 (cf. also Fig. 3 in the next section). There is only one single ^{1}H resonance for the Cp protons in **4b**, indicating equivalence of the two $CpNb(CO)_3$ moieties or rapid exchange between two inequivalent sites, as suggested for $[\{Cp_2Nb(CO)\}_2\text{-}\mu\text{-}H]^+$ [21], for which only one Cp signal was observed despite the presence of an asymmetrical Nb–H–Nb bridge revealed by an X-ray structure analysis. As expected, **4a** exhibits two Cp signals in the ^{1}H NMR spectrum in the integration ratio 1/1.

The ^{51}V NMR spectrum of **4a** shows a resonance at −1202 ppm, compared to −1129 ppm for **4c** [12]. The ^{51}V nucleus is deshielded with respect to $CpV(CO)_4$ (−1534 ppm) and $[CpV(CO)_3H]^-$ (−1730 ppm) [12] and also with respect to other dinuclear vanadium complexes such as $Cp_2V_2(CO)_5$ (−1666 ppm) [23] and

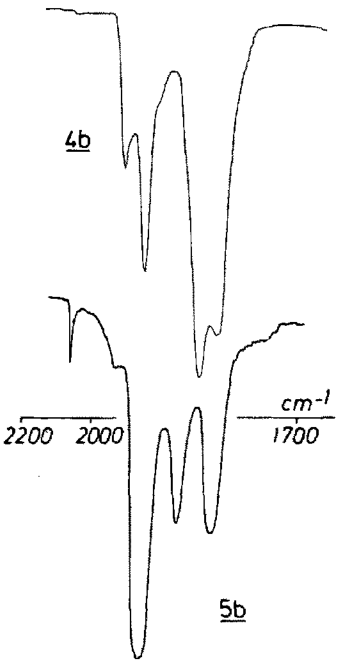

Fig. 1. IR spectra (ν(CO) region) of THF solutions of $[P_2N][\{CpNb(CO)_3\}_2$-μ-$H]([P_2N]$-**4b**) and $[P_2N][CpNb(CO)_3$-μ-$HMo(CO)_5]([P_2N]$-**5b**).

$[CpV(Me_2P(CH_2)_2PMe_2)]_2(\mu$-$H)_2$ (−1370 ppm) [24]; it is also shielded with respect to $CpV(CO)_3THF$ (−217 ppm) [12]. The chemical shift for **4a** is "normal" in the sense that this complex can be regarded as a monosubstitution product of $CpV(CO)_4$, i.e. $CpV(CO)_3L$ with $L = \{HNb(CO)_3Cp\}^-$, falling into the category of moderately polarizable ligands [12,25]. The resonance is comparatively broad ($W_{1/2}$ 190 Hz) and does not permit direct observation of $^1J(^1H-^{51}V/^{93}Nb)$. $^1J(^1H-^{51}V)$ for $[CpV(CO)_3H]^-$ is 22.8 Hz (see also ref. 26; the J value reported there, 20.3 Hz, is too small by about 10%). $^1J(^1H-^{93}Nb)$, estimated from the line widths of $[CpNb(CO)_3H]^-$ and **5a**, amounts to 40 to 60 Hz (see next section).

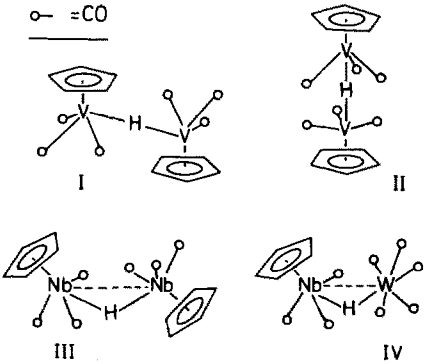

Fig. 2. Proposed structures for the anions $[(CpV(CO)_3)_2$-μ-$H]^-$ (**4c**: I and II) [14], $[\{CpNb(CO)_3\}_2$-μ-$H]^-$ (**4b**, III) and $[CpNb(CO)_3$-μ-$HM(CO)_5]^-$ (**5a**, **5b**, **5c**, IV).

[CpNb(CO)$_3$μ-HM(CO)$_5$]$^-$ (5) and [{M(CO)$_5$}$_2$-μ-H]$^-$ (7); M = Cr (a), Mo (b), W(c)

For M = Cr or W the red solutions obtained on treatment of [P$_2$N]-**2** with M(CO)$_5$THF at 195 K contain a mixture of the hetero- and homo-bimetallic complexes in the approximate molar ratio 10/1, from which **5a**/**5c** can be precipitated with pentane in the form of light-red powders that are fairly stable when stored under inert gas at low temperatures. The solutions decompose during several days to form the homodinuclear anions **7**. IR and ^{1}H NMR information is contained in Tables 1 and 2.

