Organometallics 1985, 4, 1334–1340

Pentacarbonylvanadates(I−) of Mono- and Oligodentate Phosphines: Synthesis and IR and ^{31}P and ^{51}V NMR Characterization

Klaus Ihmels and Dieter Rehder*

Institut für Anorganische Chemie der Universität, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Federal Republic of Germany

Received October 19, 1984

The complexes $[Et_4N][V(CO)_5PR_3]$ have been prepared by ligand exchange from $[Et_4N][V(CO)_5Me_2SO]$ (PR_3 = PH_2Cy, $PHCy_2$, PCy_3, PH_3, PMe_3, $P(i\text{-}Bu)_3$, $P(t\text{-}Bu)_3$, PPh_3, $P(OMe)_3$, $P(OPh)_3$, PR_2R' (R' = $CH_2CH_2PPh_2$, $CH_2CH_2PEt_2$, $CH_2CH_2AsPh_2$, $CH_2CH_2PPhCH_2CH_2PPh_2$, $CH_2CH_2P(CH_2CH_2PPh_2)_2$)), $[Et_4N][V(CO)_5THF]$ ($P(NEt_2)_3$, $P(SiMe_3)_3$), or $[Et_4N][V(CO)_5NC_5H_5]$ ($(P\text{-}t\text{-}Bu_2)_2Te$) or by daylight induced reaction between $[Et_4N][V(CO)_6]$ and $Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2$. They were characterized by their CO stretching frequencies, ^{51}V NMR parameters ($\delta(^{51}V)$ and $^1J(^{51}V-^{31}P)$), and, in the case of oligodentate phosphines, ^{31}P NMR data of the uncoordinated P functions. The arphos ligand $Ph_2As(CH_2)_2PPh_2$ and the tri- and tetradentate phosphines are almost exclusively coordinated via the PPh_2 group, while $Et_2P(CH_2)_2PPh_2$ coordinates about equivalently via PEt_2 and PPh_2. The $^{51}V-^{31}P$ coupling constants increase in the order PH_3, $P(alkyl)_3$, PPh_3 (around 210 Hz) < $P(NEt_2)_3$ (293) < $P(SiMe_3)_3$, $P(OMe)_3$ (366) < $P(OPh)_3$ (415), and $\delta(^{51}V)$ ranges from −1806 ($[V(CO)_5P(NEt_2)_3]^-$) to −1928 ($[V(CO)_5P(OMe)_3]^-$; ppm relative to $VOCl_3$). The shift trends correlate with the integral ligand strength as quantified by Graham's σ and π parameters (with a predominance in π) and reflect, in accord with theory, electronic and steric effects imposed by the substituents R.

Introduction

Phosphine derivatives of $[V(CO)_6]^-$ are reactive intermediates in the synthesis of various carbonylvanadium species. Examples are the conversion of $[V(CO)_{6-n}(PR_3)_n]^-$ to $[V(NO)(CO)_{5-n}(PR_3)_n]$[1,2] or $[V(NO)_2L_4]X$[2,3] through $[Co(NO)_2X]_2$, the conversion to $[V(H)(CO)_{6-n}(PR_3)_n]$ by ion exchange on silica gel,[4,5] the photogeneration of η^3-allyl[6] and η^2-acyl complexes[7] in the presence of allyl, benzoyl, and cyclopropylcarbonyl chloride, the oxidation to paramagnetic neutral species,[8,9] and the coupling reaction with group 14[56] triorganyls to seven-coordinate species such as $[V(SnPh_3)(CO)_5PPh_3]$.[10] In these reactions, n is usually 1–3 and PR_3 a monodentate or $1/n$ of an n-dentate phosphine.

Several routes have been proposed for the preparation of pentacarbonyl(phosphine)vanadates, the more important ones being photosubstitution in the $[V(CO)_6]^-/PR_3$ system[11-15] and ligand replacement in $[V(CO)_5NH_3]^-$[16] or $[V(CO)_5Me_2SO]^-$.[17] The labile ligand method bears the advantage that it is more specific (only pentacarbonyl species are formed even with oligodentate phosphines) and can be employed in cases where irradiation would lead to decomposition or side reactions (as for $P(p\text{-}C_6H_4Cl)_3$ and $PHPh_2$[16]) or where the ligand is too bulky to allow its photochemical introduction in reasonable yields (PCy_3[17]). Preparative routes to $[V(CO)_5PR_3]^-$ of minor importance are the reduction of $[V(CO)_5PPh_3]$[8] and $[V(CO)_4(PPh_3)_2]$,[18] thermally induced replacement of a medium by a strong π-accepting phosphine ($PPh_3/P(OPh)_3$),[19] and the disproportionation of $[V(CO)_5PR_3]$ in the presence of bases such as THF, Et_2O, or MeCN (PR_3 = $P(n\text{-}Bu)_3$, PPh_3, $P(OMe)_3$).[20,21] The reduction of *trans*-$[V(CO)_4(PPh_3)_2]$ by Na/Hg lead to the first member of the now large family of pentacarbonyl(phosphine)vanadates(I−).[18]

In the present work, pentacarbonylvanadates with mono- and oligodentate phosphines covering a wide range of varying electronic and steric characteristics are described. For the first time, a comprehensive study on the relations between the IR spectrochemical and the metal NMR magnetochemical series of ligand strengths is provided. Several of the ^{51}V shielding parameters introduced in this paper have recently been included in a review.[22]

Experimental Section

General Data. All operations were carried out under N_2 and in absolute, oxygen-free solvents. For irradiations, a high-pressure mercury lamp (Philips HPK 125) in a water-cooled quarz immersion well was used. The lamp was placed in the immediate proximity of a borosilicate vessel containing the reaction mixture. During irradiation, a slow N_2 stream was passed through the solution via a gas inlet tube fitted with a porous filter disk.

---

(1) Schiemann, J.; Weiss, E.; Näumann, F.; Rehder, D. *J. Organomet. Chem.* **1982**, *232*, 219.

(2) Näumann, F.; Rehder, D.; Pank, V. *Inorg. Chim. Acta* **1984**, *84*, 117.

(3) Näumann, F.; Rehder, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1647, 1654.

(4) Puttfarcken, U.; Rehder, D. *J. Organomet. Chem.* **1978**, *157*, 321; **1980**, *185*, 219.

(5) Rehder, D.; Puttfarcken, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem. 37B*, 348.

(6) Franke, U.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 355.

(7) Schiemann, J.; Weiss, E. *J. Organomet. Chem.* **1983**, *255*, 179.

(8) Ellis, J. E.; Faltynek, R. A.; Rochfort, G. L.; Stevens, R. E.; Zank, G. A. *Inorg. Chem.* **1980**, *19*, 1083.

(9) Ihmels, K.; Rehder, D. *J. Organomet. Chem.* **1981**, *218*, C54.

(10) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 113.

(11) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1971**, *31*, 239.

(12) Rehder, D. *J. Organomet. Chem.* **1972**, *37*, 303.

(13) Rehder, D.; Schmidt, J. *J. Inorg. Nucl. Chem.* **1974**, *36*, 333.

(14) Talay, R.; Rehder, D. *Chem. Ber.* **1978**, *111*, 1978.

(15) Rehder, D.; Bechthold, H.-Ch.; Keçeci, A.; Schmidt, H.; Siewing, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 139.

(16) Fjare, K. L.; Ellis, J. E. *Organometallics* **1982**, *1*, 1373.

(17) Ihmels, K.; Rehder, D. *J. Organomet. Chem.* **1982**, *232*, 151.

