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IX *. DERIVATIVES OF $[Nb(CO)_6]^-$ AND $[NbH(CO)_6]$, STABILIZED BY OLIGODENTATE PHOSPHINES

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Summary

UV induced CO substitution in $[Et_4N][Nb(CO)_6]$ by $Ph_2P(CH_2)_2PPh_2$ (p_2), $PhP(CH_2CH_2PPh_2)_2$ (p_3) or $P(CH_2CH_2PPh_2)_3$ (pp_3), L, yields *cis*-$[Et_4N]$-$[Nb(CO)_4L]$ via $[Et_4N][Nb(CO)_5L]$. Only chelate-5 ring structures are observed. The carbonylniobates are converted on silica gel into $[NbH(CO)_4p_2]$, $[NbH(CO)_3p_3]$ and $[NbH(CO)_3pp_3]$. IR, ^1H, ^{31}P and ^{93}Nb NMR spectral data are presented and there is ^1H and ^{31}P NMR evidence for a rigid structure of $[NbH(CO)_3p_3]$ below 200 K.

Introduction

While the chemistry of carbonylvanadium complexes has rapidly expanded during the last decade (see refs. 1–4 for some of the more recent reports), little is known about the carbonyl niobium and tantalum systems. $[Nb(CO)_6]^-$ is the only binary Nb–CO compound known under ordinary conditions; an early report on $Nb_2(CO)_{12}$ [5] has not been verified. In contrast to $[V(CO)_6]^-$, which on treatment with acids in ether solution yields $[HOR_2][V(CO)_6]$ [6] ("$HV(CO)_6$"), or $[V(CO)_6]$ when the reaction is carried out in solvent-free systems, $[Nb(CO)_6]^-$ is converted into, e.g., $[H(THF)_2][Nb_2(CO)_8(\mu\text{-}Cl)_3]^-$ [7]. It is possible, however, to stabilize the hypothetical $[NbH(CO)_6]$ by replacing CO ligands by chelating phosphines. Up to now $[NbH(CO)_2(dmpe)_2]$ (dmpe = $Me_2P(CH_2)_2PMe_2$) prepared by high-pressure synthesis from $[Nb(H)_5(dmpe)_2]$ and CO, was the only representative of this class of compounds [8]. More information is available on phosphine (and arsine) derivatives of $[Nb(CO)_6]^-$. Ellis [9] obtained $[Nb(CO)_5PPh_3]^-$ and $[Nb(CO)_4p_2]^-$ (p_2 = $Ph_2P(CH_2)_2PPh_2$) and we have recently described a large number of carbonylniobates(–I) containing bis(phosphines) and $Ph_2As(CH_2)_2PPh_2$ [10]. In the present

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* See ref. 25 for part VIII.

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TABLE 1

IR DATA (CO stretching region) FOR THF SOLUTIONS

Complex [a]	ν(CO) (cm^{-1})
$[Nb(CO)_6]^-$	1858, 1885sh [b]
$[Nb(CO)_5p_2]^-$ [c]	1965m, 1825vs
$[Nb(CO)_5p_3]^-$ [c]	1965m, 1820vs
$[Nb(CO)_5pp_3]^-$ [c]	1965m, 1811vs
cis-$[Nb(CO)_4p_2]^-$	1903s, 1798vs, 1780sh, 1750sh
cis-$[Nb(CO)_4p_3]^-$	1900s, 1795vs, 1775sh, 1745sh
cis-$[Nb(CO)_4pp_3]^-$	1898s, 1790vs, 1770sh, 1745sh
$[NbH(CO)_4p_2]$	1998w, 1875vs,br
$[NbH(CO)_3p_3]$	1920m,br 1820vs
$[NbH(CO)_3pp_3]$	1920m,br 1815s

