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[†]

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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

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[†] 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.)

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Table I. Preparative Details and Analytical Data for $[Et_4N][V(CO)_5CNR]$

R	$[Et_4N][V(CO)_6]$, g (mmol)	Me_2SO, mL (mmol)	CNR, mL (mmol)	yield, g (%)	emperical formula (mol mass)	anal. calcd (found) C	H	N	V
i-Pr	0.48 (1.37)	0.49 (6.87)	0.14 (1.79)	0.42 (78)	$C_{17}H_{27}N_2O_5V$ (391.4)	52.17 (52.0)	6.95 (7.0)	7.15 (7.2)	13.01 (13.2)
t-Bu	0.48 (1.37)	0.49 (6.87)	0.18 (1.80)	0.43 (78)	$C_{18}H_{29}N_2O_5V$ (404.4)	53.47 (53.2)	7.22 (7.1)	6.92 (7.0)	12.60 (12.1)
Cy	0.44 (1.26)	0.45 (6.30)	0.20 (1.64)	0.44 (82)	$C_{20}H_{31}N_2O_5V$ (430.4)	55.80 (55.3)	7.30 (7.3)	6.50 (6.2)	11.83 (12.2)
CH_2CO_2Et	0.44 (1.26)	0.45 (6.30)	0.18 (1.64)	0.41 (75)	$C_{18}H_{27}N_2O_7V$ (434.4)	49.77 (49.8)	6.27 (6.1)	6.45 (6.3)	14.73 (11.8)

identification of labile species.

In the present work, the ligand exchange method is extended to the preparation of a variety of hitherto unknown or insufficiently characterized pentacarbonylvanadates with ligands covering a wide range of electronic conditions including the weak acceptor properties encountered with amines and group 16 donors. Incorporating data from ref 1 and 16, a general and comprehensive concept for the description of the factors influencing ^{51}V shielding is developed on the basis of correlations between metal shielding and IR parameters. $\delta(^{51}V)$ values for some of the compounds have been reported in two preliminary notes.[22,23]

Experimental Section

The general procedure has been described in the preceding paper.[1] The ligands, obtained from commercial sources, were purified according to standard procedures[24] and kept under N_2 or Ar; liquid ligands were recondensed under Ar. SO_2 was washed with concentrated H_2SO_4 and distilled under Ar. IR and ^{51}V NMR spectra were obtained as described.[1] For broad ^{51}V resonances (half-widths $W_{1/2} >$ ca. 500 Hz), a Bruker SWL 3-100 wide line spectrometer was employed: Spectra were scanned for probes contained in 10-mm diameter vials at 11.0 MHz (central magnetic field, 0.984 T; sweep width, 3 mT), with a modulation of 0.5 mT and 10-μT field strength of the high-frequency field. Typically, 20 scans every 2 min (time constant 1 s) were sufficient to provide a signal-to-noise ratio of > 5/1. Estimated error for $\delta(^{51}V)$ measured on this instrument (and given in italics in Table III) is ±15 ppm. Spectroscopic data for the following $[V(CO)_5L]^-$ anions were taken from the literature: L = phosphine and phosphite;[1,20c] arsine and stibine;[6] alkene, alkyne, CS_2, and N_2;[16] Me_2SO;[10,13] CO;[17] $SnPh_3^-$ and $PbPh_3^-$;[14,15] NH_3;[25] H^-.[26] $[Et_4N][V(CO)_5DMSO]$ was prepared as described previously.[10]

