Carbonylniobium Chemistry, IV [1] Derivatives of $\eta^5\text{-C}_5\text{H}_5\text{Nb(CO)}_4$ with Tridentate Phosphines

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Z. Naturforsch. **38b**, 446–448 (1983); received December 17, 1982

Carbonylniobium, 1,4,7-Triphosphaheptanes, ^{31}P NMR, ^{93}Nb NMR

The photo-induced reaction between CpNb(CO)_4 and $\text{Ph}_2\text{P(CH}_2)_2\text{PR(CH}_2)_2\text{PPh}_2$ (L; R = Ph, Cy) yields the chelated five-membered ring complexes *cis*- $[\text{CpNb(CO)}_2\text{L}]$ (two isomers in the case of R = Cy). The uncoordinated PPh_2 group reacts with $\text{CpNb(CO)}_3\text{THF}$ to form $\text{CpNb(CO)}_2(\mu\text{-L})\text{CpNb(CO)}_3$. IR, ^{31}P and ^{93}Nb NMR spectra are discussed and compared with corresponding data of the analogous vanadium complexes.

Recent investigations into the coordinative properties of oligodentate phosphorus ligands towards carbonylvandium and -niobium complexes in our laboratory have lead to a large body of systematic IR, ^{31}P and metal NMR data, including those on CpV(CO)_4 and CpNb(CO)_4 derivatives with ditertiary [2–5] and tritertiary phosphines [6, 7]. In this communication, we report on the reaction pattern observed in the system $\text{CpNb(CO)}_4/\text{Ph}_2\text{P(CH}_2)_2\text{PR(CH}_2)_2\text{PPh}_2$ (R = Ph: L¹, R = Cy: L²), emphasizing the spectral properties

of the new carbonylcyclopentadienylphosphine-niobium complexes in the context of comparative studies within the vanadium triad. The data are collected in Table I; data on representative complexes containing the ligands $\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2$ ($n = 2$: p₂(2), $n = 5$: p₂(5)) are included.

The complexes *cis*- $[\text{CpNb(CO)}_2\text{L}]$ are formed during UV irradiation of THF solutions containing CpNb(CO)_4 and L in equimolar amounts. The ^{31}P NMR spectra clearly reveal that chelating five-membered rings are formed exclusively: the sole

Table I. Spectral parameters.

Complex ^a	$\nu(\text{CO})^b$ [cm ⁻¹]				$\delta(\text{M})^c$ [ppm]		$\delta(^{31}\text{P})^d$ [ppm]		
	M = Nb		M = V		$\delta(^{93}\text{Nb})$	$\delta(^{51}\text{V})$	M = Nb	M = V	
CpM(CO) ₃ L ¹	1957m	1850s					M–PPh ₂ PPh M–PCy PCy	58 —17.1(m) 53 —12.0(m)	79 ^e
CpM(CO) ₃ L ²	1962m	1852s	1953m	1845s ^e				75 ^f 97 ^f	^g 112 ^h
CpM(CO) ₂ p ₂ (5)	1864s	1771s ^f	^g						
CpM(CO) ₂ p ₂ (2)	1875s	1800s ^f	1870s	1799s ^f	—1220 ^f	—1110 ^f			114 ^h
CpM(CO) ₂ L ¹	1875s	1802s	1862s	1792s ^h	—1340	—1176 ^h	M–PPh ₂ PPh ₂ M–PPh M–PPh ₂ PPh ₂	99 —14.6(29.5) 84 97 —13.3(34.5)	—15.0(27) ^h 102 ^h 113 ^e —13.5(dd) ^e
CpM(CO) ₂ L ²	1878s	1804s	1868s	1792s ^e				—14.5(17.8) M–PCy	99 ^e 122 ^h
CpM(CO)L ¹	(1735w)		1796m	1758s ^h				85 104	