[a] Abbreviations: $p_2 = Ph_2PCH_2CH_2PPh_2$, $p_3 = PhP(CH_2CH_2PPh_2)_2$, $pp_3 = P(CH_2CH_2PPh_2)_3$. [b] See also ref. 23. [c] The first band is A_1 (equatorial), the second E; A_1 (axial) is hidden under E.

work, we show that photochemically produced tetracarbonylniobates(−I), containing the oligodentate phosphine ligands p_2, $PhP(CH_2CH_2PPh_2)_2$ (p_3) and $P(CH_2CH_2PPh_2)_3$ (pp_3), p_m, can be employed to generate stable hydridoniobium complexes by a procedure somewhat similar to that we have described previously for the preparation of analogous complexes derived from $[VH(CO)_6]$ [11].

Results and discussion

Carbonylniobates(−I)

The complexes were prepared according to eq. 1:

$$\left[Nb(CO)_6^- + p_m \xrightarrow{h\nu} [Nb(CO)_5p_m]^- \xrightarrow{h\nu} cis\text{-}Nb(CO)_4p_m\right] \qquad (1)$$

The pentacarbonylniobates, which are formed as intermediates in the photochemical reaction between $[Et_4N][Nb(CO)_6]$ and p_m can be detected by their IR pattern in the CO stretching region (Table 1). The final product of reaction is the *cis*-disubstituted, pseudo-octahedral anion. No trisubstituted product is formed with p_3 or pp_3, contrasting what has been observed with the vanadium system, where *mer*-$[V(CO)_3p_m]^-$ are obtained [12].

^{31}P coordination shifts (Table 2) are ca. 14 ppm less than in the corresponding vanadium compounds. The high-field (low-frequency) shift of the ^{31}P resonances on going down a group is a typical feature in transition metal phosphine chemistry (see, e.g. refs. 13–15), and possibly accounts for the increasing non-local diamagnetic contribution to the overall shielding of the ^{31}P nucleus. The position of the resonances in the p_3 and pp_3 complexes is the same as in $[Nb(CO)_4p_2]^-$, indicating that in all three cases stable chelate-five rings are formed. This is further evidenced by the signal pattern for the uncoordinated phosphorus functions (PPh_2; cf. Table 2). Only one signal is observed for $[Nb(CO)_4p_3]^-$ and $[Nb(CO)_4pp_3]^-$, although two inequivalent phosphorus atoms are coordinated to the niobium center. Since an accidential coincidence of $\delta(PPh_2)$, δ(PPh) and δ(P) is unlikely (in fact, more than one signal is observed in the hydrido complexes; vide infra), the P functions appear to be equilibrated by rapid fluxional processes even at 210 K. It is not possible to obtain satisfactorily distinct ^{31}P resonances at temperature above ca. 220 K because of effective scalar and quadrupole interaction with the ^{93}Nb nucleus ($I = 9/2$). However, for the p_2, p_3 and pp_3 derivatives, ^{93}Nb resonances have been obtained (Table 2) which indicate the expected deshielding with respect to $[Nb(CO)_6]^-$. Because of the widths of the signals (several kHz), the parameter $\delta(^{93}Nb)$ as a tool in structure assignment is, in these cases, of restricted value. Nonetheless, the position of the Nb resonance supports the five ring structure of the metallacyclic groups (see the discussion in ref. 9).

Hydridoniobium(I)

On silica gel, THF solutions of $[Et_4N][Nb(CO)_4p_m]$ are converted to hydrido complexes (eq. 2a and 2b):

$$[Et_4N][Nb(CO)_4p_m] \xrightarrow{\sim SiOH} [NbH(CO)_4p_m] + \{Et_4N\} \qquad (2a)$$

$$[NbH(CO)_4p_m] \xrightarrow{(THF)} [NbH(CO)_3p_m] + CO \quad (p_m = p_3, pp_3) \qquad (2b)$$

