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PREPARATION AND IR, ^{31}P, AND ^{93}Nb NMR SPECTROSCOPIC INVESTIGATION OF PHOSPHINE DERIVATIVES OF η^5-$C_5H_5Nb(CO)_4$

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Summary

UV irradiation of η^5-$C_5H_5Nb(CO)_4$ in the presence of the phosphine ligands L (L = 2 PEt_3, $Ph_2P(CH_2)_nPPh_2$ ($p_2(n)$, n = 1—5), *cis*-$Ph_2PCH{=}CHPPh_2$ (c-dpe)), and the mixed arsine-phosphine ligands $Ph_2AsCH_2CH_2PPh_2$ (arphos) and *o*-$C_6H_4(AsPh_2)(PPh_2)$ (pab) yields the well defined complexes *cis*-[η^5-$C_5H_5Nb(CO)_2L$]. The monosubstituted species η^5-$C_5H_5Nb(CO)_3L$ have been characterized spectroscopically. P_2Ph_4 forms mono- and dinuclear, mono- and biligate carbonylniobium complexes.

Shielding of the ^{93}Nb nucleus increases in the sequences (i) Ph_2As- < Ph_2P-, (ii) chelate 4-ring < chelate 5-ring and (iii) η^5-$C_5H_5Nb(CO)_2L$ < η^5-$C_5H_5Nb(CO)_3L$ < η^5-$C_5H_5Nb(CO)_4$, and ^{31}P coordination shifts decrease in the order c-dpe > pab > arphos > $p_2(2)$ > $p_2(5)$ > $p_2(4)$ ~ PEt_3 > $p_2(3)$ > $p_2(1)$. The trends generally parallel those for the corresponding NMR parameters of the vanadium complexes. Paramagnetic contributions to the overall shielding are smaller for the ^{93}Nb than for the ^{51}V nucleus, and this is explained in terms of increased covalency and decreased π-interaction in the niobium complexes.

Introduction

While the chemistry of phosphine, arsine and stibine derivatives of $CpV(CO)_4$ has been studied extensively [1—6], there have been only a few reports on phosphine-niobium complexes. To date, the compounds $CpNb(CO)_3L$ (L = PCy_3 [7], PPh_3, $AsPh_3$, $SbPh_3$ [8]), $CpNb(CO)_2L_2$ (L_2 = 2 PPh_3, $Ph_2P(CH_2)_2PPh_2$) [8] and $Cp_2Nb(CH_3)L$ (L = $P(OMe)_3$, PEt_3) [9] have been characterized, and Ellis et al. have described the preparation of $[Et_4N][Nb(CO)_5PPh_3]$ and $[Et_4N][Nb(CO)_4Ph_2P(CH_2)_2PPh_2]$ [10]. Carbonylniobium complexes have now become more readily available, through a high-yield synthesis of $CpNb(CO)_4$ described recently by Herrmann et al. [11], who also characterized the niobium cluster $Cp_3Nb_3(CO)_7$ [12,16].

TABLE 1

NMR DATA

Complex [a]	$\delta(^{93}Nb)$ (ppm) rel. $NbCl_5/MeCN$	$\delta(^{93}Nb)$ (ppm) rel. $NbOCl_3/MeCN$	$\delta(^{51}V)$ [b] (ppm) rel. $VOCl_3$	$\delta(^{31}P)$ coord. [c] (ppm)	$\Delta(\delta p)$ [d] (ppm)	$\delta(^{31}P)$ uncoord. [c] (ppm)	$J(^{31}P-^{31}P)$ (Hz)
$CpM(CO)_4$ 1	—2016	—1566	—1532				
$CpM(CO)_3PEt_3$ 2	—1865	—1415	—1410	+24.3	47		
$CpM(CO)_2(PEt_3)_2$ 3	—1645	—1195	—1160	+52.6	75		
$CpV(CO)_3P_2Me_4$ 4B			—1381(d) [e]	+37(d) [e]	96	—43(d)	276
$CpM(CO)_3p_2(O)$ 5			—1410(d) [f]	+32.5(d)	50	—28.0(d)	217
$\{CpNb(CO)_3\}_2\mu\text{-}p_2(0)$ 6A				+35.7	54		
$CpNb(CO)_2\{p_2(0)\}_2$ 7A				+53.4(d)	71	—3.4(d)	325
$\{CpNb(CO)_2\}_2\{\mu\text{-}p_2(0)\}_2$ 8A				+80.8	99		
$CpNb(CO)_3p_2(1)$ 9A				+51.1(d)	82	—27.9(d)	94
$CpM(CO)_2p_2(1)$ 10	—1360	—910	—870	+27	52		
				+52	78		
$CpNb(CO)_3p_2(2)$ 11A				+77.5	93	—15.9	
$CpM(CO)_2p_2(2)$ 12	—1670	—1220	—1110	+94.7	110		
				+112	127		
$CpNb(CO)_3p_2(3)$ 13A				+31	51	—20	