(18) Werner, R. P. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 477.

(19) Darensbourg, M. Y.; Hanckel, J. M. *Organometallics* **1982**, *1*, 82.

(20) Hieber, W.; Peterhans, J.; Winter, E. *Chem. Ber.* **1961**, *94*, 2572.

(21) Richmond, T. G.; Qi-Zhen Shi; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 76.

(22) Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125.

0276-7333/85/2304-1334$01.50/0

For irradiations at 195 K, both the reaction vessel and UV lamp were placed in a dry ice/ethanol bath. Isolated products, before analysis, were dried for 4 h under high vacuum (0.01 torr, room temperature).

Starting materials ($[Na(diglyme)_2][V(CO)_6]$, phosphines) were purchased (Ventron). $Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2$ and $Te(P\text{-}t\text{-}Bu_2)_2$ were generously provided by Dr. Dahlenburg (University of Hamburg) and Prof. du Mont (University of Oldenburg), respectively. $[Na(diglyme)_2][V(CO)_6]$ was converted to $[Et_4N][V(CO)_6]$ as described previously.[23] For the synthesis of $[Et_4N][V(CO)_5DMSO]$ see also ref 17.

Spectra. IR spectrta were obtained on a Perkin-Elmer 577 spectrometer as 0.01 M THF solutions in 0.1-mm KBr cuvettes. For low-temperature spectra, a Beckmann unit (VLT-2 RIIC, 0.12-mm cuvette with ZnS windows) was employed. $^{31}P\{^1H\}$ (at 305 K) and $^{51}V\{^1H\}$ NMR spectra (at 300 K) were scanned on a Bruker WH 90 spectrometer at 36.44 and 23.66 MHz, respectively, in 7.5-mm diameter vials fitted into 10-mm vials containing acetone-d_6 as external lock. External standards were 80% H_3PO_4 and $VOCl_3$ neat. Typical conditions for the ^{51}V NMR spectra are the following: pulse width, 10 μs; repetition time, 0.04 s; resolution, 23 Hz/point (sweep width, 23.81 kHz); number of pulses, 2500. Estimated errors for the spectral parameters are as follows: $\nu(CO) \leq \pm 2\ cm^{-1}$; $(\pi - \sigma)\ \pm 4\ Nm^{-1}$; $\delta(^{31}P)\ \pm 0.2$; $\delta(^{51}V)\ \pm 1$ ppm; $^1J(^{51}V\text{-}^{31}P) = \pm 10$ Hz; $W_{1/2} = \pm 10\%$. Variations of $\nu(CO)$ with the solvent (THF, MeCN) are within the limits of error.

$[Et_4N][V(CO)_5PR_3]$ (PR_3 = $P(OMe)_3$, $P(OPh)_3$, PH_2Cy, $PHCy_2$, PCy_3, PMe_3, $P(i\text{-}Bu)_3$, $P(t\text{-}Bu)_3$, and PPh_3). A 0.35-g (1.0-mmol) sample of $[Et_4N][V(CO)_6]$ dissolved in 70 mL of THF were treated with 0.36 mL (5.04 mmol) of Me_2SO and irradiated for 4 h. THF was then removed in vacuo (room temperature) and the resulting oil ($[Et_4N][V(CO)_5Me_2SO]$ in Me_2SO) redissolved in 20 mL of THF. A 2-mL portion of this solution, containing 0.1 mmol of $[Et_4N][V(CO)_5Me_2SO]$, was transferred to a brown borosilicate vessel, treated with a ca. 5-fold molar excess of phosphine and stirred for 12 h at room temperature. During this time, the red-orange solution turned to yellow (formation of $[V(CO)_5PR_3]^-$). NMR measurements were carried out with these samples; IR spectra were obtained after 10-fold dilution with THF.

$[Et_4N][V(CO)_5PH_3]$. Through 10 mL of a THF solution containing 0.26 mmol of $[Et_4N][V(CO)_5Me_2SO]$ (from the UV irradiation of 90 mg of $[Et_4N][V(CO)_6]$ and 0.10 mL of Me_2SO) was passed a PH_3 stream via a gas inlet tube, until the solution had turned to a light yellow (ca. 10 min). To absorb unreacted PH_3, a gas washing bottle with aqueous $K[MnO_4]$ was placed between reaction vessel and a 10-mm mercury valve.

$[Et_4N][V(CO)_5P(NEt_2)_3]$ and $[Et_4N][V(CO)_5P(SiMe_3)_3]$. A 90-mg (0.26-mmol) sample of $[Et_4N][V(CO)_6]$ was dissolved in 10 mL of THF, cooled to 195 K, and irradiated for 1 h (Ar atmosphere to avoid formation of $[V(CO)_5N_2]^-$[24]). While the low temperature was maintained, 0.80 mL of $P(NEt_2)_3$ or 0.81 mL of $P(SiMe_3)_3$ (2.60 mmol) was added. The solution was removed from the cold bath and, with continuous stirring, slowly brought to room temperature which resulted in a conversion of the red-violet $[V(CO)_5THF]^-$[24] to yellow $[V(CO)_5PR_3]^-$.

$[Et_4N][V(CO)_5(P\text{-}t\text{-}Bu_2)_2Te]$. This labile compound was obtained at 195 K from 80 mg (0.15 mmol) of $[Et_4N][V(CO)_5py]$[25] (py = pyridine), dissolved in 2 mL of THF, and 21 mg (0.05 mmol) of $Te(P\text{-}t\text{-}Bu_2)_3$ or as a suspension with brown decomposition products, at 273 K from a solution of 60 mg (0.15 mmol) of $[Et_4N][V(CO)_5Me_2SO]$ in 1.5 mL of acetone and 80 mg (0.19 mmol) of $Te(P\text{-}t\text{-}Bu_2)_2$.

$[Et_4N][V(CO)_5dppe]$ (dppe = $Ph_2P(CH_2)_2PPh_2$). A 0.35-g (1.0-mmol) sample of $[Et_4N][V(CO)_6]$ was dissolved in 70 mL of THF, treated with 0.36 mL (5.0 mmol) of Me_2SO, and irradiated for 4 h. The resulting solution of $[Et_4N][V(CO)_5Me_2SO]$ was concentrated to 20 mL and added dropwise with stirring to 50 mL of a THF solution of 0.87 g (2.17 mmol) of dppe contained in a brown Schlenk tube to exclude light. Stirring was continued for 16 h (room temperature). The yellow solution was concentrated to 10 mL and immediately treated with 50 mL of pentane to afford a red oil and white flakes of excess dppe. This white precipitate and the supernatant solution were jointly removed by decantation.

The remaining oil was triturated four times with 3-mL portions of CS_2 at 195 K and the supernatant CS_2 discarded each time. Finally, the oil was dissolved in 10 mL toluene, and after filtration 40 mL of pentane was added dropwise with vigourous stirring. A yellow powder and a red-brown oil separated out. After the mixture was left standing for 4 days at 243 K, the solvent was poured off and the residue stirred with 30 mL of pentane (4 h, room temperature), upon which the product solidified to give a yellow powder. This was filtered off, washed twice with 2-mL portions of pentane and diethyl ether, and dried in vacuo; yield 0.30 g (42%). Anal. Calcd for $C_{39}H_{44}NO_5P_2V$ (719.7): C, 65.09; H, 6.16; N, 1.95; P, 8.60; V, 7.08. Found: C, 64.5; H, 6.4; N, 2.13; P, 8.3; V, 6.9.

