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VI *. DERIVATIVES OF $[Nb(\eta^5\text{-}C_5H_5)H(CO)_3]^-$ CONTAINING A NIOBIUM-METAL BOND

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Summary

The complexes $[Et_4N][Nb(Cp)M'R_n(CO)_3]$ ($M'R_n = AuPPh_3$; $SnEt_3$, $SnBz_3$, $SnPh_3$; $GePh_3$; $PbEt_3$, $PbPh_3$) have been prepared from $[Nb(Cp)H(CO)_3]^-$ generated in situ, and characterized by IR and ^{93}Nb NMR spectroscopy. ^{93}Nb shielding increases in the order $AuPPh_3 < PbPh_3 < GePh_3 < SnPh_3 \approx SnBz_3$. The possible formation of intermediate contact ion-pairs $[R_nM']^+[Nb(Cp)H(CO)_3]^-$ is discussed.

Introduction

Metal–metal bonds in carbonyl complexes involving a metal of the vanadium triad have been known for several years. The complexes can be regarded as being derived from $[MH(CO)_6]$ (examples for M = Nb are $[Nb(SnPh_3)(CO)_5PPh_3]$, $[Nb(AuPPh_3)(CO)_6]$, $[Nb(HgEt)(CO)_6]$ [1,2] and $[M(H)_3(CO)_5]$ or $[MH(CO)_5]^{2-}$ ($[Nb(SnPh_3)(CO)_5]^{2-}$ [3]), with the transition metal M in the formal oxidation state +I and −I, respectively, if the $M'R_n$ ligand is taken to be negative.

Isoelectronic with the seven-coordinate, neutral complexes are the systems $[MCp(M'R_n)(CO)_3]^-$. To date, only a few examples with vanadium in the coordination center have been described, namely $[VCp(SnPh_3)(CO)_3]^-$ [4], $[VCp(M'Cl_3)(CO)_3]^-$ (M' = Sn, Ge) [5], and $[VCp(SnCl_3)_2(CO)_2]^{2-}$ [6]. We have now obtained several niobium complexes of the general formula $[NbCp(M'R_n)(CO)_3]^-$, which may be considered to be related to a parent compound $[NbCp(H)(CO)_3]^-$ or $[NbCp(H)_2(CO)_3]$. The ^{93}Nb NMR parameters of these complexes are of interest in the light of the continuing discussion of the factors influencing variations in metal shielding.

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* See ref. 17 for part V.

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Preparation

We recently showed that reduction of $[NbCp(CO)_4]$ by sodium amalgam in THF gives the hydrido complex $[NbCp(H)(CO)_3]^-$ [7], presumably (IR evidence) via a short-lived $[NbCp(CO)_3]^{2-}$ with a niobium center of substantial basic character. Treating a THF solution of $Na[NbCp(H)(CO)_3]$ with $R_nM'Cl$ yields intermediates which are characterized by their CO stretching frequencies and by ^{93}Nb NMR patterns very similar in several respects, to $[NbCp(H)(CO)_3]^-$. These intermediates may be formulated as $[R_nM']^+[NbCp(H)(CO)_3]^-$ (vide infra). Addition of $[Et_4N]Cl$ in CH_3CN and a trace of water immediately produces solutions with different IR and NMR characteristics, from which the complexes $[Et_4N][NbCp(M'R_n)(CO)_3]$ can be isolated in the form of oxygen-sensitive, yellow to red powders or crystalline products *. The same conversion occurs when the THF solution is allowed to stand for several hours. The overall reaction can be tentatively represented by the Scheme 1.

$$\begin{tikzcd}
{[NbCp(CO)_4]} \arrow[r, "Na/Hg", "THF"'] & \{Na_2[NbCp(CO)_3]\} \arrow[r] & Na[NbCp(H)(CO)_3] \arrow[d, "R_nM'Cl", "(THF)"'] \\
 & & R_nM'[NbCp(H)(CO)_3] \arrow[d, "{[Et_4N]Cl}", "{CH_3CN,H_2O}"'] \\
 & & {[Et_4N][NbCp(M'R_n)(CO)_3]}
\end{tikzcd}$$

$M'R_n =$		
	$GePh_3$	light-yellow
	$SnPh_3$	yellow
	$SnBz_3$	canary-yellow
	$PhPh_3$	red
	$AuPPh_3$	red-brown

SCHEME 1

Discussion

The IR (ν(CO)) and ^{93}Nb NMR data are listed in Table 1.