$CpNb(CO)_2p_2(3)$ [g] **14A**				+44	64		
$CpNb(CO)_3p_2(4)$ **15A**				+30	48	−17.7	
$CpM(CO)_2p_2(4)$ **16**	−1330	−880	−1360	+55.9	74		
				+72	90		
$\{CpV(CO)_3\}_2\mu\text{-}p_2(5)$ [h] **17B**			−1357	+74	92		
$CpNb(CO)_3p_2(5)$ **18A**				+54.8	73	−18.9	
"$CpV(CO)_2\{p_2(5)\}$" [h, i] **19B**			−1140	+86	105		
$CpNb(CO)_2p_2(5)$ **20A**				+75.2	93		
$CpNb(CO)_3$c-dpe **21A**				+62.6(d)	76	−31.1	22
$CpM(CO)_2$c-dpe **22**	−1650	−1200	−1143	+106.8	131		
				+120	143		
$CpNb(CO)_3$arphos **23A**				+28.4	44		
$CpM(CO)_2$arphos **24**	−1530	−1080	−1030	+101.1	116		
				+117	133		
$CpNb(CO)_3$pab **25A**				+66.6	81		
$CpM(CO)_2$pab **26**	−1610	−1160	−995	+110.2	124		
				+126	140		

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[a] Abreviations for ligands: $p_2(n) = Ph_2P(CH_2)_nPPh_2$ (n = 0—5), arphos = $Ph_2As(CH_2)_2PPh_2$, pab = $o\text{-}C_6H_4(AsPh_2)(PPh_2)$, c-dpe = *cis*-$Ph_2PCH{=}CHPPh_2$. A relates to niobium, B to vanadium complexes. [b] From ref. 23, if not indicated otherwise. [c] At 210 K; d = doublet. ^{31}P NMR data are for the niobium complexes, data for the vanadium complexes are given in square brackets (from ref. 23 if not indicated otherwise). [d] ^{31}P coordination shift $\Delta(\delta P) = \delta(^{31}P)$[coordinated ligand] $- \delta(^{31}P)$[free ligand]. [e] Ref. 5; $^1J(^{51}V\text{—}^{31}P) = 165$ Hz. [f] $^1J(^{51}V\text{—}^{31}P) = 155$ Hz (from ref. [5]). [h] Like the corresponding vanadium compound [2], the complex is only sparingly soluble. [h] From ref. [30]. [i] The actual composition of the complex is $CpV(CO)_3\mu\text{-}p_2(5)CpV(CO)_2p_2(5)$.

Extension of carbonylphosphineniobium chemistry is of interest in the light of the potential catalytic behaviour of these complexes in homogeneous H- and CO-transfer reactions. Additionally, comparison of the kinetics of formation, stability, chemical and electrochemical behaviour and spectroscopic parameters of carbonylphosphine-niobium and -vanadium complexes may provide further insight into the chemistry, structural features, and the nature of the bonding in these compounds.