$[Et_4N][V(CO)_5CNR]$ (R = Cy, *i*-Pr, *t*-Bu, CH_2CO_2Et). Approximately 0.45 g of $[Et_4N][V(CO)_6]$ and a 5-fold molar excess of Me_2SO dissolved in 70 mL of THF were irradiated for 4 h to generate $[V(CO)_5Me_2SO]^-$. The solution was concentrated to 30 mL and added dropwise with stirring to a brown Schlenk tube containing a 1.3-fold molar excess (relative to $[Et_4N][V(CO)_6]$) of the isonitrile in 20 mL of THF. The reaction mixture was stirred until the IR indicated completion of the Me_2SO/CNR exchange (ca. 20 h). The yellow solution, still kept away from light, was then concentrated to 15 mL and treated with 50 mL of *n*-pentane to produce a dark oil. After 30 min of stirring, the supernatant and almost colorless solution was poured off and the oil was triturated for 10 min with 5 mL of toluene. The oil partially dissolved and was reprecipitated with 20 mL of pentane. After decantation of the pentane/toluene solution, the oil was dissolved in 15 mL of THF and placed in a cold bath (ca. 240 K). Dropwise addition of a total amount of 50 mL of pentane now produced lemon yellow powders of $[Et_4N][V(CO)_5CNR]$ which, in the case of R = Cy, *i*-Pr, and *t*-Bu, were filtered off at room temperature and dried in vacuo. In the case of $CNCH_2CO_2Et$, filtration was carried out at 253 K to avoid conversion to an oil. Once freed from solvent, the compound remains solid, turning brown at room temperature, within a few minutes without apparent changes in the spectroscopic characteristics. Experimental details, yields, and analytical data are contained in Table I.

$[Et_4N][V(CO)_5py]$ (py = NC_5H_5). I. A 0.44-g (1.10-mmol) sample of $[Et_4N][V(CO)_5Me_2SO]$ was dissolved in 30 mL of pyridine cooled to 268 K and stirred for 3 h at 268–273 K and 15 min at room temperature. The violet solution was then placed in a cold bath (230 K) and treated dropwise with 20 mL of toluene, followed by ca. 100 mL of pentane to yield a carmine red powder. After 30 min of stirring (230 K), 50 mL of the supernatant solution was removed and discarded. The remaining suspension was immediately filtered and the powder washed with five 3-mL portions of cold pentane (residual pentane was removed by passage of N_2 through the filter plate) and dried under high vacuum (230 K, 6 h). At room temperature, the complex slowly decomposes: yield 0.32 g (72%). Anal. Calcd for $C_{18}H_{25}N_2O_5N$ (400.3): C, 51.36; H, 6.29; N, 6.99; V, 11.46. Found: C, 50.85; H, 5.7; N, 6.7; V, 11.6.

II. A 0.12-g (3.44-mmol) sample of $[Et_4N][V(CO)_6]$ was dissolved in 30 mL of py and irradiated for 4 h to yield the pyridine derivative.

III. The complex was also obtained by irradiation (8 h) of 30 mL of a THF solution containing 7 mL (0.688 mol) of py and 0.12 g (0.44 mmol) of $[Et_4N][V(CO)_6]$. The solution is stable at room temperature.

$[Et_4N][V(CO)_5py']$ (py′ = NC_5H_4R; R = 2-NH_2, 2-CN, 4-CN). I. A 8.0-mg (0.02-mmol) sample of $[Et_4N][V(CO)_5Me_2SO]$ was dissolved in 2 mL of acetone at 268 K and stirred (30 min) with 150 mg (1.44 mmol) of CN-py or 200 mg (2.13 mmol) of 2-NH_2-py, respectively, to yield red-brown solutions of the pyridine complexes, which could be kept at room temperature for several days without decomposition.

II. A 0.70-g (6.70-mmol) sample of 2-CN-py was dissolved in 1.5 mL of THF, cooled to 195 K, and treated with 40 mg (0.10 mmol) of $[Et_4N][V(CO)_5py]$ to give $[V(CO)_5\text{2-CN-py}]^-$.

III. A 90-mg (0.26-mmol) sample of $[Et_4N][V(CO)_6]$ dissolved in 15 mL of THF was irradiated for 1 h (195 K, Ar atmosphere) to yield $[V(CO)_5THF]^-$. While maintaining the low temp., this solution was added to 1.5 g (14.4 mmol) of py′ and stirred for 10 min, followed by 15 min of stirring at 268 K to yield blue-violet (2-CN-py), deep blue (4-CN-py), or brown-red (2-NH_2-py) solutions of the pyridine complexes identical in their spectroscopic data with those obtained by method I.