As shown previously for an analogous conversion of carbonylvanadates [11], silica gel exhibits its dual character as an ion exchanger (via the potentially acidic silanol groups) and as a carrier for absorption chromatography, thus allowing elution of the hydrido complex (eq. 2a), which is then isolated in nearly quantitative yield. In the case of p_2, a labile complex containing four CO groups is formed. For p_3 and pp_3, stabilization by elimination of a thrid CO and formation of a bicyclic structure occurs (eq. 2b). This takes only a few minutes. Very similar behaviour has been

TABLE 2

NMR DATA

Complex [a]	$\delta(^{31}P)_c$ [b]	$\delta(^{31}P)_{uc}$ [c] ($J(PP)$)	$\Delta\delta(P)$ [d]	$\delta(^{93}Nb)$ [e]	$\delta(^1H)$	Spin system [f]	$J(HP_A)$	$J(HP_B)$ [g]
$[Nb(CO)_6]^-$				−1672 [h]				
cis-$[Nb(CO)_4p_2]^-$	53.4		68.7	−1490				
cis-$[Nb(CO)_4p_3]^-$	53.4	−15.5d [35]	68.7	−1520				
cis-$[Nb(CO)_4pp_3]^-$	54.6	−14.8d [32]	68.1	−1620				
$[NbH(CO)_4p_2]$	45.8	61	61.1		−3.80	A_2X		18
$[NbH(CO)_3p_3]$	76.5 [i], 63.5,60.2		93.1 [i], 78.7,73.0	−1550	−2.94	A_2BX [j]	31	12
$[NbH(CO)_3pp_3]$	78.5 [k], 68.5,63.2	−15.0d [30]	96.3 [k], 82.0,76.7	−1100	−3.04	A_2BX	30.5	11
$[NbH(CO)_2(dmpe)_2]$ [l]	49, 27				−4.46	A_2B_2X	92	14

[a] Abbreviations: $p_2 = Ph_2PCH_2CH_2PPh_2$, $p_3 = PhP(CH_2CH_2PPh_2)_2$, $pp_3 = P(CH_2CH_2PPh_2)_2$, dmpe $= Me_2PCH_2CH_2PMe_2$. [b] For coordinated P (PPh_2 if not indicated otherwise) at 210 K. [c] For uncoordinated P, d = doublet. [d] Coordination shift = $\delta(^{31}P)_c - \delta(^{31}P)$ [free phosphinel]. [e] Relative to $NbOCl_3$ at 302 K. [f] X is the hydride ligand. The spin systems indicated (room temperature spectra) give rise to a triplet (p_2), a doublet of triplets (intensity ratio 1/1/2/2/1/1; p_3 (cf. Fig. 1b) and pp_3) and a triplet of triplets (dmpe). [g] In the case of p_3 and pp_3, P_B is the bridgehead phosphorus. [h] From ref. 10. [i] Bridge-head PPh. [j] At 225 K, a triplet due to line broadening is observed; the triplet coalesces around 210 K, and at 190 K, there is a four-line system (ABCX, $J(HP_A)$ 20, $J(HP_C)$ 24 Hz, $J(HP_B)$ unresolved; see Fig. 1b) at 2.48 ppm. [k] Bridge-head P. [l] From ref. 8.

observed for the [VH(CO)$_n$p$_m$] complexes except that monocyclic structures (p$_m$ = p$_2$) are rather stable, and the formation of metallabicyclic groups (p$_m$ = p$_3$, pp$_3$) takes hours to days.

The ^{31}P NMR spectra of [NbH(CO)$_3$p$_3$] and [NbH(CO)$_3$pp$_3$] at 210 K show three signals of like intensities (Fig. 1a). The low-field (high-frequency) resonance at ca. +77 ppm corresponds with the bridge-head phosphorus of the bicyclic structure, while the two adjacent resonances at higher field, cf. Table 2, come from the two PPh$_2$ groups, the non-equivalence of which appears to be achieved by a fixed, asymmetrical position of the hydride ligand at low temperatures. This is illustrated in Fig. 1b, where the hydride region of the ^{1}H NMR spectrum of [NbH(CO)$_3$p$_3$] is given at room temperature (A_2BX) and at 190 K (A^1A^2BX). B is the bridge-head P and A^1 and A^2 are the PPh$_2$ groups.