One of the problems encountered with NMR studies on heavier nuclei is the extent to which local dia- and para-magnetic terms contribute to variations in the overall shielding of the nucleus. Both vanadium and its heavier homologue, niobium, have nuclei accessible to NMR (the natural abundance of the magnetic nuclei is almost 100%; the relative receptivities are 0.38 and 0.48, and the nuclear spin quantum numbers 7/2 and 9/2, respectively), and a comparison of data in which all variables but the nucleus in question are kept constant should help to solve this problem. Various ^{51}V NMR studies on vanadium complexes of the type $CpV(CO)_{4-n}L_n$ have already been carried out [2—5,13,14]. In the present work, in addition to preparative and IR and ^{31}P NMR spectroscopic aspects, ^{93}Nb NMR data of several phosphine-substituted $CpNb(CO)_4$ complexes are presented. Except for two recent investigations concerned with $[Et_4N][NbL_6]$ (L = CO, PF_3) [15], $CpNb(CO)_4$ and $Cp_3Nb_3(CO)_7$ [16], ^{93}Nb measurements until now have been restricted to niobium(V) complexes containing halogen and pseudo-halogen ligands [17,18].

Results and discussion

NMR and IR spectral data are listed in Tables 1 and 2. For comparison, data for the analogous vanadium compounds are included.

Preparation and IR spectra

The complexes $CpNb(CO)_2L$ (L = $Ph_2P(CH_2)_nPPh_2 \equiv p_2(n)$, n = 1—5, *cis*-$Ph_2PCH{=}CHPPh_2$ (c-dpe), $Ph_2As(CH_2)_2PPh_2$ (arphos), o-$C_6H_4(AsPh_2)(PPh_2)$ (pab) and 2 PEt_3; for discussion of the P_2Ph_4 complexes vide infra) are prepared by UV irradiation (Duran filter) of THF solutions containing equimolar amounts of $CpNb(CO)_4$ and L. Isolation from the red-brown solutions by heptane precipitation affords ochre, orange or red microcrystalline, air-sensitive powders of the disubstituted products. The reaction proceeds in two steps via the monosubstituted species, and probably follows a S_N1 mechanism analogous to photo-induced CO substitution in $CpV(CO)_4$ [1]. Monosubstitution products could not be isolated pure, but were characterized by their CO stretching frequencies and ^{31}P NMR spectra.

The IR patterns for $CpNb(CO)_3L$ and $CpNb(CO)_2L$ are consistent with the local C_s symmetry (i.e. *cis* configuration in the case of disubstitution). The monosubstituted compounds sometimes exhibit only two absorptions in the $\nu(CO)$ region because of accidential degeneracy of the $A'^{(1)}$ and A'' modes. The same accidential coincidence of band positions has been reported for $CpV(CO)_3L$ complexes (where L is, e.g. PPh_3 and $AsPh_3$) [3]. The IR results for the niobium complexes are in accord with those reported by Nesmeyanov et al. [7] and by Lokshin et al. [8] for $CpNb(CO)_3PPh_3$ and $CpNb(CO)_2p_2(2)$.

TABLE 2

IR DATA [a]

Complex	ν(CO) (A) (cm^{-1})			ν(CO) (B) (cm^{-1}) [b]		
1	2032	1918				
2	1954	(1850)	(1850)	1947	1844	1858
9A	1957	1867	1843			
11A	1957	1847	(1847)			
13A	(1960)	(1847)				
15A	1956	(1862)	1845			
18A	1955	1862	1844			
21A	1957	1847	(1847)			
23A	1960	1866	1856			
25A	1958	1866	1852			
3	(1850)	1757	(1734)	(1851)	1772	
10	1889	1810		1871	1809	
12	1875	1800		1870	1799	
14	1833	1754				
16	1861	1779		1860	1774	
20A	1864	1771				
24	1874	1795		1867	1796	
26	1884	1812		1871	1802	
22	1882	1810		1874	1806	
5	1992	1921	1908	1958	1865	1858 [c]
6A	1960	1869	1855			
7A, 8A	1823	1783				

[a] In THF except for 14 (Nujol). A refers to Nb, B to V complexes. Bands in brackets are shoulder or estimated positions. [b] From ref. 23 if not indicated otherwise. [c] Ref. 5.

CO stretching frequencies of the CpNb(CO)$_2$L complexes are consistently higher than those of the corresponding vanadium compounds. The shift of ν(CO) towards higher wave numbers as going down a group has been established, e.g., for the Group VI pentacarbonylphosphine complexes [19,20], and is accounted for in terms of a more efficient π-interaction between the phosphine and the heavier metal, or of a diminished tendency of the heavier metal to delocalize electron density into the ligand system. In this context, Lokshin's observation concerning the basicities of CpM(CO)$_3$L (V $<$ Nb) [8] is of interest.