^a Abbreviations: L¹ = $\text{Ph}_2\text{P(CH}_2)_2\text{PPh(CH}_2)_2\text{PPh}_2$, L² = $\text{Ph}_2\text{P(CH}_2)_2\text{PCy(CH}_2)_2\text{PPh}_2$, Cy = C₆H₁₁, Cp = $\eta^5\text{-C}_5\text{H}_5$, p₂(2) = $\text{Ph}_2\text{P(CH}_2)_2\text{PPh}_2$, p₂(5) = $\text{Ph}_2\text{P(CH}_2)_5\text{PPh}_2$; ^b ca. 0.01 M in THF; ^c ^{51}V : relative to VOCl_3 neat, ^{93}Nb : quoted relative to NbOCl_3 ; see refs. [4] and [5] for further details; ^d 36.44 MHz $^{31}\text{P}\{^1\text{H}\}$ relative to phosphoric acid at 220 K, ca. 0.002 M THF/ CH_3CN 9/1. At room temperature, the signals for coordinated P are broadened almost beyond detection. In parentheses: $^3J(^{31}\text{P}\text{--}^{31}\text{P})$, m = complex multiplet, dd = two doublets; ^e ref. [4]; ^f ref. [5]; ^g with CpV(CO)_4 , no disubstituted complex is formed (cf. ref. [4]); ^h ref. [6].

phosphorus species found in the region of uncoordinated P is the diphenylphosphine function. The signals for coordinated PPh_2 , PPh and PCy are typically broadened by the adjacent quadrupolar nucleus ^{93}Nb (nuclear spin = $9/2$, electric nuclear quadrupole moment = $-0.2 \cdot 10^{-28} \text{ m}^2$), and characteristically shifted to higher frequency. The coordination shifts are *ca.* 114 (PPh_2) and 98 (PPh and PCy) ppm and comparable to those of *cis*- $[\text{CpNb}(\text{CO})_2\text{p}_2(2)]$. The deshielding of P on coordination is less than in the vanadium complexes (by 15 to 18 ppm). The commonly observed increase of ^{31}P shielding in the transition metal triads as going from the lighter to the heavier metal center probably accounts for an increasing non-local diamagnetic contribution to the overall shielding of the ^{31}P nucleus.

The ^{93}Nb resonance, although within the expected range [5], is shifted to lower frequency by 120 ppm with respect to $\text{CpNb}(\text{CO})_2\text{p}_2(2)$. A (less pronounced) low-frequency shift has also been observed for the V complexes (*cf.* Table I) and may reflect enhanced electronic interaction and perhaps diminished steric hindrance in the case where a dialkylphenylphosphorus (the central P in the triphos ligand) takes part in the coordination [3].

There are two chiral centers in the molecule (Nb and PR) and one should expect two doublets for PPh_2 in the ^{31}P NMR, corresponding to the pairs of diastereomers. In fact, two doublets (though of quite different coupling constants) are observed for L^2 (see Table), but not for pentaphenyltriphosphahexane (L^1), paralleling findings on *cis*- $[\text{CpV}(\text{CO})_2\text{L}]$ [4, 5], but contrasting with what has been reported for $\text{CpMn}(\text{CO})\text{L}^1$ [8] and

cis- $[\text{CpV}(\text{CO})_2\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}(\text{CH}_2)_3\text{PPh}_2]$ [7].

Whether the two ^{31}P signals actually arise from the chirality of the molecule or from conformational isomerism (position of R relative to the cyclopentadienyl ring; normal and twisted conformation of the metallacycle) cannot yet be stated unambiguously.

While *cis*- $[\text{CpV}(\text{CO})_2\text{L}^1]$ dissolved in CH_3CN is slowly converted to $\text{CpV}(\text{CO})\text{L}^1$ [6], no such reaction occurs with *cis*- $[\text{CpNb}(\text{CO})_2\text{L}]$. However, IR and ^{31}P NMR spectra of the reaction products obtained from the irradiation of $\text{CpNb}(\text{CO})_2(\mu\text{-L})\text{CpNb}(\text{CO})_3$ in the presence of excess L exhibit weak signals which can be allocated to a trisubstituted species,