The ^{1}H NMR spectral patterns in the hydride region at room temperature are consistent with a pseudo-octahedral {Nb(CO)$_n$p$_m$} unit and H$^-$ wandering between all those faces which do not contain edge-spanning chelate back-bones. This model of restricted fluxionality has been applied successfully to interpret the spectra of [VH(CO)$_n$p$_m$] complexes [11]. On the basis of structural similarities to [TaH(CO)$_2$(dmpe)$_2$], which has been characterized by an X-ray analysis [16], the face-capped octahedron has also been proposed for the structure of the related [NbH(CO)$_2$(dmpe)$_2$] [8]. Alternatively, a pentagonal bipyramid as established for the solid state structures of [VH(CO)$_4$p$_2$] [17] and [TaH(PPh$_3$)$_2$(dmpe)$_2$] [18] with

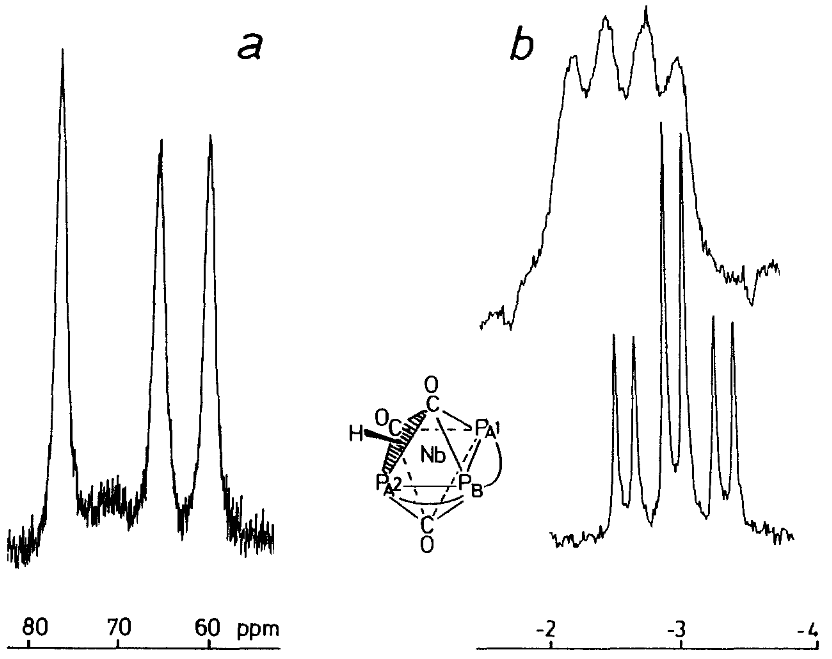

Fig. 1. ^{31}P{^{1}H} (a) and ^{1}H (hydride region) (b) NMR spectra of [NbH(CO)$_3$PhP(CH$_2$PPh$_2$)$_2$]$^-$. The spectra were obtained at 210 (a), 302 and 190 K (b). A structure based on the face-capped octahedron is assumed, and one of the "allowed" [11] position for the hydride ligand is indicated. At room temperature, there are four equivalent positions for H$^-$, and P$_{A^1}$ and P$_{A^2}$ are equilibrated. At ca. 210 K, the structure becomes rigid.

H^- occupying one of the corners of the basic pentagon, might be considered.