Strained ring systems (p$_2$(1), c-dpe, pab) give rise to an increase of ν(CO) with respect to the chelate 5-ring formed with p$_2$(2), while large ring systems (p$_2$(4), p$_2$(5)) exhibit the opposite tendency. These trends are more pronounced in the Nb than in the V complexes. Similar observations were made with M(CO)$_4$p$_2$(n) complexes (M = Cr, Mo, W; n = 1—3) [20].

^{31}*P NMR spectra*

In contrast to the ^{31}P NMR spectra of phosphinevanadium complexes, which show very broad absorptions (if any), ^{31}P signals of the niobium complexes are, sharp at 200 K. This difference in behaviour is apparently due to the greater electric nuclear quadrupole moment of the niobium (—0.2 [18]) than of the vanadium nucleus (0.05 × 10^{-28} m^2 *), which (in association with a considerable

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* There is some disagreement in the literature over the value of the quadrupole moment of vanadium. The reported values vary from 0.05 to 0.5 × 10^{-28} m^2 [21]. We have argued on the basis of a comparative study of ^{55}Mn, ^{51}V and ^{31}P NMR parameters for the isoelectronic and isostructural complexes [Mn(CO)$_5$PR$_3$]$^+$ and [V(CO)$_5$PR$_3$]$^-$ that vanadium falls into the low quadrupole category [22].

increase in the molecular correlation time at low temperatures) results in relaxation rates sufficiently high to cause complete decoupling of the ^{31}P and ^{93}Nb nuclei.

The signals for the coordinated PPh_2 groups usually appear as singlets, except for the monosubstitution products formed with c-dpe, $p_2(1)$ and $p_2(0)$, where, due to the inequivalence of the two PPh_2, doublets are seen both for the coordinated and the uncoordinated phosphorus. The coupling constants are 22, 94 and 217 Hz, respectively, for the three-bond (c-dpe), two-bond ($p_2(1)$) and one-bond ($p_2(0)$) phosphorus couplings. Since the other diphosphines do not give split signals, coupling apparently occurs via the bonds within the ligand itself and not via the niobium centre. One-bond P—P coupling of this order of magnitude has also been observed for monosubstituted $CpV(CO)_3p_2(O)$ complexes ([5] and Table 2).

All the ^{31}P signals for coordinated phosphorus ligands are shifted to low field with respect to the uncoordinated ligand. ^{31}P coordination shifts $\Delta(\delta p) = \delta(^{31}P)$ [coordinated PPh_2] — $\delta(^{31}P)$ [free ligand] for the $CpNb(CO)_3L$ complexes cover a range of ca. 50 ppm. With the exception of arphos, ligands with a 5- and 6-membered backbone produce a smaller down-field shift than $p_2(0)$ and $p_2(1)$. This may reflect steric influences from the part of the non-coordinated PPh_2 in the case of the latter.