Of the four ν(CO) bands (for **5b** see Fig. 1,b), the three absorptions at higher wavenumbers can be assigned to the {M(CO)$_5$-μ-H} moiety of local C_{4v} symmetry, with the E band also incorporating the two high frequency CO vibrations of the {CpV(CO)$_3$} fragment. A weak shoulder at ca. 1950 cm^{-1} may correspond to the (IR-forbidden) B_1 that is sometimes observed for M(CO)$_5$L complexes when L is a bulky ligand. In KBr, the ν(CO) and at 1825 cm^{-1} belonging to {CpNb(CO)$_3$} is split (1825 and 1810 cm^{-1}).

The ^{1}H(hydride) resonances for the complexes **7** are sharp, but those for **5a**, **5b** and **5c** are broadened as a consequence of quadrupolar interaction by the nucleus ^{93}Nb (vide supra) and exhibit the typical temperature dependence of $W_{1/2}$ shown in Fig. 3 for **5c**/**7c**. The magnetic nucleide ^{183}W (natural abundance 14.3%, $I = 1/2$)

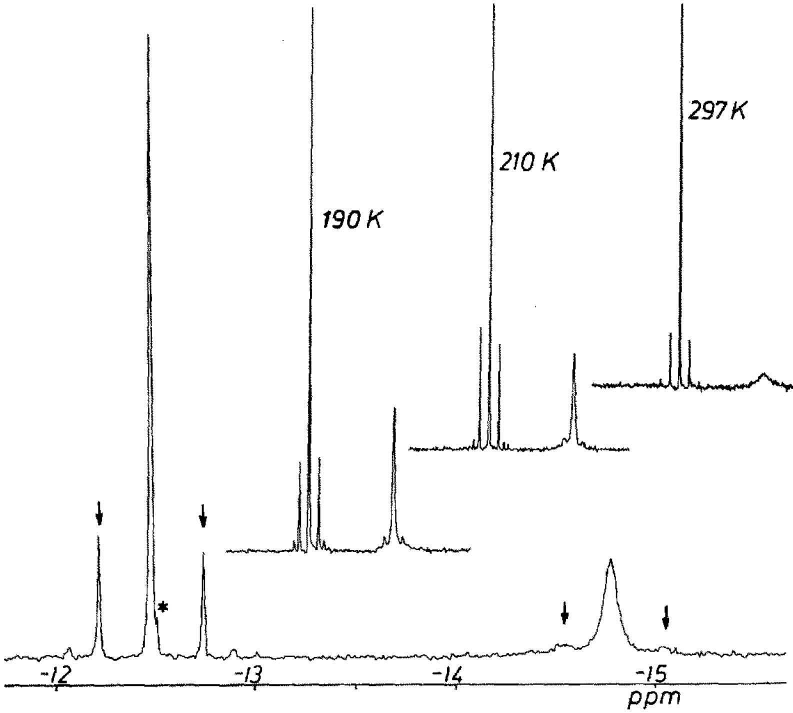

Fig. 3. 80 MHz ^{1}H NMR spectrum of a mixture of [CpNb(CO)$_3$-μ-HW(CO)$_5$]$^-$ (**5c**) and [{W(CO)$_5$}$_2$-μ-H]$^-$ (**7c**) in THF-d_8 at variable temperatures, showing the temperature dependence of the line widths for **5c**, the ^{183}W satellite doublets (arrows) and also the high-field (low-frequency) component of the ^{13}C (natural abundance) doublet (asterisk). The bottom spectrum is the expansion of the spectrum scanned at 210 K.

gives rise to a satellite system [27,30]; the $^1J(^1H-^{183}W)$ coupling constants are 39 Hz (**5c**) and 42 Hz (**7c**), respectively, and these values are consistent with a model in which the bent Nb–H–W linkage is represented as a closed three-centre bond, i.e. a bond involving metal–metal overlap [19,30]. From the spectroscopic evidence and the structural information available for **7** and related compounds [1,2,5,16–21,28], we propose structure IV in Fig. 2 for the heterobimetallic complexes **5**.

In the case of **5c** the satellite splitting, is only resolved at low temperature, since only under these conditions is there effective relaxation decoupling between ^1H and ^{93}Nb and hence a sufficiently narrow ^1H resonance. As in the case of **4a** and **4b**, the two nuclei are still partially decoupled at elevated temperatures, and this again prevents direct observation of niobium-hydrogen coupling. However, in this situation, with relaxation mainly due to scalar relaxation of the second kind, the magnitude of $^1J(^1H-^{93}Nb)$ can be estimated, in the limit of motional narrowing and for Lorentzian line shapes, from eq. 7:

$$W_{1/2}(^1H) = \tfrac{4}{3}J^2 I(I+1)\left[W_{1/2}(^{93}Nb)\right]^{-1} \qquad (7)$$

