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## III *. TRICARBONYL-$\eta^5$-CYCLOPENTADIENYLHYDRIDONIOBATE(–I): PREPARATION AND $^{93}$Nb NMR SPECTROSCOPIC INVESTIGATION OF $[Et_4N][CpNb(H)(CO)_3]$ AND $[Et_4N][CpNb(D)(CO)_3]$

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### Summary

The complexes $[Et_4N][CpNb(X)(CO)_3]$ (X = H, D) have been prepared by reduction of $CpNb(CO)_4$ in THF and subsequent treatment with $CX_3CN/[Et_4N]Cl$. There is IR-spectroscopic evidence for the formation of an intermediate $[CpNb(CO)_3]^{2-}$. The isotope effect ($^1H$, $^2H$) on the $^{93}Nb$ shielding (6 ppm) and the temperature dependencies of $\delta(^{93}Nb)$ (0.25 ppm/deg) and the line widths are discussed.

### Introduction

We have recently shown that $[CpV(CO)_3]^{2-}$, obtained by the reduction of $CpV(CO)_4$ in THF [1], liquid $NH_3$ [2] or HMPA [3] is converted to the hydrido complex $[CpV(H)(CO)_3]^-$ in the presence of acetonitrile [4]. This anion, which can be stabilized by precipitation with $[Et_4N]^+$, was also obtained by Bergman and co-workers by reaction of $Na_2[CpV(CO)_3]$ with $H_2O/THF$ [5]. Bergman has extensively studied the chemistry of this anionic hydridovanadium species [5,6].

### Results and discussion

We have now successfully applied our method for the preparation of $[Et_4N][CpNb(X)(CO)_3]$, where X = H or D. The complexes are formed according to equation 1.

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$$\mathrm{CpNb(CO)_4} \xrightarrow[\mathrm{THF}]{\mathrm{Na/Hg}} [\mathrm{CpNb(CO)_3}]^{2-} \xrightarrow{\mathrm{CX_3CN}} [\mathrm{CpNb(X)(CO)_3}]^{-} \tag{1}$$

It appears that the niobium centre in the dianion is more basic than the vanadium centre in the analogous vanadium complex, i.e. the intermediate $Na_2[CpNb(CO)_3]$ cannot be isolated in pure form. There are, however, absorptions in the CO stretching region which clearly indicate that this yet unknown anion is formed (Table 1). Two additional bands at 1850 and 1812 $cm^{-1}$, which appear after 10 min of reduction and slowly dissappear in the course of the reaction, may be attributed to a hydrido-bridged species $[\{CpNb(CO)_3\}_2\mu\text{-}H]^-$ by analogy with a corresponding vanadium complex suggested by Bergman [5] and Jones [10] (cf. Table 1). The complete conversion into the hydrido complex is readily brought about by addition of a solution of $[Et_4N]Cl$ in acetonitrile.

If the reaction is carried out in TDF and $CD_3CN$, an approximate 1/1 mixture of $[CpNb(H)(CO)_3]^-$ and $[CpNb(D)(CO)_3]^-$ is obtained, which is stable in its composition at room temperature. If the $CD_3CN$ solution is kept at elevated temperatures (320 K and more), the $H^-$ ligand is progressively replaced by $D^-$. The H/D exchange is revealed by the $^{93}Nb$ NMR spectra (Fig. 1). Similarily, a solution of $[CpNb(H)(CO)_3]^-$ in $CD_3CN$ is stable below 305 K in absolutely dry $CD_3CN$, but immediate conversion to the deuterido complex occurs (even at room temperature), if small amounts (ca. 1%) of $D_2O$ are added. This exchange does not take place in a solution of $[CpNb(H)(CO)_3]^-$ in $CH_3CN$ + ca. 1% $D_2O$.

The formation of considerable amounts of $[CpNb(H)(CO)_3]^-$ during the reaction in deuterated solvents suggests that hydrogen reacts more readily than deuterium. This observation can be accounted for in terms of $H^+$ being the more electrophilic agent, or by kinetic considerations (i.e. a greater mobility of $H^+$ as compared to $D^+$ and/or a sterically reduced tendency for the niobium centre to ligate the larger D). Since there is no exchange of H for D at room temperature in the absence of $D_2O$, hydrogen transfer to $[CpNb(CO)_3]^{2-}$ is probably achieved by direct reaction between $[CpNb(CO)_3]^{2-}$ and $CX_3CN$ rather than by interaction of (catalytically acting) proton-active impurities such as $X_2O$.