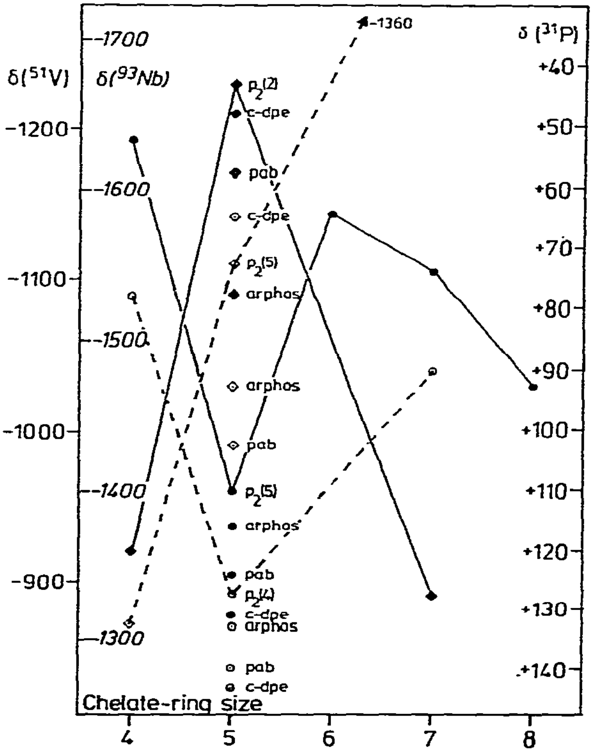

Fig. 1. Chelate-ring size (abscissa) of the complexes $CpM(CO)_2p_2(n)$ vs. $\delta(^{31}P)$ (right ordinate circles) and $\delta(M)$ (left ordinate squares) for M = ^{93}Nb (solid lines and full symbols) and M = ^{51}V (broken lines and open symbols). Shielding of the ^{31}P, ^{51}V and ^{93}Nb nuclei increases from bottom to top.

$\Delta(\delta p)$ values for the disubstituted chelate complexes show a maximum value (minimum ^{31}P shielding) for the chelate 5-ring, and a minimum value (maximum ^{31}P shielding) for the chelate 4-ring, paralleling an analogous trend of the $\Delta(\delta p)$ values of various carbonylphosphinevanadium and other transition metal diphosphine complexes ([23] and refs. cited herein). The shielding of the metal nuclei (vide infra) shows the opposite trend. The situation is illustrated graphically in Figure 1, which also shows that within the 5-ring systems $\Delta(\delta p)$ decreases in the sequence c-dpe > pab > arphos > $p_2(2)$.

^{93}Nb NMR spectra

To a close approximation, the paramagnetic contribution σ_{para} to the overall shielding $\sigma = \sigma_{dia} + \sigma_{para}$ (the diamagnetic term σ_{dia} is practically constant for a given nucleus [24]) is expressed by

$$\sigma_{para} = -\text{const.}\ \overline{\Delta E}^{-1} < r^{-3} >_{nd} k'^2 \qquad (1)$$

where r_{nd} is the distance of the valance-*d* electrons from the nucleus ($\langle r^{-3} \rangle$ is the quantum mechanical expectation value of r^{-3}), k' the orbital reduction factor, and $\overline{\Delta E}$ the mean excitation energy for electronic singlet transitions from the ground state to symmetry-allowed excited states. ΔE correlates with the integral ligand strength (σ-donor + π-acceptor power in this case), $\langle r^{-3} \rangle_{nd}$ with the nephelauxetic effect, and k'^2 with the covalency of the metal—ligand bond [3,23,24]. High second-order paramagnetic contributions lead to low overall shielding, hence a decrease of $|\delta|$, where δ is the chemical shift and quoted negative for signals upfield of the standard.

In Table 1, $\delta(^{93}Nb)$ values are listed relative to a standard of $NbCl_5$ in CH_3CN; $NbCl_5$ is readily available and gives a sharp ^{93}Nb signal at extreme low field (high frequency), and so is a suitable standard. For direct comparison with the $\delta(^{51}V)$ values, which are quoted relative to $VOCl_3$, Table 1 also contains the $\delta(^{93}Nb)$ relative to $NbOCl_3$ in CH_3CN ($\delta(NbOCl_3)$ = ca. —450 ppm rel. $NbCl_5$/CH_3CN [18]).

Except for the parent compound $CpNb(CO)_4$ itself, all the niobium signals are very broad (half widths $\Delta\nu_{1/2}$ are around 6000 Hz) and thus clearly differ in appearance from the ^{51}V NMR signals of the vanadium compounds, the line widths of which are one order of magnitude less, presumably because of the smaller nuclear electric quadrupole moment of vanadium. Comparison of the shift values $\delta(^{93}Nb)$ and $\delta(^{51}V)$ relative to $MOCl_3$ shows that within the limits of error there are no distinct differences. Since the diamagnetic contribution σ_{dia}, which depends chiefly upon the terms $P_i\langle r^{-1} \rangle_i$ (P_i = electron population of the *i*-th orbital) of the core electrons, aquires a greater value for the heavier Nb *, the paramagnetic contribution to σ is smaller in the Nb than in the V complexes. This could be due to smaller values of k' and $\langle r^{-3} \rangle$ in eq. 1 (increase of the covalency and of r) in the case of the niobium complexes, and to an increase of ΔE, caused by stabilisation of the Nb 4*d* relative to the V 3*d* orbitals, and relative to the interacting acceptor system of the ligands. We have shown by

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* Free atom values for σ_{dia} are: $\sigma_{dia}(^{93}Nb) = 3870$, $\sigma_{dia}(^{51}V) = 1727$ ppm [25]; calculated values for $\sigma_{dia}(^{51})$ in several vanadium compounds are 1708 to 1718 ppm [24,26].