Freshly prepared THF solutions of $R_nM'Cl/Na[NbCp(H)(CO)_3]$ exhibit three CO stretching frequencies, at about 1900, 1815, and 1760 cm^{-1}, which are closely related to the ν(CO) bands of $Na[NbCp(H)(CO)_3]$ (in $[Et_4N][NbCp(H)(CO)_3]$, the two CO bands at lower wave numbers combine to one broad absorption signal), and hence may still contain the $[Nb(H)(CO)_3]$ moiety. This view is supported by the fact that sharp ^{93}Nb NMR signals at -1540 ($GePh_3$ and $SnPh_3$), -1598 ($PbPh_3$) and -1480 ppm ($AuPPh_3$) are observed, comparable to the halfwidth of $Na[NbCp(H)(CO)_3]$. The substantial downfield shift of the resonance signals relative to the parent compound, on the other hand, indicates a significant influence of the triorganyl metal unit. Such an influence reflects direct Nb–M′ contact. This direct interaction can be achieved either by strong contact ion-pair formation (eq. 1), with

$$[R_nM']^+\cdot solv + [NbCp(H)(CO)_3]^-\cdot solv \rightleftharpoons [R_nM']^+[NbCp(H)(CO)_3]^- + solv \tag{1}$$

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* *Note added in proof*: An X-ray structure analysis of the triphenyltin compound showed that the unit cell contains one molecule $[Et_4N][NbCp(SnPh_3)(CO)_3]$ plus a statistical number of 2.4 H_2O. The complex crystallizes in the space group $P2_1/n$. The three CO groups and the $SnPh_3$ ligand span a plane parallel to the Cp ring. The Nb–Sn bond length is 282 pm (F. Näumann, J. Kopf and D. Rehder, unpublished).

TABLE 1

ν(CO) AND ^{93}Nb NMR DATA FOR $[NbCp(H)(CO)_3]^-$ DERIVATIVES[a]

Complex		ν(CO) (cm^{-1})	Phase	$\delta(^{93}Nb)$ (ppm)[b]	$\Delta\nu_{1/2}$ (kHz)[c]
$[Et_4N][VCp(H)(CO)_3]$		1889s, 1775vs,br	MeCN	−1730	0.13
$[Et_4N][NbCp(H)(CO)_3]$[d]		1900vs, 1789vs,br	MeCN	−1802	0.16
$Na[NbCp(H)(CO)_3]$		1897s, 1799vs,br, 1739vs	THF	−1735	sharp
$[R_nM']^+/Na[NbCp(H)(CO)_3]$[e]					
R_nM' =	Ph_3Ge	1903s, 1815vs, 1760s	THF	−1541	sharp
	Ph_3Sn	1897vs, 1806vs, 1759s	THF	−1540	sharp
	Et_3Sn	1887vs, 1800vs, 1750s	THF		
	Ph_3Pb	1909s, 1820vs, 1770s	THF	−1598	sharp
	Et_3Pb	1894vs, 1869s, 1812vs	THF		
	Ph_3PAu	[f]	THF	−1480	sharp
$[Et_4N][VCp(SnPh_3)(CO)_3]$		1891s, 1895s,br	hmpa, THF	−2054	<100
$[Et_4N][NbCp(M'R_n)(CO)_3]$					
$M'R_n$ =	$GePh_3$	1900vs, 1795vs,br	THF/MeCN	−1625	10.1
		1893vs, 1797sh/1776vs[g]	KBr		
	$SnPh_3$	1897vs, 1800/1781vs[g]	THF	−1700	9.3
		1890vs, 1799/1770vs[g]	KBr		
	$SnBz_3$	1881vs, 1782/1764vs[g]	KBr	−1700	11.4
	$SnEt_3$	1881vs, 1780vs,br	THF/MeCN		
		1882vs, 1787/1769vs[g]	KBr		
	$PbPh_3$	1907vs, 1811/1800vs[g]	THF	−1510	18.7
		1899vs, 1807vs,1788/1766vs[g]	KBr		
	$PbEt_3$	1897vs, 1805vs,br	THF/MeCN		
	$AuPPh_3$	1896vs, 1847/1827vs[g]	THF/MeCN	−1390	10.3
		1899vs,br, 1812vs,br	KBr		