$[Et_4N]_2[V(CO)_5CN]$. I. A 50-mg (0.14-mmol) sample of $[Et_4N][V(CO)_6]$ was dissolved in 10 mL of acetonitrile and irradiated, at 195 K, for 30 min. This solution was treated in the cold with 43 mg (0.28 mmol) of $[Et_4N]CN$, removed from the cold bath, and stirred for 30 min at room temperature, upon which the cyano complex was formed, accompanied by a color change from yellow-orange to ocher.

II. A 50-mg (0.14-mmol) sample of $[Et_4N][V(CO)_6]$ and 0.05 mL (0.70 mmol) of Me_2SO dissolved in 10 mL of THF were irradiated for 4 h. The solvent was distilled off and the remaining red oil ($[Et_4N][V(CO)_5Me_2SO]/Me_2SO$) treated with 10 mL of a CH_3CN solution of 0.55 g (3.50 mmol) of $[Et_4N]CN$. Since the cyano complex has been described previously,[7,12] no attempts were undertaken for its isolation.

$[Et_4N][V(CO)_5L]$ (L = NCR, $OCMe_2$, $S(O)Ph_2$, $E^{16}Ph_2$, SO_2, NR_3). The preparations closely follow those of the pyridine complexes and are summarized, together with colors and decomposition points, in Table II. The solutions of these complexes

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Table II. Experimental Details for the Preparation of $[V(CO)_5L]^-$ Complexes and Selected Properties

L	method[a]	$[Et_4N][V(CO)_6]$ mg (mmol)	ligand mL (mmol)	solvent (mL)	color	decomp temp[b]
NCMe	A	80 (0.23)		MeCN (15)	yellow-orange	258
NCPh[c]	A′	90 (0.26)	3.0 (29.4)	THF (12)	red-violet	243
	B	20 (0.06)	2.0 (19.6)	THF (10)	red-violet	
$OCMe_2$	A	80 (0.23)		$OCMe_2$ (15)	wine red	218
OPh_2	A′	90 (0.26)	4.3 (26.0)	THF (10)	red-violet	233
SPh_2	B	80 (0.23)	5.8 (54.5)	THF (11)	brown	248
SMePh	B	100 (0.29)	6.8 (42.0)	THF (0)	brown	263
$SePh_2$	B	90 (0.26)	3.0 (17.4)	THF (15)	dark brown	263
$TePh_2$	B	5 (0.014)	0.8[d]	THF (0.75)	brown	stable
SO_2	B	90 (0.26)		THF (10)	gray-green	238
$S(O)Ph_2$	C	40 (0.10)	50[e] (0.25)	THF (1.5)	light red	stable
NEt_3	A′	70 (0.20)	5.7 (40.0)	THF (10)	red-violet	228
$NHEt_2$	A′	100 (0.29)	4.5 (43.5)	THF (10)	wine red	263
NH_2Ph	A′	70 (0.20)	4.0 (40.0)	THF (11)	cherry red	228
$NHPh_2$	A′	70 (0.20)	45[e] (0.27)	THF (15)	red-violet	228
NEt_2Ph	A′	100 (0.29)	7.0 (43.5)	THF (10)	red-violet	233

[a] A, 30-min irradiation of $[Et_4N][V(CO)_6]$ dissolved in L at 195 K under N_2; A′, 60-min irradiation of $[Et_4N][V(CO)_6]$ + L in THF at 195 K under Ar; B, dropwise addition of L to a solution of $[Et_4N][V(CO)_5THF]$ obtained by 30–60 min irradiation of $[Et_4N][V(CO)_6]$ in THF at 195 K; C, addition of L to $[V(CO)_5py]^-$ in THF at 195 K and warming to room temperature. [b] Approximate decomposition temperature in K. [c] Also obtained by ligand exchange from $[V(CO)_5Me_2SO]^-$/NCPh at room temperature. [d] Density not reported. [e] Amount of ligand in mg.

which, except of L = NCPh and $TePh_2$, are thermolabile have been measured directly at 200–220 K.

Attempted Preparations. The reaction between $[V(CO)_5THF]^-$ and CSe_2 at 195 K leads to black decomposition products. A characterization by IR and/or ^{51}V NMR could not be carried out.