$[Et_4N][V(CO)_5pepe]$ (pepe = $Ph_2P(CH_2)_2PEt_2$). The reaction was carried out with 0.17 g (0.48 mmol) of $[Et_4N][V(CO)_6]$ in 20 mL of THF, 0.17 mL (2.40 mmol) of Me_2SO, and 0.45 mL (1.2 mmol) of pepe in analogy to the procedure described above. Reaction time for the exchange of Me_2SO for pepe was 8 h. The red oil obtained after addition of pentane was separated from the solution, dissolved in 10 mL of toluene, filtered, and treated once more with 50 mL of pentane. The supernatant pentane was then decanted, the oil washed twice with 2-mL portions of Et_2O, and residual solvent removed under high vacuum (4 h at room temperature). The complex can be precipitated as a yellow powder with pentane from a toluene solution cooled to 195 K; the melting point is around 263 K.

$[Et_4N][V(CO)_5arphos]$ (arphos = $Ph_2As(CH_2)_2PPh_2$). The procedure follows that described for the dppe complex. Amounts of reactants were 0.54 g (1.55 mmol) of $[Et_4N][V(CO)_6]$, 0.55 mL (7.75 mmol) of Me_2SO, and 1.52 g (3.40 mmol) of arphos. The workup of the red oil obtained after extraction of excess ligand with CS_2 was more direct; the oil was redissolved in 15 mL of toluene and agitated, at −195 K, with 70 mL of *n*-heptane to yield a yellow powder of the complex. This was filtered off at room temperature, washed twice with pentane and Et_2O, and dried; yield 0.49 g (43%). Anal. Calcd for $C_{39}H_{44}AsNO_5PV$ (763.6): C, 61.34; H, 5.81; N, 1.83; P, 4.05; V, 6.67; As, 9.81. Found: C, 60.8; H, 5.8; N, 1.84; P, 3.95; V, 7.0; As, 9.9.

$[Et_4N][V(CO)_5p_3]$ (p_3 = $PhP(CH_2CH_2PPh_2)_2$). A 0.15-g (0.43-mmol) sample of $[Et_4N][V(CO)_6]$ in 20 mL of THF was treated with 0.15 mL (2.1 mmol) of Me_2SO and irradiated for 4 h. This solution was dropped slowly to 0.92 g (1.72 mmol) of p_3 in 50 mL of THF contained in a brown Schlenk tube and stirred for 16 h. The yellow solution was concentrated to 10 mL, and 100 mL pentane was added in one batch to precipitate a red oil and minor amounts of white, unreacted phosphine which, together with the pentane, was decanted. (On standing of the decantate for several days at 243 K, most of the unreacted phosphine crystallized and was recovered by filtration and several washings with CH_3CN.) The oil was dissolved in 10 mL of CH_3CN and filtered and the acetonitrile removed in vacuo. This procedure was repeated with 10 mL of toluene and 100 mL of pentane at 195 K. The oil thus obtained was further purified by three washings with 5-mL portions of Et_2O. After decantation of the ether, residual solvent was removed in vacuo, leading to spontaneous solidification of the (now yellow) product; yield 0.18 g (48%). Anal. Calcd for $C_{47}H_{53}NO_5P_3V$ (885.8): C, 65.96; H, 6.24; N, 1.64; P, 10.86; V, 5.95. Found: C, 66.0; H, 6.2; N, 1.77; P, 10.1; V, 5.8.

$[Et_4N][V(CO)_5pp_3]$ (pp_3 = $P(CH_2CH_2PPh_2)_3$). The procedure is essentially the same as described for $[Et_4N][V(CO)_5p_3]$. Amounts of reactants: 0.18 g (0.51 mmol) of $[Et_4N][V(CO)_6]$, 0.18 mL (2.58 mmol) of Me_2SO, and 2.04 g (3.04 mmol) of pp_3. Yield: 0.22 g (44%). Anal. Calcd for $C_{55}H_{62}NO_5P_4V$ (991.9): C, 66.60; H, 6.30; N, 1.41; P, 12.49; V, 5.14. Found: C, 66.2; H, 6.2; N, 1.57; P, 12.8; V, 5.6.

$[Et_4N][V(CO)_5p'_3]$ (p'_3 = $PhP(CH_2CH_2CH_2PPh_2)_2$). A 0.5-g sample of (1.4 mmol) of $[Et_4N][V(CO)_6]$ and 0.8 g (1.4 mmol) of p'_3 were dissolved in 30 mL of THF and exposed to diffuse daylight (direct sunlight was avoided). After 2 days, the originally yellow solution had turned to a dark red. Stirring for 4 weeks afforded a light yellow powder of the desired complex. This was filtered off, washed twice with 10-mL portions of heptane, and

---

(23) Rehder, D.; Dahlenburg, L.; Müller, J. *J. Organomet. Chem.* **1976**, *122*, 53.

(24) Ihmels, K.; Rehder, D. *Chem. Ber.* **1985**, *118*, 895.

(25) Ihmels, K.; Rehder, D., following paper in this issue.

dried; yield 0.51 g (41%). Anal. Calcd for $C_{49}H_{57}NO_5P_3V$: C, 66.59; H, 6.50; N, 1.59; P, 10.51; V, 5.76. Found: C, 66.8; H, 6.7; N, 1.52; P, 9.8; V, 5.8.

If a THF solution containing equimolar amounts of $[V(CO)_6]^-$ and p'_3 is irradiated by UV for several hours, an approximate 1/4/1 mixture (by ^{51}V NMR) of $[V(CO)_5p'_3]^-$ ($\delta(^{51}V)$ -1845 (d, J = 226 Hz); ν(CO) 1960 and 1814 cm^{-1}), *cis*-$[V(CO)_4p'_3]^-$ (δ -1742 (t, J = 213 Hz); ν 1890, 1780, 1765, 1740 cm^{-1}), and *mer*-$[V(CO)_3p'_3]^-$ (δ -1573 (br s); ν 1930 cm^{-1} (others obscured)) is obtained. The spectroscopic data compare favorably to the corresponding complexes with tri- and tetradentate phosphines.[23,26]

Results and Discussion

General and Preparation. The problems that usually arise with the photoinduced introduction of phosphines into the carbonylvanadate system are manifold: (i) π-Accepting phosphines such as PMe_3, $P(OMe)_3$, or PF_3 readily replace CO in $[V(CO)_6]^-$; however, mixtures of multiply substituted complexes $[V(CO)_{6-n}(PR_3)_n]^-$ (n = 1, 2, PMe_3; n = 1–4, $P(OMe)_3$ and related phosphines;[15,27] n = 1–6, PF_3[15,28]) are obtained. (ii) Bulky phosphines (cone angle >160°) give rise to photolabile vanadium–phosphorus bonds. Only small amounts of $[V(CO)_5PR_3]^-$ are formed, and prolonged UV irradiation leads to gradual degradation of the carbonyl complex. (iii) The phosphine itself might be photolabile. This is the case with phosphines containing chlorine or a P–H bond. (iv) An additional problem arises with oligodentate phosphines which, under the conditions of UV irradiation, exhibit a strong tendency to form chelate structures (vide infra).