The ^1H nucleus of the hydride ligand is deshielded with respect to the analogous vanadium hydrides by 1.2 (p_2) to 1.6 (p_3) ppm. This is in accord with proposals by Buckingham and Stephens [19,20], according to which the ^1H shielding in a series of similar complexes decreases with increasing H–metal bond length. The coupling observed in the ^1H spectra is merely due to scalar interaction between ^1H and ^{31}P. Coupling to the ^{93}Nb nucleus, as observed in $[Nb(Cp)H(CO)_3]^-$ [21,22], is suppressed by fast relaxation. The presence of a H–Nb bond is, however, established by a (comparatively broad) $\nu(NbH)$ at 1600 cm^{-1} of medium intensity, which compares with $\nu(NbH)$ 1550 cm^{-1} in $[NbH(CO)_2(dmpe)_2]$ [17]. Thermolysis of the hydrido complexes in toluene yields a red-brown, still unidentified powder characterized by a single IR absorption at 1760 cm^{-1}.

Experimental

General

Phosphines were purchased (Ventron). $Na[Nb(CO)_6]$ was prepared according to a recently published normal pressure synthesis by Calderazzo et al. [23] from $NbCl_5$, CO and Zn/Mg in pyridine. (We did not succeed reproducing Ellis' alternative normal pressure route to $[Nb(CO)_6]^-$ via CO treatment of $NbCl_5$/lithium methylnaphthalide [24].) $[Et_4N][Nb(CO)_4p_2]$ was prepared as described previously [9,10]. Silica gel (Kieselgel 60, 70–230 mesh ASTM, Merck) was degassed for 1 h (room temperature, 1 Torr) and saturated with N_2. All operations were carried out under nitrogen and in anhydrous solvents.

Irradiations were carried out in a DEMA irradiation apparatus (Mangels, Bonn) of ca. 100 ml capacity, fitted with a water-cooled quartz immersion well and a sintered disc to allow passage of N_2 through the solution during irradiation. UV source was a high pressure mercury lamp (Hanau, 125 W at 220 V). The photo-reaction was monitored by IR and stopped, when all bands belonging to $[Nb(CO)_6]^-$ and $[Nb(CO)_5p_m]^-$ had disappeared. Prolonged irradiation times resulted in slow decomposition of the compounds; no trisubstituted species were formed. Before analysis, all complexes were dried for 4 h under high vacuum.

Spectroscopic measurements

IR: Perkin-Elmer 577, 0.02 *M* THF in 0.1 mm KBr cuvettes. ^1H-NMR: Bruker WP 80 and WH 90, THF-d_8 solutions, external lock acetone-d_6. $^{31}P\{^1H\}$: Bruker WH 90, 0.05 THF solutions, external lock acetone-d_6, external standard 80% H_3PO_4. ^{93}Nb: Bruker SWL 3-100, 0.1 *M* THF (plus a few drops of NCMe to improve the solubility) at 302(2) K, ν_0 11.0 MHz, central field B_0 1.0585 T, modulation amplitude 1 mT, external standard $NbCl_5$/MeCN (B_s 1.0564 T). $\delta(^{93}Nb)$ values are quoted relative to $NbOCl_3$ (δ 0 ppm; $\delta(NbCl_5)$ −450 ppm). Absolute error ±20 (anionic complexes) to ±70 ppm (hydrido complexes).

Preparation of complexes

$[Et_4N][Nb(CO)_6]$. 200 ml of an ether solution of $Na[Nb(CO)_6]$ obtained from 18 g (66.6 mmol) of freshly sublimed $NbCl_5$ as described in ref. 23, were treated with 200 ml of diglyme. The solution was concentrated to 200 ml and to this resulting orange solution, a solution of 14.06 g of well dried $[Et_4N]Br$ (67 mmol) in 60 ml of ethanol was added dropwise with stirring during 5 min. The stirring was maintained, and 600 ml of O_2-free water were added during 10 min to precipitate canary yellow $[Et_4N][Nb(CO)_6]$, which was immediately filtered off, washed with three 50 ml portions of water, and dried for 6 h under high vacuum to yield 8.4 g (31%) $[Et_4N][Nb(CO)_6]$. Its solutions in THF or MeCN are extremely air-sensitive. As a solid the compound is slightly light-sensitive, but can be handled in air for several minutes without apparent change.