Passage of high-grade purity CO_2 through a THF solution of $[V(CO)_5THF]^-$ at 203 K gives rise to a color change from red-violet to cherry red and precipitation of a cinnabar-red, sparingly soluble powder. We were unable to characterize this compound (which decomposes above 238 K) by spectroscopic methods. Attempts to dissolve the red powder in MeCN afforded $[V(CO)_5NCMe]^-$.

Irradiation of $[Et_4N][V(CO)_6]$ plus a threefold molar excess of $[Et_4N]Br$ in MeCN at 230 K yields a red-brown solution which, along with the signal for $[V(CO)_5NCMe]^-$ (ca. 90% intensity), showed two additional weak resonances at −1732 and −1768 ppm (253 K). Irradiation in CH_2Cl_2 at 195 K gives similar results; the main signal this time is unreacted $[V(CO)_6]^-$.

Reaction of 60.0 mg (0.15 mmol) of $[Et_4N][V(CO)_5py]$, dissolved in 2 mL of THF, and 21.0 mg (0.05 mmol) of $Te(PtBu_2)_2$ at 195 K afforded a solution which initially showed a broad signal at −1752 ppm characteristic of coordination via Te. The compound rearranges, however, to the P-coordinated complex (cf. ref 1).

Results and Discussion

Preparation and General Data. Pentacarbonylvanadates(I–) have been obtained by one of the following methods (i–iii).

(i) Irradiation of $[Et_4N][V(CO)_6]$ Dissolved in L (Eq 1). The quantitative formation of $[V(CO)_5L]^-$ is verified

$$[V(CO)_6]^- + L \xrightarrow[(L)]{h\nu} [V(CO)_5L]^- \qquad (1)$$

$$L = THF,\ 2\text{-}Me\text{-}THF,\ OCMe_2,\ NCMe,\ py$$

by the complete conversion to $[V(CO)_5PPh_3]^-$ on addition of PPh_3. Since the complexes decompose at 200–220 K (except for the pyridine compound), the irradiations are carried out at dry ice temperature and spectroscopic characterization is achieved around 200–210 K. The irradiations have to be conducted under Ar since, in the presence of N_2, $[V(CO)_5N_2]^-$[16] is formed as a temperature-labile byproduct. Although the isolated pyridine complex slowly decomposes above 240 K, its solution in pyridine can be handled and investigated spectroscopically at room temperature. The complexes noted here are excellent precursors to the preparation of a large variety of other compounds (vide infra). The THF,[8,9] py,[9] and NCMe[9,12] compounds have been identified previously in THF glasses and in solution.

(ii) Irradiation of $[Et_4N][V(CO)_6]$ Solutions in the Presence of L at 195 K (Eq 2). Except for the CN^- and

$$[V(CO)_6]^- + L \xrightarrow[(THF)]{h\nu} [V(CO)_5L]^- \qquad (2a)$$

$$L = py,\ NCPh,\ OPh_2,\ NEt_3,\ NHEt_2,\ NEt_2Ph,\ NHPh_2,\ NH_2Ph$$

$$[V(CO)_6]^- + CN^- \xrightarrow[(MeCN)]{h\nu} [V(CO)_5CN]^{2-} \qquad (2b)$$

NCPh complexes, the compounds are thermolabile and decompose between 200 and 240 K. Acetonitrile has been employed for the synthesis of the cyano complex, since $[Et_4N]CN$ is insoluble in THF. The dianion $[V(CO)_5CN]^{2-}$ has been obtained previously by UV irradiation of $Na[V(CO)_6]$ and NaCN in liquid ammonia[7] and by NH_3/CN^- exchange from $Na[V(CO)_5NH_3]$[12] and isolated as the black $[PPh_4]^+$ (in MeCN, deep red) or light yellow $[Et_4N]^+$ salt. An alternative method for its preparation is the irradiation of a MeCN solution of $[Et_4N][V(CO)_5PCy_3]$ and $[Et_4N]CN$ (unpublished).