These disadvantages of the photoreaction have recently been overcome by ligand exchange reactions in the systems $[V(CO)_5L]^-/PR_3$, where L is a weak (with respect to its acceptor ability) and hence a labile ligand. Ellis and coworkers have employed $[V(CO)_5NH_3]^-$,[16] for which a preparative route (via the superreduced $[V(CO)_5]^{3-}$[29]) completely independent of a photosource had been developed. Despite the fact that the ammine complex is now more accessible than by the photoroute earlier described by us,[12] the necessity to work in liquid ammonia still renders this method tedious. For this reason, we have proposed $[V(CO)_5Me_2SO]^-$ as a starting material.[17] This complex can be generated photochemically at room temperature and reacted, in situ, with phosphines to produce $[V(CO)_5PR_3]^-$ in satisfactory yields. These exchange reactions preferably are carried out with the exclusion of light, since phosphines such as PMe_3 or dppe convert to the disubstituted tetracarbonylvanadates when exposed to diffuse daylight. Typical reaction times for the complete exchange of Me_2SO are ca. 12 h. The complexes formed with $P(SiMe_3)_3$ and $P(NEt_2)_3$, which are labile at room temperature, can not be synthesized by this method. In these cases, we have found that $[V(CO)_5THF]^-$, which is formed during the UV irradiation of $[V(CO)_6]^-$ in THF at 195 K,[24] is more conveniently employed. THF is immediately replaced by the phosphines, and the complexes can be characterized at low temperatures (although they are sufficiently long-lived at room temperature to allow collection of spectroscopic data).

The photoreaction between $[V(CO)_6]^-$ and bi- to hexadentate phosphines, p_n, usually leads to the chelates *cis*-$[V(CO)_4p_n]^-$ and *mer*-$[V(CO)_3p_n]^-$. The intermediate formed in the first reaction step $[V(CO)_5p_n]^-$ has been identified spectroscopically in several instances.[5,23,26] In a few cases, the different reactivities of mono- and disubstituted complexes toward, e.g., Et_4N/H exchange or allyl chloride have lead to the isolation of pentacarbonylvanadates. Examples are $[V(CO)_5pp_3]^-$ (pp_3 = $P(CH_2CH_2PPh_2)_3$)[4] and $[\{V(CO)_5\}_2\mu\text{-arphos}]^{2-}$ (arphos = $Ph_2As(CH_2)_2PPh_2$).[30,31]

The complex anions $[V(CO)_5dppe]^-$ (dppe = $Ph_2P(CH_2)_2PPh_2$), $[V(CO)_5dppm]^-$ (dppm = $Ph_2PCH_2PPh_2$), and $[V(CO)_5P_2Ph_4]^-$ with one of the phosphorus functions uncoordinated have been prepared by ligand exchange from $[V(CO)_5NH_3]^-$.[16] A preliminary characterization on the basis of spectroscopic data has already been carried out for a few other pentacarbonyl(phosphine)vanadates obtained from $[V(CO)_5Me_2SO]^-$ and dppe, arphos, p_3 (p_3 = $PhP(CH_2CH_2PPh_2)_2$), pp_3, and $Ph_2P(CH_2)_2PEt_2$ (pepe).[17] These complexes have now been isolated in 40–50% yields as yellow, air-sensitive powders by precipitation with pentane from toluene solutions. The pepe complex $[Et_4N][V(CO)_5pepe]$ is an orange-red oil at room temperature. $[V(CO)_5(P\text{-}t\text{-}Bu_2)_3Te]^-$ is thermolabile and has not been isolated. Its generation from $[V(CO)_5py]^-$ at ca. 200 K yields, inter alia, a tellurium-bound intermediate, which rearranges to the P-bound species within a few hours (^{51}V NMR evidence[25]).

While the complex $[V(CO)_5p_3]^-$ is light sensitive due to the pronounced tendency to form stable, five-membered metalla–phospha cycles by chelation, the corresponding carbonylvanadate with $Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2$ (p'_3) is stable. Yellow, sparingly soluble $[Et_4N][V(CO)_5p'_3]$ is gradually produced as a mixture of $[Et_4N][V(CO)_6]$ and p'_3, dissolved in THF, is exposed to diffuse daylight for several days to weeks. UV irradiation produces an equilibrium mixture of $[V(CO)_np'_3]^-$ (n = 1–3; see Experimental Section for details and data).

Spectra. IR and ^{51}V NMR data of the $[V(CO)_5PR_3]^-$ described in this work are collected in Table I, which also contains Graham's σ and π parameters[32] calculated from the CO stretching force constants and the factor $(\sigma - \pi)^{-1}$ which will be employed as a measure of the ligand strength (see below).

The IR pattern in the CO stretching region is in accord with the local C_{4v} symmetry of the complexes. Typically, three bands are observed around 1960 (A_1^{cis}), 1810 (E), and 1790 (shoulder; A_1^{trans}, trans refering to the CO trans to PR_3). A comprehensive IR analysis for pentacarbonyl(phosphine)vanadates(I–) has been given by Darensbourg and Hanckel,[19] who showed that the extent of the separation between E and A_1^{trans} is a function of the nature of the ligand and ion-pairing phenomena. For $P(OMe)_3$, $P(OPh)_3$, and p'_3, only two ν(CO) are observed. This accidential degeneracy of E and A_1^{trans} is also a common feature in, e.g., some $[Cr(CO)_5PR_3]$ complexes.[33a] Darensbourg also clarified the nature of an absorption around 1855 cm^{-1} which is very commonly observed and actually has to be attributed to small amounts of $[V(CO)_6]^-$. Some of the earlier band assignments carried out by our group[13,14] and others[33b] are therefore incorrect. It has been shown that the IR-forbidden B_1 may also gain some intensity.[34,35]

---

(26) Rehder, D.; Puttfarcken, U. *J. Organomet. Chem.* **1980**, *184*, 343.

(27) Rehder, D.; Dorn, W. L.; Schmidt, J. *Transition Met. Chem. (Weinheim, Ger.)* **1976**, *1*, 233.

(28) Schmidt, H.; Rehder, D. *Transition Met. Chem. (Weinheim, Ger.)* **1980**, *5*, 214.

(29) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.

(30) Roose, W.; Rehder, D.; Lüders, H.; Theopold, K. H. *J. Organomet. Chem.* **1978**, *157*, 321.

(31) Borowski, R.; Rehder, D.; von Deuten, K. *J. Organomet. Chem.* **1981**, *220*, 45.

(32) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315.

(33) (a) Cotton, F. A; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Wrighton, M. S.; Handeli, D. I.; Morse, D. L. *Inorg. Chem.* **1976**, *15*, 434.

(34) Bigorgne, M.; Poilblanc, R.; Pankowski, M. *Spectrochim. Acta, Part A* **1970**, *26A*, 1217.

(35) Miller, J. R. *Inorg. Chim. Acta* **1968**, *2*, 421.