For **5a**, we find $W_{1/2}(^1H)$ 18 Hz, $W_{1/2}(^{93}Nb)$ 6100 Hz, and calculate ($I = 9/2$) a J value of 58 Hz, which agrees well with the lower limit of 40 Hz estimated from the overall line width of $[CpNb(CO)_3H]^-$ ($W_{1/2}$ 360 Hz), for which a plateau-like signal typical for a spin 1/2 resonance fully coupled to a quadrupolar nucleus [31] is observed. The position of the ^{93}Nb NMR signal of **5a**, at −1845 ppm, does not differ greatly from the $\delta(^{93}Nb)$ values for related compounds such as $CpNb(CO)_4$ (−2016 ppm) and $[CpNb(CO)_3H]^-$ (−1802 ppm) [10].

*$[CpNb(CO)_3\text{-}\mu\text{-}HMn(CO)_2C_5H_4R]^-$ (R = H: **6a**, Me: **6b**) and $[\{C_5H_4RMn(CO)_2\}_2\text{-}\mu\text{-}H]^-$ (**8a** and **8b**)*

The heterobimetallic complexes **6**, generated by reaction of **2** with $CpMn(CO)_2THF$, are labile and have not been isolated as solids. In the CO stretching region of the freshly prepared solutions there are three bands (**6a**; 1885, 1872, 1820 cm^{-1}; Table 1). The brown solutions decompose within several hours to yield $\nu(CO)$ absorptions at 1872 and 1822 cm^{-1} (**8a**) typical of the complexes $CpMn(CO)_2L$. The extreme high-field shift of the ^1H(hydride) resonances (**6a**: −21.0, **8a**: −26.5 ppm; Table 2) clearly indicates the presence of bridging hydride, and is comparable to that for e.g., $Cp_2Nb(CO)\text{-}\mu\text{-}HMn(CO)_2Cp$ (−26.1 ppm [5]). Again, the resonances are broad at room temperature, and this in the case of **8** is exclusively due to the quadrupole interaction induced by the ^{55}Mn nucleus ($I = 5/2$, Q 0.4×10^{-28} m^2).

Experimental

General, and physical measurements

All operations were conducted in highly purified solvents under N_2 atmosphere. Irradiations were carried out in Duran glassware by use of a high pressure mercury lamp (Philips HPK 125), fitted with a water-cooled quartz mantle, as external radiation source. Starting materials were from commercial sources, except for $CpNb(CO)_4$ which was prepared from $CpNbCl_4$ (synthesized from $CpSn(n\text{-}Bu)_3$ [32] and $NbCl_5$) [33] under 330 bar of CO pressure and 135 °C, with Na/Al/Cu as reductant and halogen acceptor [34]. In all cases, the benzene originally employed was replaced by toluene without loss in yield.

IR spectra: Perkin–Elmer 557, 0.01–0.02 *M* THF solutions, 0.1 mm KBr cuvettes. NMR spectra: ^{1}H: Bruker WP 80, 5 mm diameter vials, THF-d_8. ^{51}V: Bruker WH 90 (23.66 MHz), 10 mm diameter vials, THF/THF-d_8 2/1, sweep width 25 kHz (acquisition time 0.16 s), pulse width 6 μs; standard $VOCl_3$ in $CDCl_3$. ^{93}Nb: Varian DP 60/Bruker SWL 3-100 (16 MHz), 14 mm diameter vials, THF, sweep width 3 mT, modulation amplitude 0.064 mT, field strength of the radio field 23 dB (maximum setting: 0 dB); standard $[Et_4N][NbCl_6]$ in CH_3CN ($B_s = 1.5361$ T).

Preparation of complexes

*$[\{(C_6H_5)_2P\}_2N][C_5H_5Nb(CO)_3H]$($[P_2N]$-**2**).* A solution of 1.27 g (4.7 mmol) of $CpNb(CO)_4$ in 40 ml of THF was stirred for 5 h with 300 g of sodium amalgam containing 0.8% w/w of Na. During this time, the colour of the solution changed from red to brown and a fine precipitate formed. The suspension was decanted from the amalgam and the latter washed with two 5 ml portions of THF. The combined decantates were treated with 2.7 g (4.7 mmol) of $[(Ph_2P)_2N]Cl$ suspended in 20 ml of THF, and the solution filtered after 2 h of stirring. The orange-yellow filtrate * was evaporated to dryness to leave a brown oil, which solidified after trituration with three 10 ml portions of O_2-free water. After being dried under high vacuum (1 h at 30 °C) the solid was redissolved in 20 ml of THF and $[P_2N]$-**2** was gradually precipitated as an ocre powder by slow addition of n-pentane. The powder was filtered off and dried (high vacuum, 5 h, room temperature). Yields were between 1.1 and 1.35 g (45 to 55%).