The compounds produced according to eq 2a are photolabile in the sense described by equilibriums 3 and 4

$$[V(CO)_6]^- \xrightleftharpoons{h\nu} \{[V(CO)_5]^-\} + CO \qquad (3)$$

$$\{[V(CO)_5]^-\} + L \xrightleftharpoons[h\nu]{} [V(CO)_5L]^- \qquad (4)$$

(dissociative mechanism as proposed for the CO substitution in $[Cr(CO)_6]$[27]). An associative mechanism as proposed for the CO substitution in $[V(CO)_6]$[28] seems unlikely in the view of Wrighton's conclusions on photosubstitution reactions of $[V(CO)_6]^-$.[9] An approximately 100-fold molar excess of L is needed to suppress the reverse reaction to $[V(CO)_6]^-$ and to produce $[V(CO)_5L]^-$ almost quantitatively. Decomposition above ca. 240 K yields, as evidenced by IR and ^{51}V NMR, $[V(CO)_6]^-$; in the presence of PPh_3, $[V(CO)_5PPh_3]^-$ is formed.

There is no case for which disubstitution has been observed, which is not surprising in the light of the lability of complexes containing ligands with negligible π acceptor ability and also agrees with Strohmeier's investigations into

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Table III. IR and $\delta(^{51}V)$ Values for $[V(CO)_5L]^-$ Complexes

	IR data						^{51}V NMR data	
	$\nu(CO)$[a]							
L	A_1^{cis}	B_1[b]	E	A_1^{trans}	other	solv (temp[c])	$\delta(^{51}V)$[d]	solv (temp[c])
py	1960 w	1853 w	1800 s	1760 sh		py (295)	−1461	py (300)
py	1954 w		1800 s	1748 m		THF/py, 1/10		
NCMe	1965 m		1805 s	1785 m	*e*	MeCN (233)	−1615	MeCN (255)
NCPh	1957 m		1813 vs	1770 s	$\nu(CN)$ 2199 w[f]	THF/PhCN, 5/1 (203)	−1606	PhCN (300)
CNCy	1949 m		1822 vs		$\nu(CN)$ 2075 w[f]	THF (295)	−1900	MeCN (300)
CN-*t*-Bu	1942 m		1823 vs		$\nu(CN)$ 2080 w[f,g]	THF (295)	−1898	MeCN (300)
CN-*i*-Pr	1949 m		1825 vs		$\nu(CN)$ 2075 w[f]	THF (295)	−1901	MeCN (300)
$CNCH_2CO_2Et$	1948 m	1867 w	1830 vs		$\nu(CN)$ 2080 w[f,g]	THF (295)	−1906[h]	MeCN (300)
CN^-	1950 m		1790 s	1745 sh	$\nu(CN)$ 2060 w	MeCN (295)	−1864	MeCN (300)
NEt_3	1958 w		1800 s	1750 m		THF (ca. 200)	*−1482*	THF (202)
$NHEt_2$	1953 w		1792 s	1738 m		THF (ca. 200)	*−1522*	THF (202)
NH_2Ph	1950 w		1802 s	1755 m		THF (ca. 200)	*−1506*	THF (207)
$NHPh_2$	1946 w		1792 s	1735 m		THF (ca. 200)	*i*	
NEt_2Ph	1953 w		1792 s	1738 m		THF (ca. 200)	*−1505*	THF (202)
2-CN-py	1953 m		1815 s	1775 sh	$\nu(CN)$ 2179[f]	THF (295)	−1621	acetone (270)
4-CN-py	1952 w		1810 s	1770 sh		THF (295)	*−1440*	acetone (300)
$2\text{-}NH_2\text{-}py$	1955 w		1800 s	1750 sh		THF (295)	−1493	acetone (304)
THF	1948 w		1803 s	1750 sh		THF (ca. 200)	*−1390*[j]	THF (207)
2-Me-THF	*k*		*k*				*−1395*[l]	2-Me-THF (202)
$OCMe_2$	1955 w		1795 s	*m*		acetone (200)	*−1423*[n]	acetone (207)
OPh_2	*i*		1800 s	1735 m		THF (ca. 200)	*−1339*	THF (202)
SMePh	1963 w		1807 s	1770 m		THF (ca. 210)	*−1628*	THF (207)
SPh_2	1968 w		1820 s	1773 m		THF (ca. 210)	*−1618*	THF (202)
$SePh_2$	1963 w		1818 s	1780 sh		THF (ca. 210)	*−1658*	THF (207)
$TePh_2$	1958 m	1860 w	1820 s	1790 sh		THF (295)	*−1753*	THF (300)
$Te(P\text{-}t\text{-}Bu_2)_2$	*o*		*o*				*−1752*	THF (270)
$S(O)Me_2$	1977 m	1870 w	1827 vs		$\nu(SO)$ 1288	THF (295)	−1657	THF (300)
$S(O)Ph_2$	1978 w		1835 vs			THF (295)	−1657	THF (300)
SO_2	2018 w		1895 s	1940 sh		THF/SO_2 (203)	−1496	THF/SO_2 (200)