[a] For comparison, the ν(CO) and $\delta(^{51}V)$ (rel. $VOCl_3$) of $[VCp(SnPh_3)(CO)_3]^-$ and $[VCp(H)(CO)_3]^-$ are included (data from refs. 4, 8 and 12). [b] Relative to $NbOCl_3$. [c] Half-widths; signals indicated "sharp" have a maximum width of 1 kHz (modulation broadening). [d] Ref. 7. [e] See text for discussion. [f] Cannot be assigned unambiguously because the CO pattern of $[NbCp(AuPPh_3)(CO)_3]^-$ is superimposed. [g] Incompletely resolved.

the equilibrium position largely shifted to the right (for $PbPh_3$ to a lesser extent than for $GePh_3$ and $SnPh_3$), or by participation of species containing the ligand $M'R_n$ in the first coordination sphere (eq. 2).

$$[R_nM']^+\cdot \text{solv} + [NbCp(H)(CO)_3]^- \rightleftharpoons [NbCp(M'R_n)(CO)_3]^- + H^+\cdot \text{solv} \qquad (2)$$

In either case, the exchange has to be sufficiently fast to provide the narrow signals which are observed in the ^{93}Nb NMR.

Addition of $[Et_4N]Cl/CH_3CN$ and water results in removal of the hydrido ligand and its replacement by the $M'R_n$ group, which formally becomes a negatively charged, two-electron donating ligand. The solution IR spectra of the tetraethylammonium salts show a strong ν(CO) around 1900 and a very broad, poorly resolved band at ca 1790 cm^{-1}; the ^{93}Nb NMR spectra exhibit broad resonance lines (half-widths ca. 10 kHz).

The ^{93}Nb shielding for the complexes $[Et_4N][NbCp(M'R_n)(CO)_3]$ increases in the order $AuPPh_3 < PbPh_3 < GePh_3 < SnPh_3 \approx SnBz_3$. For the complexes with

Group IVa triorganyls, this is the same sequence as reported for ^{55}Mn shielding in [Mn(M'R$_3$)(CO)$_5$] [9,10], ^{59}Co shielding in [Co(M'R$_3$)(CO)$_4$] [11], and ^{51}V shielding in [V(Cp)(M'R$_3$)(CO)$_3$]$^-$ and [V(M'R$_3$)(CO)$_5$PPh$_3$] [12]. This shielding pattern is also reminiscent of the sequence BiR$_3$ < AsR$_3$ < SbR$_3$ for carbonylvanadium [13] and carbonylmolybdenum complexes [14]. In both series the ligand belonging to the fifth period induces the largest metal shielding.

To explain this phenomenon we must briefly consider the theory of metal shielding. The overall shielding σ' is usually expressed as the sum of three terms, i.e.

$$\sigma' = \sigma_{para} + \left(\sigma^{\text{local}} + \sigma^{\text{non-local}}\right)_{\text{dia}}$$

The local diamagnetic contribution, which is dominated by the core electrons, is practically constant for a given nucleus. The non-local diamagnetic term is assumed to increase with increasing nuclear charge on the ligand function attached to the metal in the coordination center. In our case, an increase of ^{93}Nb shielding in the order Ge < Sn < Au $\lesseqgtr$ Pb is to be expected. While the non-local term, which is commonly considered to be negligibly small, may add to the observed ordering of the Ge and Sn complexes, it clearly cannot explain the inverted orders of Ge,Sn/Pb and Pb/Au and the large gap between Pb and Au. In fact, the variations in $\delta(^{93}\text{Nb})$ are dominated by variations in the paramagnetic deshielding term which, in the closure approximation, can be given as

$$\sigma_{para} = \text{const.}\overline{\Delta E}^{-1} \cdot \langle r^{-3} \rangle_{4d} \cdot C^2_{\text{Nb}(4d)},$$

where $\overline{\Delta E}$ is the mean excitation energy, r the distance of the Nb-4d electrons from the Nb nucleus, and C the Nb(4d) LCAO coefficient.

Apparently there are two counter-acting effects upon σ', namely (i) influences via ΔE, i.e. an increase of σ_{para} (decrease of σ') with decreasing ligand strength down Group IVa, and (ii) influences via $\langle r^{-3} \rangle C^2$. This latter factor represents nephelauxetic and covalency effects and should lead to a fall in σ_{para} (enhanced σ') as the polarizability (or the Pearson basicity) of the ligating function increases and its electronegativity χ * decreases. Thus, while the low-field position of the complex containing the weakly interacting lead ligand is a consequence of the small ΔE, the sequence SnR$_3$ > GeR$_3$ reflects the large nephelauxetic effect (small $\langle r^{-3} \rangle$) and small C_{Nb} for the tin complex, which over power the influences arising from the ligand field splitting.