Table I. IR and ^{51}V NMR Data of Pentacarbonyl(phosphine)vanadates [Et_4N][$V(CO)_5PR_3$][a] in THF

PR_3[b]	ν(CO),[c] cm^{-1}				k^{trans}, Nm^{-1}	k^{cis}, Nm^{-1}	π,[d] Nm^{-1}	σ,[d] Nm^{-1}	$(\pi - \sigma)^{-1}$, 10^2 N^{-1} m	$\delta(^{51}V)$[e]	$^1J(^{51}V-^{31}P)$, Hz
	A_1^{cis}	B_1	E	A_1^{trans}							
1, $P(OMe)_3$	1971 w		1827 vs		1369	1414	81	−48	0.78	−1928	366
2, $P(OPh)_3$	1981 w	1882 sh	1845 vs		1395	1437	84	−32	0.86	−1899	415
3, $PHCy_2$	1959 w		1811 s	1790 sh	1313	1392	47	−38	1.20	−1886	213
4, PH_2Cy	1967 w		1818 s	1800 sh	1327	1398	55	−38	1.08	−1884	202
5, PMe_3	1957 w		1810 s	1790 sh	1313	1390	49	−40	1.12	−1875	214
6, PH_3	1968 w		1823 s	1800 sh	1327	1409	44	−16	1.67	−1868	200
7, $P(SiMe_3)_3$	1951 w		1804 s	1773 sh	1287	1382	31	−30	1.64	−1867	366
8, $P(i\text{-}Bu)_3$	1955 w		1809 s	1780 sh	1298	1389	35	−27	1.61	−1856	211
9, PCy_3	1956 w	1852 w	1807 s	1775 sh	1291	1387	30	−24	1.85	−1854	211
10, $P(t\text{-}Bu)_3$	1958 w		1813 s	1785 sh	1305	1394	37	−24	1.64	−1833	210
11, $(t\text{-}Bu_2P)_2Te$	1957 w		1810 s	1780 sh	1298	1391	33	−23	1.79	−1834	215
12, PPh_3	1963 w		1823 s	1790 sh	1311	1407	30	−4	2.94	−1813	204
13, $P(NEt_2)_3$	1958 w		1810 s	1775 sh	1290	1391	25	−15	2.50	−1806	293
14, pepe	1959 m		1816 s	1790 sh	1312	1398	40	−23	1.59	−1842 −1891	*f* 208
15, dppe	1958 w		1814 s	1790 sh	1312	1395	43	−29	1.39	−1848	*f*
16, arphos	1958 w		1820 s	1790 sh	1311	1401	36	−16	1.92	−1849	*f*
17, p_3	1961 m	1860 w	1818 s	1793 sh	1316	1401	41	−21	1.61	−1849	*f*
18, p'_3	1960 m		1814 s		1350	1395	81	−67	0.68	−1845	214
19, pp_3	1961 m	1859 w	1817 s	1792 sh	1315	1399	42	−24	1.52	−1886	*f*

[a] PR_3 is a one or oligodentate phosphine. [b] Abbreviations: pepe = $Ph_2P(CH_2)_2PEt_2$, dppe = $Ph_2P(CH_2)_2PPh_2$, arphos = $Ph_2P(CH_2)_2AsPh_2$, p_3 = $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, p'_3 = $Ph_2P(CH_2)_3PPh(CH_2)_3PPh_3$, pp_3 = $P(CH_2CH_2PPh_2)_3$. [c] In THF except for p'_3 (in MeCN). [d] Graham's π and σ parameters relative to [$V(CO)_5NEt_3$]$^-$. [e] Relative to $VOCl_3$ at 300 K in THF or toluene (pepe, dppe, arphos, p_3, pp_3) or MeCN (p'_3). [f] Not resolved. Half-widths are 510 (pepe), 710 (pepe, V-PPh_2), 500 (arphos), 1100 (p_3), and 1300 (pp_3) Hz.

Here, this vibration mode is observed with the bulky phosphines p_3, pp_3, and PCy_3 and with the excellent π acceptor $P(OPh)_3$ (Table I). The weak absorptions for [$V(CO)_5PCy_3$]$^-$ (1852 cm^{-1}) and [$V(CO)_5P(OPh)_3$]$^-$ (1882 cm^{-1}) are in good agreement with the calculated[36] B_1 (1855 and 1887 cm^{-1}, respectively).

The ^{51}V NMR spectra exhibit well-resolved doublets ($^1J(^{51}V-^{31}P)$ coupling) with shift values typical of [$V(CO)_5PR_3$]$^-$, i.e., between −1806 (PR_3 = $P(NEt_2)_3$) and −1928 ppm ($P(OMe)_3$). The complexes with oligodentate phosphines and arphos fall within this range. There is a clear tendency for a decrease of ^{51}V shielding (decrease of $|\delta(^{51}V)|$) as the bulk of the phosphine increases (PMe_3 > $P(i\text{-}Bu)_3$ > $P(t\text{-}Bu)_3$; $PH_2Cy \cong PHCy_2$ > PCy_3) and the electronegativity of R decreases ($P(OMe)_3$ > PMe_3), the low-field (high-frequency) position of the $P(NEt_2)_3$ derivative being a consequence of the joint effects of the steric requirement of the NEt_2 group and its low effective electronegativity (vide infra). Comparable trends have been noted earlier for [$V(Cp)(CO)_3PR_3$] and [$V(Cp)(NO)_2PR_3$] (Cp = η^5-C_5H_5)[22,37] and the phosphine derivatives of [$Mo(CO)_6$] and [$W(CO)_6$].[38-41] Coupling constants are around 210 Hz for alkyl- and arylphosphines and go up to 415 Hz in the case of $P(OPh)_3$. This dependence upon the substituent electronegativity has been rationalized in terms of increasing Fermi contact contributions due to an increase of the s-electron densities at the two coupling nuclei caused by V(3d) → P(3d) → OR π delocalization.[22,27,37,42]

The ^{31}P NMR spectra should exhibit, for the coordinated phosphorus, an eight-line pattern (the nuclear spin of ^{51}V is 7/2) as observed in the ^{31}P NMR of [$V(PF_3)_6$]$^-$,[22,43] in the ^{13}C NMR of [$V(^{13}CO)_{6-n}(^{12}CO)_n$]$^-$,[44,45] or in the ^{1}H NMR of [$V(H)(CO)_5$]$^{2-}$.[46] However, in complexes of lower than O_h symmetry, quadrupole relaxation becomes effective (the nuclear quadrupole moment of ^{51}V is −0.052 × 10^{-28} m^2) and only very broad ^{31}P NMR signals are observed which still might bear the coupling information[5] but usually are unspecific due to partial relaxation decoupling. This is also the case with the compounds described here, which show broad signals usually centered around +70 (20) ppm.

For oligodentate phosphines, one or more PR_2 groups remain uncoordinated, and the ^{31}P NMR spectra give sharp resonances in the region around −20 ppm. The coupling and intensity patterns, along with the resonance positions of the ^{51}V NMR signals, allow insight into the coordination behavior of phosphines which contain two differing, competing functions. The ^{31}P NMR data are summarized in Table II; representative spectra are shown in Figures 1–3.

Let us first consider the bidentate ligands dppe, arphos, and pepe. The ^{31}P data for the uncoordinated PPh_2 group

---

(36) Dalton, J.; Paul, I.; Smith, J. G.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 1195.

(37) Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33 and references cited therein.

(38) Andrews, G. T.; Colquhoun, I. J.; McFarlane, W.; Grim, S. O. *J. Chem. Soc., Dalton Trans.* **1982**, 2353.

(39) Masters, A. F.; Bossard, G. E.; George, T. A.; Brownlee, R. T.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1983**, *22*, 908.

(40) Gray, G. M.; Gray, R. J. *Organometallics* **1983**, *2*, 1026.

(41) Gray, G. M.; Kraihanzel, C. S. *Inorg. Chem.* **1983**, *22*, 2959.

(42) Rehder, D.; Schmidt, J. *Transition Met. Chem.* (*Weinheim, Ger.*) **1977**, *2*, 41.

(43) Rehder, D.; Bechthold, H.-Ch.; Paulsen, K. *J. Magn. Reson.* **1980**, *40*, 305.

(44) Ihmels, K.; Rehder, D.; Pank, V. *Inorg. Chim. Acta* **1985**, *96*, L69.

(45) Warnock, G. F. P.; Philson, S. B.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1984**, 893.

(46) Warnock, F. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5016.