On the other hand, $H^-$ is easily replaced by $D^-$ at elevated temperatures in dry deutero-acetonitrile, or at room temperature in the presence of $D_2O$. Since the $D_2O$-induced conversion of $[CpNb(H)(CO)_3]^-$ to $[CpNb(D)(CO)_3]^-$ does not occur in $CH_3CN$, the position of the exchange equilibrium is obviously dependent upon the overall H/D ratio, showing that there is no pronounced preference for the bonding of either the $H^-$ or the $D^-$ ligand once the basicity of the metal center is reduced by the attachment of hydrogen.

The overall NMR results are summarized in Table 1 together with IR and NMR data on vanadium complexes of the general formula $[CpV(Y)(CO)_3]^-$. Figure 2 is a graphical presentation of the temperature dependencies of the $^{93}Nb$ chemical shift values, $\delta(^{93}Nb)$ and the half-widths of the NMR signals, $\Delta\nu_{1/2}$. The smooth curves indicate that temperature-dependent exchange equilibria between different Nb species can be excluded. The temperature gradient for $\delta(^{93}Nb)$, 0.25 ppm/deg is somewhat smaller than that for $CpNb(CO)_4$ (0.38 ppm/deg [11]). In accord with theory, shielding of the $^{93}Nb$ nucleus decreases as the temperature increases. The considerable broadening of the resonances at low temperatures is consistent with an increase in the molecular correlation time [12].

The shielding difference between $[CpNb(H)(CO)_3]^-$ (−1802 ppm) and

TABLE I

IR AND NMR DATA FOR $[CpM(CO)_3]^{2-}$ AND $[CpM(Y)(CO)_3]^-$ (M = Nb, V)

| Complex | $\nu(CO)(cm^{-1})$ | | | Phase | $\delta(H^-)$ (ppm) $[\Delta\nu_{1/2}(Hz)]^a$ | $\delta(C_5H_5^-)$ (ppm) | $\delta(M)^b$ (ppm) $[\Delta\nu_{1/2}(Hz)]^a$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| $Na_2[CpNb(CO)_3]^c$ | 1750vs (br) | 1615m (vbr) | | THF | | | | d |
| $Na_2[CpV(CO)_3]$ | 1742s | 1619s | | HMPA | | 4.32 | | 3,5 |
| $[Me_4N]_2[CpV(CO)_3]$ | 1742s | 1630s | | $CH_3CN$ | | | | |
| $Cs_2[CpV(CO)_3]$ | 1748 | 1645 | | Nujol | | | | 8 |
| $[Et_4N][CpNb(H)(CO)_3]$ | 1900vs | 1789vs(br) | | $CH_3CN$ | − 5.6 [360] | 5.38,<br>5.08 | − 1802 [160] | d |
| $[Et_4N][CpNb(H)(CO)_3]$ | 1888s | 1780–1755vs | | Nujol | | | | d |
| $[Et_4N][CpNb(D)(CO)_3]$ | 1899s | 1887vs (br) | | $CD_3CN$ | | | − 1808 [130] | d |
| $[Et_4N][CpV(H)(CO)_3]$ | 1889s | 1775vs (br) | | $CH_3CN$ | − 6.3 [160] | | − 1730 $^e$ | 4 |
| $[P_2N][CpV(H)(CO)_3]$ | 1890 | 1780 | | $CH_3CN$ | − 6.1vbr | 4.57 | | 5 |
| $[P_2N][CpV(CH_3)(CO)_3]$ | 1895 | 1855 | 1775(sh) | THF | | 4.43 | | 5 |
| $[CpV(Br)(CO)_3]^-$ | 1948 | 1855 | 1810 | THF | | 4.83 | | 5 |
| $[(CpV(CO)_3)_2\mu\text{-}H]^-$ | 1857 | 1817 | | THF | | 4.67 | | 5 |
| $[Et_4N][CpV(SnPh_3)(CO)_3]$ | 1891s | 1795s (br) | | HMPA | | | | 3 |
| $[Et_4N][CpV(SnCl_3)(CO)_3]$ | 1950s | 1889m (sh) | 1851vs | $CH_2Cl_2$ | | | | 9 |

[a] Half-width of the resonance signal. [b] M = V: relative to $VOCl_3$. M = Nb: relative to $NbOCl_3$. [c] Not isolated; see text for discussion and for additional bands. [d] This work. [e] Doublet ($^1J(V\text{-}H) = 20$ Hz); $\Delta\nu_{1/2}$ ($^1H$) = 60 Hz.