Experimental

Spectroscopic measurements

IR spectra were recorded on a Perkin–Elmer 577 spectrometer under the conditions indicated in Table 1. The ν(CO) were recorded to ± 1 cm^{-1}, but for broad and poorly resolved bands, the absolute error may amount to ± 5 cm^{-1} or more.

The ^{93}Nb NMR spectra were recorded on a Bruker wide-line SWL 3-100 spectrometer fitted with an adapted Varian 4230B (8–16 MHz) probe head, at 16.0 MHz and a central magnetic field of 15.38 T, as ca. 0.1 *M* THF of THF/CH$_3$CN solutions in 14 mm diameter vials. The probe temperature was 298–300 K, and the

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* χ values for the four ligand functions are: Ge$^{\text{IV}}$ 1.78, Sn$^{\text{IV}}$ 1.58, Pb$^{\text{IV}}$ 1.56, Au$^{\text{I}}$ 1.26 [15].

reference was a saturated solution of $NbCl_5$ in dry CH_3CN. The resonances were obtained as the first derivative of the absorption signal. Typical measuring conditions are: sweep width 6 mT, modulation amplitude 0.4 mT (0.1 mT for signals indicated "sharp" in Table 1), *rf* field at maximum setting, scan number 30. $\delta(^{93}Nb)$ are quoted relative to $NbOCl_3$ (δ 0; $\delta(NbCl_5)$ +450 ppm), with a negative sign for signals at high field of the reference. The absolute error is ca. ± 10 ppm. Peak-to-peak line widths were converted to half-widths by multiplication with $\sqrt{3}$; absolute error ±0.7 kHz.

Preparative procedure

All operations were carried out under N_2.

A solution of 220 mg of $[NbCp(CO)_4]$ [16] (0.81 mmol) in 10 ml THF was treated with 20 g of 0.8% sodium amalgam. After 3 h stirring (room temperature) the brown solution (of $Na[NbCp(H)(CO)_3]$) was decanted from the excess Na/Hg and added to a solution of 390 mg Ph_3SnCl (1.0 mmol) in 5 ml THF at −20°C. The solution was stirred for 15 min, during which it was allowed to warm to +5°C, and than showed the IR and NMR pattern noted for $[SnPh_3]^+/Na[NbCp(H)(CO)_3]$ in Table 1. A solution of 150 mg $[Et_4N]Cl$ (0.90 mmol) in 3 ml CH_3CN and 0.1 ml of O_2-free water were then added, and the suspension was stirred for a few minutes. The solution, which contained $[Et_4N][NbCp(SnPh_3)(CO)_3]$, was evaporated to dryness (in vacuo, at room temperature), and the residue was triturated with 5 ml water and filtered off. This procedure was repeated three times, the filtrates being discarded. Residual water was then removed in vacuo, and the powdery product was dissolved in 5 ml THF. The solution was filtered and the filtrate decanted from small amounts of metallic impurities. To the yellow-orange solution thus obtained n-heptane (ca. 1 ml) was added with stirring until the solution turned turbid. After several days at −18°C yellow, needle-like crystals separated. These were filtered off, washed with 3 ml n-heptane, and dried for 5 h under high vacuum. Found: C, 55.50; H, 5.62; N, 2.36. $C_{34}H_{40}NNbO_3Sn$ (722.28) calcd.: C, 56.54; H, 5.58; N, 1.97%.

The reactions with Bz_3SnCl and Ph_3PbCl were carried out analogously to yield yellow (tribenzyltin complex) or red (triphenyllead complex) needle-like crystals. $[Et_4N][NbCp(SnBz_3)(CO)_3]$: Found: C, 56.96; H, 6.32; N, 2.11. $C_{37}H_{46}NNbO_3Sn$ (764.31) calcd.: C, 58.14; H, 6.07; N, 1.83%. $[Et_4N][NbCp(PbPh_3)(CO)_3]$: Found: C, 50.53; H, 5.23; N, 1.74. $C_{34}H_{40}NNbO_3Pb$ (810.80) calcd.: C, 50.37; H, 4.97; N, 1.73%.

The reactions with Et_3SnCl, Ph_3GeCl, Et_3PbCl and Ph_3PAuCl were carried out analogously to yield yellow ($GePh_3$) and red-brown ($AuPPh_3$) powders. The complexes could not be isolated in analytically pure form; the germanium and gold complexes tend to decompose in the presence of CH_3CN and during the isolation procedure. No reaction was observed with Ph_3SiCl; addition of $AlCl_3$ resulted in complete decomposition.

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