Table II. ^{31}P **NMR Data for the Uncoordinated** PR_2 **Groups in** $[V(CO)_5phosphine]^-$ [a]

	δ(^{31}P) [J(^{31}P–^{31}P), Hz][c]		
phosphine[b]	free phosphine[d]	$[V(CO)_5phosphine]^-$	ratio $VPPh_2/VPR_2$
dppe[e]	−13.4	−12.5 [d, 40]	
pepe PPh_2	−12.6 [25]	−11.9 [d, 32]	4/3
PEt_2	−20.0	−18.6 [d, 25]	
p_3			
	a. PPh_2-Bound Isomer, ABX		
PPh_2	−13.6 [29]	−12.2 [d, 28]	4/1
PPh	−17.8	−16.8 [t, 29]	
	b. PPh-Bound Isomer, A_2X		
PPh_2	−13.6	−13.6[f]	
p'_3 PPh_2	−18.2 [0.9[g]]	−19.8 [<2]	h
PPh	−28.8	−29.0	
pp_3			
	a. PPh_2-Bound Isomer, A_2BX		
PPh_2	−13.9 [26]	−13.3 [d, 25]	10/1
P	−16.6	−18.4 [q, 26]	
	b. P-Bound Isomer, A_3X		
PPh_2	−13.9	−12.2[f]	

[a] In toluene at 305 K except for p'_3 (MeCN, 300 K). [b] For abbreviations see footnote *b* in Table I. [c] d = doublet; t = pseudotriplet; q = pseudoquartet. [d] Under the same conditions as for the complex. [e] Cf. also ref 16. [f] Partly obscured. [g] From ref 51. [h] Only one isomer is observed ($VPPh_2$).

of $[V(CO)_5dppe]^-$ agree with those given by Ellis.[16] For $[V(CO)_5arphos]^-$, no ^{31}P NMR signal appears in this region. The ^{51}V NMR of the compound shows only one signal at −1849 ppm, split into a doublet (280 Hz). Hence the ligand exclusively bonds via PPh_2. This has also been noted for $[Cr(CO)_5arphos]$[47] and is in accord with the better π acceptor ability of phosphine than arsine ligands.

Phosphine ligand exchange reactions in pentacarbonyl(phospine)vanadates have been shown to follow a dissociative, first-order mechanism.[19] This is also true for the photosubstitution of CO by PR_3 in the isoelectronic $[Cr(CO)_6]$ (although, at high ligand concentrations, a second-order term gains influence)[48] and should also prevail for the labile ligand syntheses carried out here in the carbonylvanadium systems.

The ambidentate pepe ligates about equally via PPh_2 and PEt_2 (Figure 1), giving rise to two ^{51}V signals at −1843 (V–PPh_2) and −1891 ppm (V–PEt_2, doublet, *J*(VP) = 208 Hz). Two doublets at −18.6 (PEt_2, *J*(PP) = 25 Hz) and −11.9 ppm (PPh_2, *J*(PP) = 32 Hz) for the uncoordinated PR_2 groups are shifted slightly to lower field of the free ligand.

The situation is more complex with the compounds formed by the tri- and tetradentate ligands. Two isomers may be expected with p_3, depending on whether the phosphine bonds via its terminal PPh_2 or the central PPh. The (unstructured) ^{51}V NMR signal at −1849 ppm does not allow for a distinction; the chemical shift differences for complexes such as $[V(CO)_5PEtPh_2]^-$ (−1849 ppm) and $[V(CO)_5PMe_2Ph]^-$ (−1855 ppm)[5,22] are close to the limits of error. However, the ^{31}P NMR is in favor with the PPh_2 bonded isomer being the main product. For this isomer, an ABX pattern (A = uncoordinated PPh_2; B = uncoordinated PPh; X = coordinated PPh_2) is expected. The B part is a pseudotriplet (as observed in the corresponding tungsten complex[49]) at −16.8 ppm and the A part a doublet at −12.2 ppm, partly overlapping with the doublet for the PPh bound isomer (A_2X) at −13.6 ppm. Integration yields a ratio of the two isomers of 4/1. Simulated and experimental spectra are shown in Figure 2.

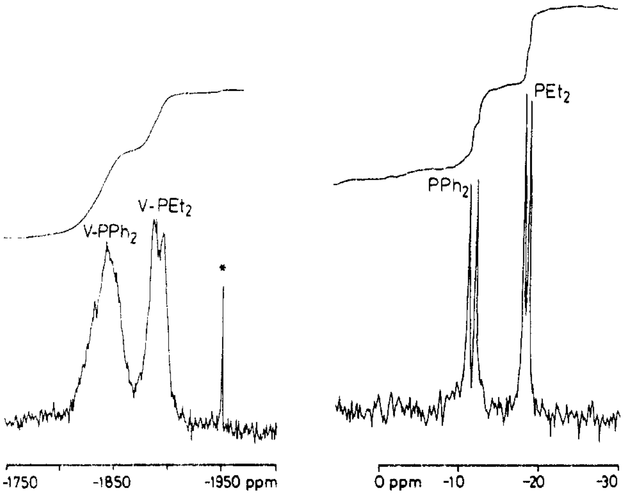

Figure 1. $^{51}V\{^1H\}$ (left) and $^{31}P\{^1H\}$ (for uncoordinated PR_2; right) NMR spectra of $[Et_4N][V(CO)_5pepe]$ (pepe = $Ph_2PCH_2CH_2PEt_2$) at 300 K in toluene (asterisk = $[V(CO)_6]^-$).

The monosubstituted complex $[V(CO)_5p'_3]^-$, which has been prepared by light-induced reaction (vide supra), shows a well-resolved doublet (*J*(VP) = 214 Hz) at −1845 ppm in the ^{51}V NMR. The ^{31}P NMR exhibits two singlets (^{31}P–^{31}P coupling <2 Hz) at −19.8 (PPh_2) and −29.0 ppm (PPh) of the intensity ratio 1/1, indicating that only PPh_2 coordination occurs.

The ^{31}P NMR spectrum of the pp_3 complex (Figure 3) shows a pseudoquartet (−18.4 ppm; apical P) and a doublet (−13.3 ppm; PPh_2). The intensity ratio is 1/2.3, and this corresponds with an isomeric mixture of V–P and V–PPh_2 bound phosphine of 1/10.

The Correlation between IR and Shielding Data. Shielding variations for metal nuclei are dominated by variations in the paramagnetic deshielding term, which contains the energy separation between HOMOs and LUMOs (Δ*E*) and quantities associated with the expansion of the metal d cloud and the covalency of the metal–ligand bond. If, in a first approximation valid for a series of complexes with ligands coordinating via the same function (PR_3 in our case), all parameters except Δ*E* are taken as constant (*B*), then the shielding/Δ*E* relation can be written in the form of a linear equation[50]

$$\sigma' = A - B\Delta E^{-1}$$

where σ' is the overall shielding, *A* the (constant) diamagnetic, and $B\Delta E^{-1}$ the paramagnetic contribution to σ'. The validity of this equation has been verified for, inter alia, sundry $^{59}Co^{3+}$ complexes of octahedral geometry[52] and also for *cis*-$[^{95}Mo(CO)_4(PR_3)_2]$,[41] which exhibit linear correlations between the metal shifts and the lowest d–d transitions in the electron absorption spectra. Metal shielding as a function of the nature of phosphine ligands has also been discussed for various pentacarbonyl(phosphine)molybdenum and -tungsten complexes by McFarlane et al.[37,53] and will further be presented, together with

---

(47) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, K. G. *J. Chem. Soc., Dalton Trans.* **1973**, 347.