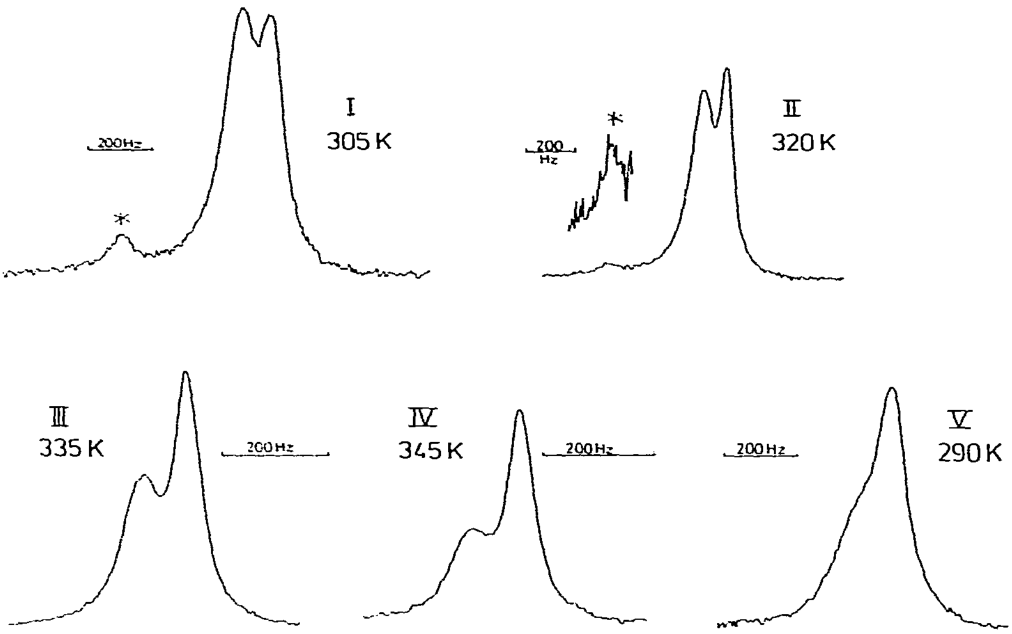

Fig. 1. $^{93}$Nb NMR spectra of [Et$_4$N][CpNb(X)(CO)$_3$] in CD$_3$CN (X = H: left signal, X = D: right signal), showing the substitution of H for D with increasing temperature (I to IV) and the situation after freezing-in (V). The signal indicated * (−1779 ppm at 305 K) is not assigned.

[CpNb(D)(CO)$_3$]$^-$ (−1808 ppm), which can be regarded as an isotope effect upon $^{93}$Nb shielding, is produced by (i) an increase of non-local diamagnetic contributions to the overall shielding [13], and (probably to a much greater extent) (ii) by the decrease of the population of excited vibronic states (decrease of the paramagnetic deshielding contribution [14,15]) on going from H to D. The greater shielding for the deuterium compound is thus an electronic and/or steric effect induced by the apparently more nucleophilic D$^-$ (less electrophilic D$^+$, see above) and the larger deuterium ligand, and compares to the isotope effect observed for CpW(X)(CO$_3$) [22].

Due to the greater line widths of the $^{93}$Nb resonances compared to the $^{51}$V resonances (as a result of the larger electric nuclear quadrupole moment of the former), $^1$H–$^{93}$Nb coupling is not resolved in the $^{93}$Nb spectra. The $^1$H resonance for the H$^-$ is, however, typically broadened by scalar ($I(^{93}\text{Nb}) = 9/2$) and quadrupolar interaction with the niobium. The lower limit for the coupling constant $^1J(^1\text{H}-^{93}\text{Nb})$ as estimated from the line width (360 Hz) is ca. 36 Hz, and hence about twice that for $^1J(^1\text{H}-^{51}\text{V})$ in [CpV(H)(CO)$_3$]$^-$ (20 Hz [4]); this is in accord with observations on the relation between $^1J(^{19}\text{F}-\text{M})$ and $^1J(^{31}\text{P}-\text{M})$ in fluoro and phosphine complexes of the respective metals [17–19]. From the observability of the H–Nb coupling it is also clear that fast inter- or bond-dissociative intramolecular exchange does not occur.

There are two $^1$H resonances for the cyclopentadienyl protons, possibly indicating that the Cp–Nb axis is slightly off the axis of the {Nb(X)(CO)$_3$} moiety, or that rotation of the cyclopentadienyl ring is restricted, and is in contrast with observa-