MO calculations of the SCCC type that the acceptor systems of the ligands are destabilized with respect to the V 3*d* orbitals in $CpV(CO)_4$ and $[CpV(CO)_3CN]^-$ [24]. Thus, stabilization of the Nb 4*d* orbitals leads to diminished π-interaction which, for the interaction with the CO ligands, is manifested by an increase of ν(CO) for Nb complexes.

With the exception of the $p_2(4)$ complexes, the trends in metal chemical shift are similar for the Nb and V complexes (see also Fig. 1): shielding increases in the several series:

$CpM(CO)_2L < CpM(CO)_3L < CpM(CO)_4$

$Ph_2As\text{-} < Ph_2P\text{-}$

chelate 4-ring < chelate 5-ring

The decrease of shielding on introducing a CO in place of a phosphine ligand has been explained in terms of an increase of the energy of the relevant transitions in complexes of low point symmetry, plus destabilization of π- and σ-type molecular orbitals as M—PR_3 interaction becomes increasingly important relative to M—CO interactions [24]. Anisotropy effects may also contribute to the lower shielding in C_s complexes [27]. The higher shielding of the metal nucleus in phosphorus compared with arsenic complexes is in accord with the greater ligand strength of phosphines (increase of ΔE in eq. 1) [3,4,13]. The low shielding in the $p_2(1)$ complexes reflects ring strains and angle deformations in the chelate 4-ring structures, which hinder the metal phosphorus overlap [23]. As a result, ΔE decreases and the metal-*d* character of the orbitals involved in the electronic transitions increases (k' increases), and hence there is an increase in σ_{para} and a decrease in σ (and $|\delta|$).

At the same time, deviation from the tetrahedral bond angles at the phosphorus leads to an increase in the *s*-contribution to the phosphorus donor function and thus to an increase in ^{31}P shielding (decrease of $\Delta(\delta p)$) of $p_2(1)$ relative to $p_2(2)$ complexes (Fig. 1). Restricted σ-overlap between Nb and the phosphorus functions in $CpNb(CO)_2p_2(1)$ should result in diminished electron density at the niobium centre and thus may release the π^* acceptor orbitals located on the CO ligands; hence the higher ν(CO) value (cf. Table 2).

The reaction between $CpNb(CO)_4$ and Ph_2PPPh_2

Figure 2 illustrates the ^{31}P NMR spectrum of the products present after 20 minutes irradiation. The relevant data are listed in Table 1 and 2.

The first product, which can be identified after brief irradiation times (ca. 5 min), is apparently the mononuclear, monoligate species $CpNb(CO)_3P_2Ph_4$ (5A), characterized by two doublets ($^1J(^{31}P—^{31}P)$ = 217 Hz) at +32.5 (coordinated PPh_2) and —28.0 ppm (uncoordinated PPh_2; free ligand: —17.8 ppm). The second step may be either displacement of a second CO and formation of a mononuclear, biligate species $CpNb(CO)_2(P_2Ph_4)_2$ (7A), or reaction of 5A with a second $CpNb(CO)_4$ to yield the dinuclear, monoligate complex $\{CpNb(CO)_3\}_2\mu\text{-}P_2Ph_4$ (6A). Both complexes were identified by their IR and ^{31}P NMR spectroscopic characteristics. Thus, 6A exhibits a singlet due to the equivalency of the P atoms, while 7A is characterized by two doublets (+53.4 and —3.4 ppm, $^1J(^{31}P—^{31}P)$ = 325 Hz). The ν(CO) absorptions for 5A are at