(48) Pardue, J. E.; Dobson, G. R. *Inorg. Chim. Acta* **1976**, *20*, 207.

(49) Keiter, R. L.; Brodack, J. W.; Borger, R. D.; Cary, L. W. *Inorg. Chem.* **1982**, *21*, 1256.

(50) Harris, R. K.; Mann, B. E. Eds. "NMR and the Periodic Table"; Academic Press: New York, 1978.

(51) DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc. Dalton Trans.* **1975**, 1011.

(52) Juranič, N. *Inorg. Chem.* **1983**, *22*, 521.

Table III. Shielding Parameters $\delta(^{51}V)$ and Ligand Parameters for Alkylphosphines in $[V(CO)_5PR_3]^-$

parameter[a]	PH_2Cy	$PHCy_2$	PMe_3	PH_3	$P(i\text{-}Bu)_3$	PCy_3	$P(t\text{-}Bu)_3$
$\lvert\delta(^{51}V)\rvert$	1884	1886	1875	1868	1856	1854	1833
θ	111	142	118	87	143	170	182
π	55	47	49	44	35	30	37
σ	−38	−38	−40	−16	−27	−24	−24

[a] θ = Tolman's cone angle in deg; π and σ = Graham's π and σ parameters in Nm^{-1} (cf. Table I).

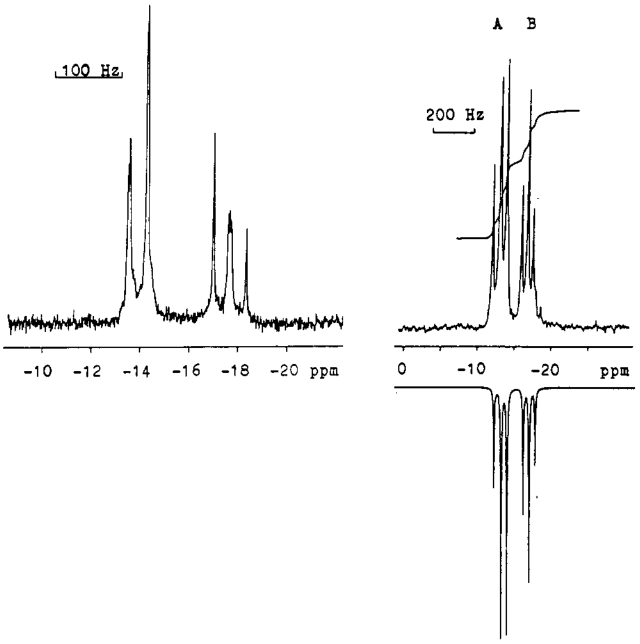

Figure 2. $^{31}P\{^1H\}$ NMR spectra of p_3 (p_3 = $PhP(CH_2CH_2PPh_2)_2$; left) and $[V(CO)_5p_3]^-$ (experimental, upper right; computed, lower right) in toluene at 305 K. The computation had been carried out for a 4/1 ratio of the two isomers (PPh_2- and PPh-bound ligands, respectively).

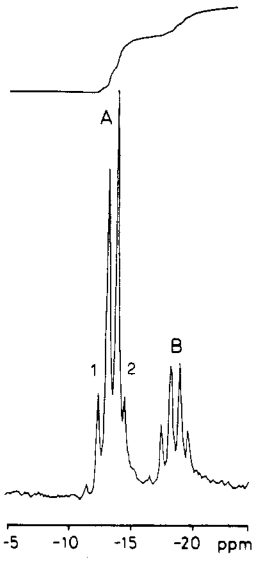

Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[V(CO)_5pp_3]^-$ (pp_3 = $P(CH_2CH_2PPh_2)_3$) in toluene at 305 K, showing the A_2BX pattern for the main component (the PPh_2-bound isomer). 1 is the P-bound isomer, and 2 is an impurity of the free ligand.

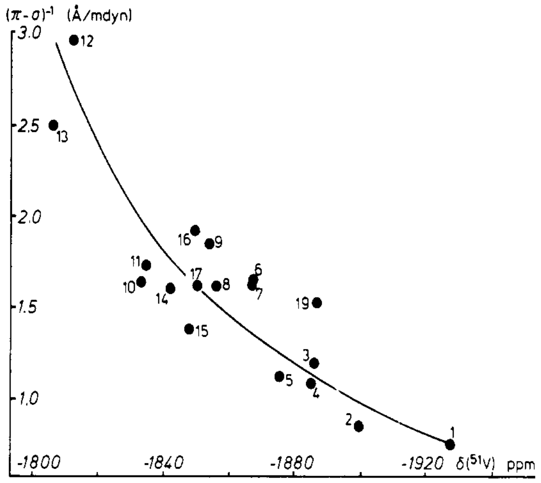

Figure 4. Plot of $(\pi - \sigma)^{-1}$ vs. $\delta(^{51}V)$ for $[V(CO)_5PR_3]^-$ complexes. π and σ are the Graham parameters (here in mdyn/Å = 10^{-2} N/m); $(\pi - \sigma)$ is a measure for the total ligand strength and is related to the ligand field splitting ΔE. The correlation is nonlinear since, by definition, π and $\sigma \rightarrow 0$ for $\delta(^{51}V) \rightarrow -1456$ ppm (see text). Data were taken from Table I.

a more detailed treatment of the background theory, for a larger variety of $[V(CO)_5L]^-$ complexes in the succeeding paper.[25]

Since ΔE is a measure for the integral ligand strength, parameters describing the σ donor and π acceptor ability of the phosphine may be taken as a substitute for ΔE to correlate shielding data. Thus, if $\delta(^{51}V)$ is used as the parameter quantifying σ'

$$\delta(^{51}V) = A - B(\pi - \sigma)^{-1}$$

where π and σ are the Graham parameters calculated from the CO stretching force constants *k*(cis) and *k*(trans)[32,33] relative to the complex $[V(CO)_5NEt_3]^-$ ($\pi = 0$, $\sigma = 0$; $\delta(^{51}V)$ −1456[22,25]). The *k*, σ, and π values are contained in Table I, the results represented graphically in Figure 4. The slight curvature is due to the fact that, per definition, $\pi,\sigma \rightarrow 0$ for $\delta(^{51}V) \rightarrow -1456$. Disregarding this deviation from linearity, a straight line with the correlation coefficient 0.87 is obtained.

Since the phosphines limiting the $\delta(^{51}V)$ range for $[V(CO)_5PR_3]^-$ complexes $P(NEt_2)_3$ and $P(OR)_3$ are characterized by extremes in the IR spectroscopic π parameters, vanadium–phosphorus π interaction might be considered to be the main factor influencing ΔE (and σ'). The extremely low σ parameter for PPh_3 agrees with investigations carried out by Romm et al.,[54] according to which the free electron pair on P is conjugated to the aromatic systems and hence less available. The relatively low π parameter in turn is compatible with $\pi(Ph)$–$\pi^*(CO)$ interligand interaction as discussed, e.g., in ref 55. The influence of steric factors is evidenced by the parallelity of the trends for $\delta(^{51}V)$, σ, π, and Tolman's cone angles in alkylphosphine complexes (Table III). Generally, steric

---

(53) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.

(54) Romm, I. P.; Sadykova, E. M.; Gur'yanova, E. N.; Kolli, I. D.; Kocheshkov, K. A. *Dokl. Chem.* **1970**, *195*, 820.

(55) Hengefeld, A.; Kopf, J.; Rehder, D. *Organometallics* **1983**, *2*, 114.