[a] A_1^{cis} and A_1^{trans} correspond with $A_1^{(2)}$ (k_2) and $A_1^{(1)}$ (k_1). [b] In most cases, the B_1 region is obscured by the $\nu(CO)$ of $[V(CO)_6]^-$ (1855 cm^{-1}), which is usually present as an impurity. For B_1(calcd), see Table IV. [c] Measuring temperature in K. [d] Relative to $VOCl_3$ neat. Values in italics (broad lines) have been obtained on a wide line spectrometer (see Experimental Section). [e] $\nu(CN)$ not observed. [f] Free ligand: NCPh, 2230; CNCy, 2132, CN-*t*-Bu, 2130; CN-*i*-Pr, 2135; $CNCH_2CO_2Et$, 2126; 2-CN-py, 2232 cm^{-1}. [g] Shoulder at 2040–2045 cm^{-1}. [h] A ^{13}C sattelite doublet, slightly shifted to high field, is observed. [i] Not observed. [j] A second, broad signal at −854 ppm (not assigned) has erroneously been attributed to the THF complex in ref 24. [k] Not characterized by IR since only minor amounts of this complex are formed. [l] A second signal is observed at −546 ppm (not assigned). [m] Obscured by $\nu(CO)$ of uncoordinated acetone. [n] For a second signal at −536 ppm see the discussion in the text. [o] Not identified unambiguously because the complex rearranges to the P-bound isomer.

the systems $[M(CO)_6]$/py, where the reaction rate for disubstitution is sufficiently slow to practically prevent, in the case of M = Cr, the introduction of a second pyridine ligand.[29] Good π accepting ligands such as CNR should form disubstituted complexes comparable to those observed with the phosphines PMe_3 and $P(OMe)_3$.[20a,d] However, attempts to prepare disubstituted isonitrile complexes $[V(CO)_4(CNR)_2]^-$ either by UV irradiation of $[V(CO)_6]^-$/CNR or by action of the catalytic system PdO/$[Mn_2(CO)_{10}]$ proposed by Coville[30] upon $[V(CO)_5CNR]^-$ have not yet been successful. In the latter case, $[Mn_2(CO)_9CNR]^{31}$ is formed.

(iii) Ligand Exchange without Irradiation (Eq 5).

$$[V(CO)_5L']^- + L \rightarrow [V(CO)_5L]^- + L' \qquad (5)$$

This method allows for the mild preparation of a variety of complexes. Commonly, $[V(CO)_5L']^-$ is generated in situ, and L′ may be THF, Me_2SO, py, MeCN, or NH_3. Me_2SO and pyridine complexes can also be used as isolated materials. The following compounds have been prepared in this work: L′ = THF and L = 2-CN-py, 4-CN-py, $2\text{-}NH_2\text{-}py$, NCPh, SPh_2, SMePh, $SePh_2$, $TePh_2$; L′ = Me_2SO and L = CNCy, CN-*i*-Pr, CN-*t*-Bu, $CNCH_2CO_2Et$, py, 2-CN-py, 4-CN-py, $2\text{-}NH_2\text{-}py$, NCPh, CN^-; L′ = py and L = 2-CN-py, $S(O)Ph_2$, $Te(P\text{-}t\text{-}Bu_2)_2$; L′ = MeCN and L = CN^-.