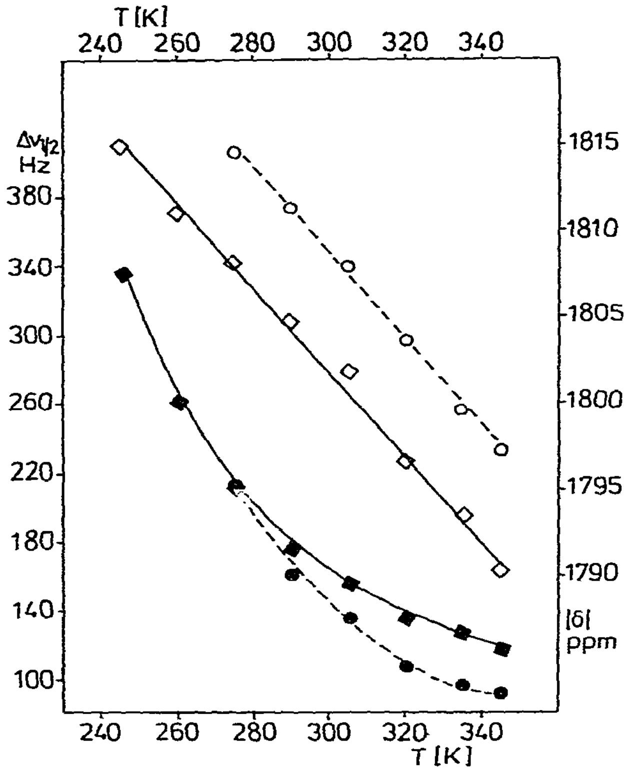

Fig. 2. Temperature vs. $^{93}$Nb chemical shift (right ordinate, open symbols) and half widths of the resonance lines (left ordinate, full symbols) for $[CpNb(X)(CO)_3]^-$: X = H: squares, X = D: circles.

tions on $CpNb(CO)_4$, for which a recent X-ray analysis [16] reveals ideal tetragonal symmetry (3 : 4 geometry). There is only one $^1$H resonance in the corresponding hydrido (and related) vanadium complexes (Table 1).

Another interesting feature is the difference in shielding, $\Delta\delta(M)$, between the hydrido complexes on the one hand and the parent carbonyl $CpM(CO)_4$ on the other. For M = V, the difference is 196 ppm for M = Nb 234 ppm (where the resonance for the hydrido complexes is shifted to higher field). The difference between the two $\Delta\delta(M)$ values, 38 ppm, is of the same order of magnitude as that observed in various phosphine derivatives of $CpM(CO)_4$ [21], and may be accounted for in terms of more predominant local diamagnetic shielding contributions in the Nb complexes or of structural differences between the hydrido complexes of vanadium and niobium, respectively, resulting in different paramagnetic contributions to the overall shielding.

## Experimental

All operations were carried out in dry, oxygen-free solvents under $N_2$. $CpNb(CO)_4$ was prepared according to Herrmann et al. [11,16].

IR spectra were run on a Perkin Elmer 337 spectrometer as ca. 0.01 *M* $CX_3CN$ solutions (0.1 mm KBr cuvettes) or as Nujol mulls. $^1$H NMR spectra were obtained on a Bruker DP 80, $^{93}$Nb NMR spectra on a Bruker WH 90 spectrometer at 22.00 MHz in 7.5 mm diameter vials relative to $NbCl_5/CH_3CN$. $^{93}$Nb chemical shifts are quoted relative to $NbOCl_3$ ($\delta = 0$; $\delta[NbCl_5] = +450$ ppm); absolute error at constant (± 1 deg) temperature is less than 1 ppm.

*$[Et_4N][CpNb(H)(CO)_3]$*

A solution of 1.27 g (4.7 mmol) $CpNb(CO)_4$ in 40 ml THF was added to 300 g of sodium amalgam (containing 1% sodium) and the mixture was stirred for 3 hours. During this time, the colour changed from red to dark brown and a powder (a mixture of $Na_2[CpNb(CO)_3]$ and $Na[CpNb(H)(CO)_3]$) separated. The powder was brought into suspension, and the suspension was poured off and evaporated to dryness (room temperature). The pasty brown residue was dissolved in 35 ml $CH_3CN$ containing 0.78 g (4.7 mmol) of rigorously dried (high vacuum, 100°C) $[Et_4N]Cl$, and stirred for 15 min. The dark green solution which formed immediately was filtered (to remove most of the NaCl), and the residue on the filter extracted twice with 10 ml portions of 5% $[Et_4N]Cl/CH_3CN$. The combined filtrates were evaporated to dryness, the brown powder washed twice with 5 ml portions of $O_2$-free $H_2O$ and freed from water by suction. For purification, the moist rawproduct was redissolved in 10 ml of $CH_3CN$. Treatment with 10 ml of n-heptane produced a fluid, red-brown oil. The supernatant heptane layer was discarded, and 20 ml THF were added with vigorous stirring to the remainder. The brown powder thus obtained was filtered off and dried under high vacuum (5 hours) to yield ochre $[Et_4N][CpNb(H)(CO)_3]$. Yield 1.0 g (57%). The complex is highly air-sensitive, slightly soluble in THF (red solution) and readily soluble in $CH_3CN$ (green solution). Found: C, 45.2; H, 7.3; N, 3.8; Nb, 25.9. $C_{15}H_{26}NNbO_3$ (361.28) calcd.: C, 49.87; H, 7.25; N, 3.88; Nb, 25.72%. The repeatedly low carbon values may result from incomplete combustion of C due to the formation of niobium carbide.

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