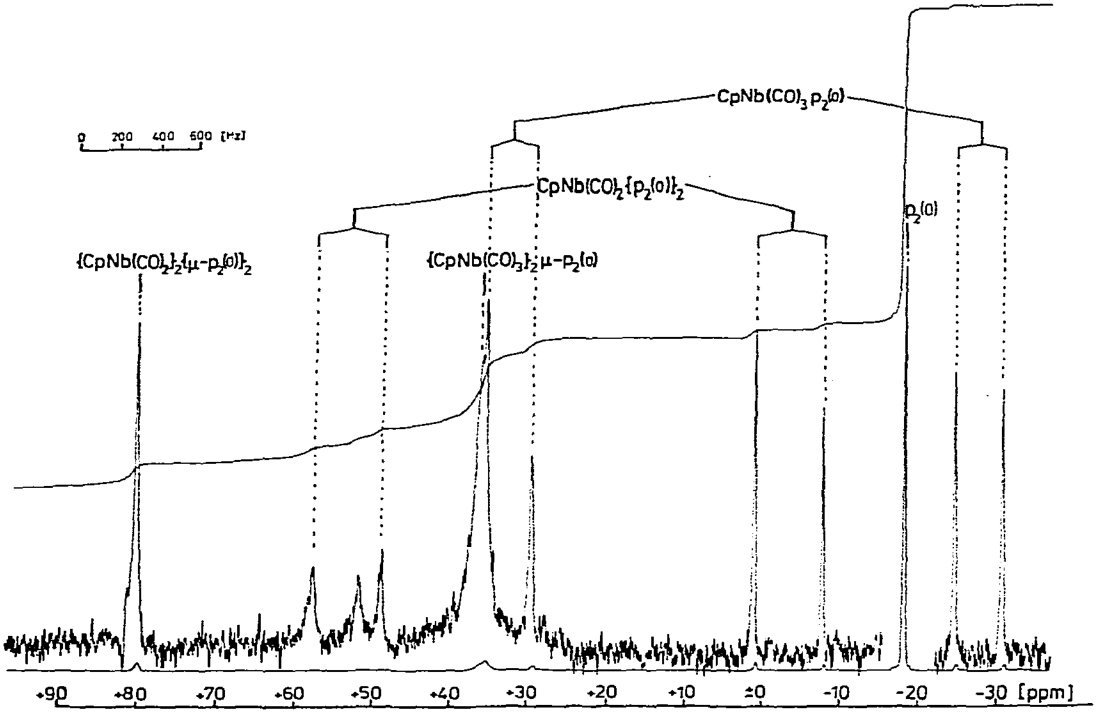

Fig. 2. 36.44 MHz $^{31}P\{^1H\}$-NMR spectrum of the reaction between $CpNb(CO)_4$ and P_2Ph_4 after 20 min of irradiation time.

markedly higher wave numbers than those for **6A**, and this can be attributed to enhanced π-delocalization with participation of the unligated PPh_2 group in the former. Further reaction of **7A** with $CpNb(CO)_4$ then affords $\{CpNb(CO)_2\}_2(\mu\text{-}P_2Ph_4)_2$ (**8A**), which again gives rise to a singlet with a ^{31}P coordination shift similar to that of $CpNb(CO)_2p_2$(**2**). All the assignments were carried out on the basis of similar results for the reaction between $CpV(CO)_4$ and diphosphanes P_2R_4 [5].

Experimental

General method and materials

All operations were carried out under nitrogen in Schlenk-tubes and in anhydrous, oxygen-free solvents. The irradiation apparatus was a Duran tube of ca. 50 ml capacity, and irradiation was carried out with a high-pressure mercury lamp (Philips HPK 125, Mangels, Bonn), fitted into a quartz cooling mantle and placed very close to the Duran vessel. During irradiation the solution was agitated by passing a weak N_2 stream through the reaction mixture by means of a gas inlet tube fitted with a G1 filter plate. N_2 and CO were released through a 10 mm mercury valve. The reactions were monitored by IR spectroscopy.