$\text{CpNb}(\text{CO})\text{L}$ (see Table). The main product of this reaction is again *cis*- $[\text{CpNb}(\text{CO})_2\text{L}]$. The dinuclear complexes $\text{CpNb}(\text{CO})_2(\mu\text{-L})\text{CpNb}(\text{CO})_3$ are obtained from the dark-reaction between $\text{CpNb}(\text{CO})_3\text{THF}$ [9] and $\text{CpNb}(\text{CO})_2\text{L}$. If $\text{CpNb}(\text{CO})_3\text{THF}$ is treated with L, a mixture of the mononuclear compounds $\text{CpNb}(\text{CO})_3\text{L}$ and *cis*- $[\text{Nb}(\text{CO})_2\text{L}]$ is obtained. The disubstituted complex is slightly less soluble in THF/heptane and can be accumulated by several successive fractional precipitations. In the monosubstituted complex, the ligand is chiefly coordinated via the terminal PPh_2 group. As commonly observed with $\text{CpM}(\text{CO})_3\text{PR}_3$ complexes, two of the three CO stretching frequencies ($A'^{(1)}$ and A'') are accidentally degenerate if R is a spacious group. In all compounds, the $\nu(\text{CO})$ absorptions are consistently higher by several cm^{-1} in the Nb than in the V complexes, and also for L^2 as compared to L^1 .

Experimental

All operations were carried out with the strict exclusion of oxygen.

cis- $[\text{CpNb}(\text{CO})_2\text{L}^1]$. 407 mg $\text{CpNb}(\text{CO})_4$ [10] (1.51 mmol) and 808 mg L^1 (1.51 mmol) were dissolved in 70 ml THF and irradiated internally with UV (see ref. [11] for details concerning the irradiation apparatus). A weak N_2 stream was passed through the solution to remove released CO. The originally orange solution turned to green after *ca.* 3 min (formation of $\text{CpNb}(\text{CO})_3\text{THF}$) and then quickly to a dark red-brown, indicating the formation of the phosphine complexes $\text{CpNb}(\text{CO})_3\text{L}^1$ and *cis*- $[\text{CpNb}(\text{CO})_2\text{L}^1]$. The reaction was monitored by IR and irradiation was stopped as the formation of the disubstituted complex was completed (*ca.* 60 min). The solution was then concentrated to 5 ml and treated dropwise and with vigorous stirring with 30 ml *n*-heptane. A brown powder precipitated which, after standing at 0 °C for 1 d, was filtered off, reprecipitated from THF/heptane, washed twice with 5 ml portions of cold heptane and dried under high vacuum (4 h at room temperature). Further product was isolated from the combined filtrates after one week of standing at -25 °C. Yield: 620 mg (64%) of an orange-brown, air-sensitive powder.

cis- $[\text{CpNb}(\text{CO})_2\text{L}^2]$ was prepared accordingly. Yield: 78%. For the preparation of L^2 see ref. [4].

$\text{C}_{41}\text{H}_{44}\text{NbO}_2\text{P}_3$ (754.6)

Calcd	C 65.26	H 5.88	Nb 12.31	P 12.31,
Found	C 65.1	H 5.9	Nb 12.5	P 12.1.

$\text{CpNb}(\text{CO})_2(\mu\text{-L}^1)\text{CpNb}(\text{CO})_3$. A solution of 210 mg $\text{CpNb}(\text{CO})_4$ (0.78 mmol) in 60 ml THF was cooled to 0 °C (ice/water bath) and irradiated until the solution became dark green and the IR showed

the bands of $\text{CpNb(CO)}_3\text{THF}$ (1961 and 1840 cm^{-1} [9]) only, which took *ca.* 25 min. A solution of 598 mg *cis*- $[\text{CpNb(CO)}_2\text{L}^1]$ (0.80 mmol) in 30 ml THF was added, instantaneously producing a red-brown colour. The solution was stirred at room temperature for 1 h, concentrated to 8 ml and treated with 40 ml *n*-heptane. 500 mg (65%) of a

dark, orange-brown, air-sensitive powder were thus isolated.

$\text{C}_{49}\text{H}_{43}\text{Nb}_2\text{O}_5\text{P}_3$ (990.6)

Calcd	C 59.41	H 4.38	Nb 18.76	P 9.38,
Found	C 59.7	H 4.5	Nb 18.3	P 9.5.

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