$[Et_4N][Nb(CO)_4PhP(CH_2CH_2PPh_2)_2]$. A solution of 396 mg (1.01 mmol) $[Et_4N][Nb(CO)_6]$ and 570 mg (1.06 mmol) of p_3 in 100 ml THF was irradiated for 4.5 h. The dark red solution was filtered, concentrated to 10 ml, then treated with 20 ml n-pentane, with vigorous stirring. The dark-red powder which separated was filtered off, washed with pentane, and dried. Yield 720 mg (82%). Analysis: Found: C, 62.9; H, 6.7; N, 1.56. $C_{46}H_{53}NNbO_4P_3$ (869.7) calcd.: C, 63.47; H, 6.10; N, 1.60%.

$[Et_4N][Nb(CO)_4P(CH_2CH_2PPh_2)_3]$. A solution of 593 mg (1.52 mmol) $[Et_4N][Nb(CO)_6]$ and 1.1 g (1.64 mmol) pp_3 in 100 ml THF was irradiated for 110 min. Concentration to 20 ml and addition of 20 ml n-pentane yielded a dark-red, viscous oil. The supernatant solution was decanted and the oil was washed twice with 3 ml portions of pentane. The tarry residue thus obtained solidified under vacuum with considerable increase in volume. After pulverization, 1.16 g (76%) of red, air-sensitive $[Et_4N][V(CO)_4pp_3]$ were isolated. Analysis: Found: C, 64.1; H, 6.0; N, 1.42. $C_{54}H_{62}NNbO_4P_4$ (1005.8) calcd.: C, 64.48; H, 6.21; N, 1.39%.

$[NbH(CO)_4Ph_2PCH_2CH_2PPh_2]$. A solution of 1.3 g $[Et_4N][Nb(CO)_4p_2]$ (1.77 mmol) in 10 ml THF/MeCN, was transferred to a silica gel column (8 × 6 cm) and eluted with 200 ml THF. The first fraction yielded an orange yellow solution of $[NbH(CO)_4p_2]$. The complex, which was characterized by its IR and NMR patterns, can be isolated by precipitation with pentane (orange yellow powder). Neither the THF solution nor the solid are stable, which is indicated by a decomposition band in the IR at 1830 cm^{-1} which rapidly increases in intensity. A red zone, which remains at the top of the column can be eluted with MeCN, and contains hydrido complex and $[Nb(CO)_6]^-$.

$[NbH(CO)_3PhP(CH_2CH_2PPh_2)_2]$. A solution of 560 mg (0.64 mmol) $[Et_4N][Nb(CO)_4p_3]$ in 10 ml THF containing a few drops of MeCN was transferred to a silica gel column (14 × 3.5 cm). During the elution, with a total of 150 ml of THF, CO was liberated. The orange yellow THF solution was concentrated to 10 ml and $[NbH(CO)_3p_3]$ was precipitated by addition of 25 ml n-pentane. Yield: 400 mg (88%) of a yellow orange, powdery product. Analysis: Found: C, 62.6; H, 5.2. $C_{37}H_{35}NbO_3P_3$ (713.5) calcd.: C, 62.29; H, 4.94%.

$[NbH(CO)_3P(CH_2CH_2PPh_2)_3]$. This compound was prepared as described for $[NbH(CO)_3p_3]$ from 500 mg (0.55 mmol) $[Et_4N][Nb(CO)_4pp_3]$ dissolved in 5 ml THF. The orange eluate was evaporated to dryness, and the residual red-orange oil was washed twice with 2 ml portions of n-pentane, and then solidified under high vacuum. Yield 290 mg (62.5%) of an orange powder. Analysis: Found: C, 63.6; H, 5.4. $C_{45}H_{43}NbO_3P_4$ (848.6) calcd.: C, 63.70; H, 5.10%.

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