*$[\{(C_6H_5)_2P\}_2N][\{C_5H_5Nb(CO)_3\}_2\text{-}\mu\text{-}H]$($[P_2N]$-**4b**).* A solution of 135 mg (0.5 mmol) of $CpNb(CO)_4$ dissolved in 30 ml of THF was irradiated for 15 min, the dark green solution cooled to −78 °C and added dropwise with vigorous stirring to a pre-cooled (−78 °C) solution of 258 mg of $[P_2N]$-**2** in 20 ml of THF. The mixture was allowed to warm slowly to 0 °C, and then filtered, and the solvent evaporated off at 0 °C under vacuum. The remaining green oil containing **4b** and $CpNb(CO)_4$, was washed twice with 10 ml portions of n-pentane. Complete removal of $CpNb(CO)_4$ was achieved by several reprecipitations from THF/pentane. 472 mg (62%) of spectroscopically pure $[P_2N]$-**4b** were finally obtained as a greyish green, extremely air-sensitive powder.

$[\{(C_6H_5)_2P\}_2N][C_5H_5Nb(CO)_3\text{-}\mu\text{-}HV(CO)_3C_5H_5$($[P_2N]$-**4a**) was prepared as described for **4b** from 114 mg of $CpV(CO)_4$ and 258 mg of $[P_2N]$-**2**. The irradiation (15 min) was carried out at dry-ice temperature. Yield: 417 mg [58%) of a grey-green powder.

*$[\{(C_6H_5)_2P\}_2N][C_5H_5Nb(CO)_3\text{-}\mu\text{-}HM(CO)_5]$ (M = Cr: ($[P_2N]$-**5a**) Mo: $[P_2N]$-**5b**, W: $[P_2N]$-**5c**).* Stock solutions containing 1.2 mmol of $M(CO)_5THF$ in 100 ml of THF were prepared by irradiation of $M(CO)_6$ (M = Cr: 264 mg, M = Mo: 317

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* The residue on the filter plate was extracted with MeCN (ca. 150 ml), to yield a deep-green solution from which, on standing at −30 °C, 320 mg of an unidentified black, crystalline anionic carbonylniobium complex (ν(CO) 1783, 1750, 1715 cm^{-1}) separated. This compound is practically insoluble in all common solvents. It decomposes in CH_2Cl_2 or $CHCl_3$ to form $CpNb(CO)_4$.

mg, M = W: 422 mg). These solutions were cooled to −78 °C and added dropwise at −78 °C to 20 ml of a THF solution containing 180 mg (0.35 mmol) of $[P_2N]$-**2** until the ν(CO) at 1785 cm^{-1} typical of the anion **2** had disappeared (some 37 to 41 ml of the stock solution, corresponding to an excess of 10–20%, were necessary for a complete conversion of **2**).

The deep-red solution was allowed to warm to room temperature and then evaporated. From the residual red oil containing the hydrido-bridged complexes and $M(CO)_6$, most of the hexacarbonyl was removed by three washings with 5 ml portions of pentane. Two consecutive reprecipitations from THF/pentane or THF/hexane yielded pale-red powders which were free from $M(CO)_6$. In the case of M = Mo, this powder was pure $[P_2N]$-**5b**. For chromium and tungsten, about 10% of $[P_2N][\{M(CO)_5\}_2\text{-}\mu\text{-}H]$ (M = Cr: $[P_2N]$-**7a**, W: $[P_2N]$-**7c**) were present in it. The chromium complex $[P_2N]$-**5a** could be purified further by additional reprecipitations; 50 mg (21% with respect to $[P_2N]$-**2**) of spectroscopically pure $[P_2N]$-**5a** was obtained by 6 such additional reprecipitations.

Column chromatography on silica-gel or magnesium silicate, with THF, THF/MeCN, or THF/CH_2Cl_2 as elutants lead to decomposition of the complexes **5**, and **7** was the main decomposition product obtained from the column.

Reaction of $[P_2N]$-2 with $C_5H_5Mn(CO)_2THF$ and $C_5H_4CH_3Mn(CO)_2THF$. A mixture of $CpMn(CO)_3$ and $CpMn(CO)_2THF$ obtained by irradiation of $CpMn(CO)_3$ in THF (1.5 mmol in 150 ml) was added dropwise with vigorous stirring at −78 °C to a solution of 0.5 mmol of P_2N-**2** in 20 ml of THF, until the characteristic ν(CO) band of the latter at 1785 cm^{-1} had disappeared. The mixture was allowed to warm to room temperature, then filtered, and evaporation of the solvent then yielded a brown oil, which was washed with pentane until the washings were colourless. The remaining solid, a mixture of **6a**/**8a** or **6b**/**8b**, was vacuum-dried and redissolved in THF-d_8 for immediate spectroscopic investigation.

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