$CpNb(CO)_4$ was prepared from Cp_2NbCl_2 [28] by the method reported by Herrmann et al. [11], but using a magnetically stirred high pressure device and a reaction time of one week. The phosphines $p_2(n)$ (n = 1—4) were prepared from $NaPPh_2$ (Na + PPh_3) and the α, ω-dichloroalkanes in liquid ammonia, and $p_2(0)$, $p_2(5)$, c-dpe and arphos were obtained from commercial sources (Strem). The synthesis of pab will be described in a separate paper [29].

Spectroscopic measurements

IR: ca. 0.02 *M* THF solutions in 0.1 KBr cuvettes (14A in Nujol); Perkin-Elmer spectrometer 337; absolute error ±1 cm^{-1}. ^{93}Nb-NMR: ca. 0.1 *M* THF, at 300 K relative to $NbCl_5/CH_3CN$ (negative sign = to high field (low frequency) of the standard); 1A and 2A: Bruker WH 90 PFT spectrometer at 22.0 MHz in rotating 7.5 mm diameter vials fitted into 10 mm vials with acetone-d_6 as external lock, pulse width 5μs (no repetition time), average sweep width 31 KHz, average number of scans 100 (1A) to 3000 (2A), absolute error <1 ppm (1A) and ca. ±5 ppm (2A), width at half height $\Delta\nu_{1/2} < 30$ (1A) and ca. 1.4 KHz (2A); 10A, 12A, 16A, 22A and 24A: Varian DP 60 wide-line spectrometer at 12.2 MHz (quartz stabilized; maximum transmitter intensity) and 1.174 T, sweep width 8.3 mT, modulation 0.4 to 0.8 mT, time constant 3 s^{-1}, average number of scans (compiled on a CAT) 100, absolute error ca. ±30 ppm, $\Delta\nu_{1/2}$ 5.2 (22A) to 9.4 KHz (24A) ±20%. $^{31}P\{^1H\}$ NMR: Bruker WH 90 at 36.44 MHz relative to H_3PO_4, ca. 0.1 *M* THF, 203 ± 2 K, absolute error ±1 ppm and less.

Procedure

The typical procedure described below was used with appropriate variations for the preparation of the complexes $CpV(CO)_2L$ (L = 2 PEt_3, $p_2(n)$, arphos, pab, c-dpe). Analytical data and colours are listed in Table 3.

A solution of 320 mg $CpNb(CO)_4$ (1.23 mmol) and 470 mg $p_2(1)$ (1.23 mmol) in 20 ml THF was irradiated for 1 hour, after which the IR spectrum indicated complete substitution of 2 CO ligands. The solution was concentrated to 2 ml and treated with 20 ml of heptane. After two days at 250 K, a micro-crystalline powder was obtained, and this was filtered off, washed with 5 ml of heptane, and dried for 6 hours under high vacuum.

Irradiation times for other ligands L varied from 30 min (PEt_3) to 6 hours (c-dpe). In a few cases (12A, 22A), precipitation of the complex occurred

TABLE 3

ANALYTICAL DATA AND COLOURS OF ISOLATED COMPLEXES

Complex	Colour	Empirical formulae	Molecular Mass	Analysis found (calcd.) (%)	
				C	H
10A	light red-brown	$C_{32}H_{27}NbO_2P_2$	598.4	64.9 (64.23)	5.2 (4.55)
12A	orange-red	$C_{33}H_{29}NbO_2P_2$	612.4	64.5 (64.72)	4.9 (4.77)
14A	brick-red	$C_{34}H_{31}NbO_2P_2$	626.5	64.4 (65.19)	5.0 (4.99)
16A	cocoa-brown	$C_{35}H_{33}NbO_2P_2$	640.5	65.7 (65.63)	5.2 (5.19)
20A	cerise	$C_{36}H_{35}NbO_2P_2$	654.5	65.5 (66.06)	5.4 (5.39)
22A	dark orange	$C_{33}H_{27}NbO_2P_2$	610.4	65.8 (64.93)	4.7 (4.45)
24A	orange	$C_{33}H_{29}AsNbO_2P$	656.4	60.9 (60.39)	6.6 (4.45)
26A	dark ochre	$C_{37}H_{29}AsNbO_2P$	704.4	64.0 (63.09)	4.9 (4.15)

during the concentration of the THF solution. 14A separated during irradiation, and is an almost insoluble compound. Yields are around 40%.

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