(56) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

crowding as encountered with bulky phosphines leads to a decrease of V–P interaction and therefore to a decrease of π and σ (and ΔE, i.e., an increase of the paramagnetic deshielding contribution and decrease of σ' and $|\delta(^{51}V)|$).

Registry No. 1, 75009-05-1; **2**, 79152-75-3; **3**, 96444-88-1; **4**, 96444-90-5; **5**, 82510-89-2; **6**, 82581-48-4; **7**, 96444-92-7; **8**, 96444-93-8; **9**, 82887-80-7; **10**, 96444-95-0; **11**, 96444-97-2; **12**, 10170-61-3; **13**, 96444-98-3; **14** (V–PPh_2), 82887-85-2; **14** (V–PEt_2), 82887-89-6; **15**, 82887-83-0; **16**, 82887-82-9; **17** (V–PPh_2), 82887-87-4; **17** (V–PPh), 75009-07-3; **18**, 96445-00-0; **19** (V–PPh_2), 73299-95-3; **19** (V–P), 73309-66-7; $[Et_4N][V(CO)_6]$, 13985-78-9; $[Et_4N][V(CO)_5Me_2SO]$, 96445-01-1; $[Et_4N][V(CO)_5Py]$, 82887-77-2; *cis*-$[V(CO)_4P'_3]^-$, 96445-02-2; *mer*-$[V(CO)_3P'_3]^-$, 96445-03-3.

Pentacarbonylvanadates(I–) Containing C, N, and Group 16 Ligands. The Relation between IR and ^{51}V NMR Shift Parameters[†]

Klaus Ihmels and Dieter Rehder*

Department of Chemistry, University of Hamburg, Martin-Luther-King-Platz 6,
D-2000 Hamburg 13, Federal Republic of Germany

Received October 19, 1984

The complexes $[Et_4N][V(CO)_5L]$ with L = CNR, CN^-, NCR, NR_3, pyridines, $S(O)R_2$, $OCMe_2$, SO_2, and ER_2 (E = O, S, Se, Te) have been prepared by ligand exchange from $[V(CO)_5THF]^-$ or $[V(CO)_5Me_2SO]^-$ or by UV irradiation of $[V(CO)_6]^-$ in THF in the presence of L at 195 K. As shown by ^{51}V NMR, substituted pyridines NC_5H_4R exhibit an ambidentate coordination behavior, ligating via the pyridine N (R = H, 4-CN), NH_2 (R = 2-NH_2), or the nitrile N (R = 2-CN). ^{51}V chemical shifts $\delta(^{51}V)$ relative to $VOCl_3$ span the range of −1339 (L = OPh_2) to −1906 ppm ($CNCH_2CO_2Et$). Shielding increases as the ligand strength (mainly the π acceptor ability) and the ligand polarizability increase. IR spectroscopic π parameters relative to NEt_3 vary from 173 (SO_2) to −7 ($NHEt_2$) and σ parameters from −75 ($CNCH_2CO_2Et$) to 21 Nm^{-1} (SPh_2). Including data for L = PR_3, N_2, $SnPh_3^-$, and others, a linear correlation (coefficient 0.95) is obtained for $\delta(^{51}V)$ vs. $\chi/(6.5 + (\pi - \sigma)$, where χ is the electronegativity of the coordinating ligand function, $(\pi - \sigma)$ a measure for the integral ligand strength, and 6.5 an empirical factor.

Introduction

Until recently, pentacarbonylvanadates(I–) containing other than phosphine ligands[1] have only been described sporadically. While ligands which are good to moderate acceptors (AsR_3, SbR_3) can still be introduced into $[V(CO)_6]^-$ by photochemical reaction paths,[2-6] the possibility of exchanging CO by L under the conditions of UV irradiation rapidly decreases as the π acceptor power of L decreases. At the same time, the complexes become more labile under ordinary conditions, i.e., at room temperature and in solution. Nonetheless, a few $[V(CO)_5L]^-$ complexes generated by UV irradiation of $[V(CO)_6]^-$ in the presence of L have been reported. Examples are L = NH_3 and CN^-,[7] Me-THF,[8,9] pyridine, and MeCN,[9] and Me_2SO.[10]

More recently, alternative methods, avoiding the sometimes problematic photochemical route, have extended the family of $[V(CO)_5L]^-$ complexes. The more promising of these new routes are ligand exchange reactions. The cyano complex $[V(CO)_5CN]^{2-}$ has thus been prepared via $[V(CO)_5Me_2SO]^-$[10] or $[V(CO)_5NH_3]^-$ (from $[V(CO)_5]^{3-}$ and $[NH_4]Cl$ in liquid ammonia)[11,12] and CN^-. Ammonia substitution has also successfully been applied to the introduction of MeCN and isonitriles,[12,13] while the complexes of several group 14 triorganyls $[V(CO)_5ER_3]^{2-}$ (E = Sn, Pb) can be obtained either by reduction of $[V(CO)_5(ER_3)_2]^-$[14,15] or via the reaction between $[V(CO)_5]^{3-}$ and R_3ECl in NH_3.[11] We have shown that thermolabile $[V(CO)_5L]^-$ species with L = η^1-N_2, η^2-CS_2, SO_2 (η^1-S), η^2-alkenes, and η^2-alkynes[16] and $[V(CO)_5(^{13}CO)]^-$[17] can be prepared by ligand exchange from $[V(CO)_5L']^-$ (L′ = THF, acetone, or (L = N_2) Me-THF). ^{51}V NMR spectroscopy, which we have developed in the past years as a versatile tool for analytical purposes, structural assignments, and the interpretation of electronic interactions in the vanadium coordination sphere[6,15-21] can be employed for the

---

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) See the preceding paper in this issue.
(2) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1971**, *31*, 239.
(3) Talay, R.; Rehder, D. *Chem. Ber.* **1978**, *111*, 1978.
(4) Talay, R.; Rehder, D. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 451.
(5) Roose, W.; Rehder, D.; Lüders, H.; Theopold, K. H. *J. Organomet. Chem.* **1978**, *157*, 311.
(6) Borowski, R.; Rehder, D.; von Deuten, K. *J. Organomet. Chem.* **1981**, *220*, 45.
(7) Rehder, D. *J. Organomet. Chem.* **1972**, *37*, 303.
(8) Braterman, P. S.; Fullarton, A. *J. Organomet. Chem.* **1971**, *31*, C27.
(9) Wrighton, M. S.; Handeli, D. I.; Morse, D. L. *Inorg. Chem.* **1976**, *15*, 434.
(10) Ihmels, K.; Rehder, D. *J. Organomet. Chem.* **1983**, *232*, 151.
(11) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100.
(12) Ellis, J. E.; Fjare, K. L. *Organometallics* **1982**, *1*, 898.
(13) Ellis, J. E.; Fjare, K. L. *J. Organomet. Chem.* **1981**, *214*, C33.
(14) Ellis, J. E.; Hayes, T. G.; Stevens, R. S.; *J. Organomet. Chem.* **1981**, *216*, 191.
(15) Talay, R.; Rehder, D. *J. Organomet. Chem.* **1984**, *262*, 25.
(16) Ihmels, K.; Rehder, D. *Chem. Ber.* **1985**, *118*, 895.
(17) Ihmels, K.; Rehder, D.; Pank, V. *Inorg. Chim. Acta* **1985**, *96*, L69.
(18) Survey on ^{51}V NMR spectroscopy: Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33.
(19) NMR of the first transition series nuclei: Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125.