The thermolabile pyridine complex and the stable isonitrile complexes have been isolated as solids in 72% (py) and 70–80% yields (CNR). Similar yields (60–85%) of isonitrile complexes have been obtained by Ellis and Fjare[12] from the exchange reaction between $[V(CO)_5NH_3]^-$ and CNR (R = Me, Cy, *t*-Bu, Ph). The isocyanide complexes $[V(CO)_5CN\text{-}n\text{-}Bu]^-$ and the labile $[Ph_4As][V(CO)_5NCMe]$ were also identified by IR.[12] The complexes formed with substituted pyridines are stable at room temperature.

IR and ^{51}V NMR Spectra. Data are collated in Table III. The CO stretching pattern typical of local C_{4v} symmetry is observed for complexes of ligands belonging to the medium to weak π acceptor category (i.e., ligands coordinating via N, O, S, Se, Te, and CN^-): (commonly) weak A_1 band around 1950–1960 cm^{-1}, allocated to the four CO groups cis to L, a A_1 band of medium intesity for the CO trans to L (around 1740 cm^{-1}), and a strong E mode at ca. 1800–1820 cm^{-1} (the SO_2 complex gives a differing pattern; vide infra). Complexes with the good π delocalizing isonitrile ligands show only two $\nu(CO)$; A_1^{trans} and E are ac-

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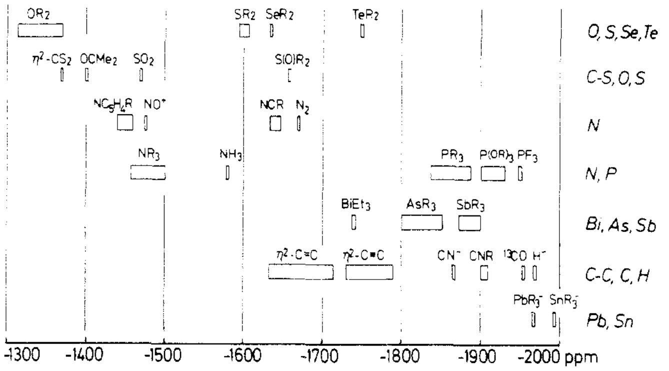

Figure 1. Chemical shift ranges ($\delta(300)$ relative to $VOCl_3$) of $[V(CO)_5L]^q$ complexes ($q = 0$, L = NO^+; q = 2–, L = CN^-, $SnPh_3^-$, $PbPh_3^-$, H^-; q = 1– for any other L). The coordinating ligand atoms are noted at the right-hand margin. ^{51}V shielding increases from left to right.

cidentially degenerate. The same phenomenon is observed with several (phosphine)vanadates.[1] In a few cases, the IR-forbidden B_1 mode is identified and assigned where it coincides with the calculated B_1 (cf. Table IV). The B_1 region is usually obscured by the ν(CO) of $[V(CO)_6]^-$ (ca. 1855 cm^{-1}) which is omnipresent as a decomposition or equilibrium product.

Due to the quadrupole moment of the ^{51}V nucleus (nuclear spin, $^7/_2$; nuclear quadrupole moment, -0.052×10^{-28} m^2), quadrupole relaxation governs the spin–lattice relaxation time T_1. Since T_1 is dependent upon the molecular correlation time τ_c and τ_c in turn largely depends on the viscosity of the system,[21b] relaxation rates increase with decreasing temperature and thus give rise to broad signals. Coordination of ^{14}N (nuclear spin = 1) adds to the broadening by scalar relaxation. Exchange phenomena (see eq 3 and 4) may also contribute. On the other hand, sharp signals (half-widths $W_{1/2}$ around 20 Hz) are observed in the room-temperature spectra of the isonitrile complexes, and in one case (L = $CNCH_2CO_2Et$), the doublet for the ^{13}C isotopomer has been identified which, in accord with what has been noted for the ^{51}V shifts of the complexes $[V(^{12}CO)_{6-n}(^{13}CO)_n]^-$,[17] is shifted slightly to low frequency (high field) of the main signal. $^1J(^{51}V-^{14}N)$ coupling constants, which have been reported for $V(N\text{-}t\text{-}Bu)(OSiMe_3)_3$,[32] $VO(NEt_2)(O\text{-}i\text{-}Pr)_2$[33] and $VO(NEt_2)Cl_2$,[21a] are around 50–110 Hz and should be resolved in $[V(CO)_5py]^-$ ($W_{1/2}$ = 132 Hz). However, only a singlet arises, and this can be traced back to relaxation decoupling as noted for other low-valent vanadium compounds, e.g., $[V(NO)(CO)_3diphos]$[34] and $[V(NO)_2L_4]^+$.[34,35]

For a set of ligands coordinating via the same function, the $\delta(^{51}V)$ ranges are relatively small (taking amines and nitriles as two different ligand sets), Figure 1, and this fact can be exploited to decide upon the coordination mode where ambidentate coordination might be expected. Since $\delta(^{51}V)$ values are temperature dependent, only data corrected for temperature effects are directly comparable. There is, in agreement with theory, a linear increase of ^{51}V shielding as the temperature decreases,[18] and this is verified for the temperature dependence of $\delta(^{51}V)$ of $[V(CO)_5CNCH_2CO_2Et]^-$ presented graphically in Figure 2. The temperature gradient is 0.25 ppm/deg and has been

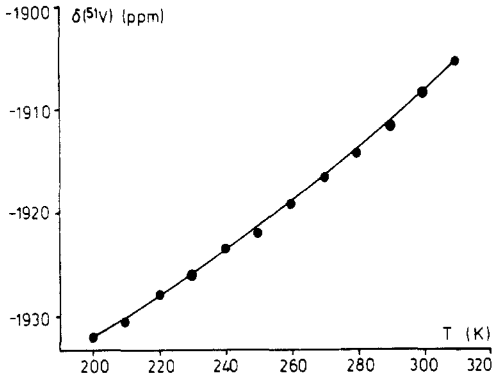

Figure 2. $\delta(^{51}V)$ vs. temperature T of $[V(CO)_5CNCH_2CO_2Et]^-$ in THF, showing the almost linear temperature dependence of ^{51}V shielding.

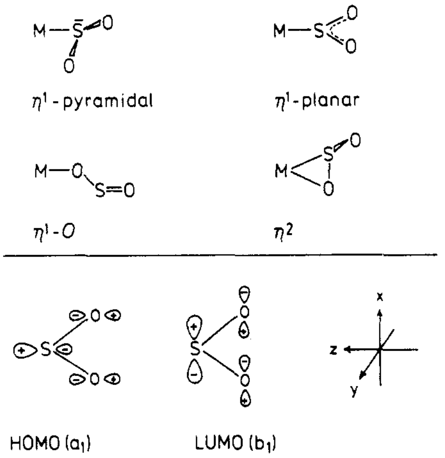

Figure 3. Coordination modes and frontier orbitals of SO_2, adapted from ref 41.

employed throughout to extrapolate $\delta(^{51}V)$ to 300 K. These $\delta(300)$ parameters are contained in Table IV (below) and have been used in Figure 1.[59]

Ambidentate coordination is expected with sulfoxides, SO_2, and substituted pyridines. As evidenced by the δ values, 4-CN-py is coordinated through the py-N and 2-NH_2-py through the NH_2 group, while 2-CN-py ligates via the nitrile N and therefore behaves as a nitrile rather than a pyridine derivative. This sight is supported by the ν(CN) which, in the case of $[V(CO)_52\text{-CN-py}]^-$, is shifted to smaller wavenumbers with respect to the free ligand by 53 cm^{-1}. The reason for the differing coordination behavior, which has also been observed in other systems,[36–38] probably is a sterically hindered coordination of the py-N in the ortho derivatives.

For dimethyl and diphenyl sulfoxide, S-coordination is suggested from NMR and IR arguments. $\delta(^{51}V)$ values are similar to those of other S-bonded ligands (SPh_2, SMePh); the ^{51}V nucleus is substantially more shielded than in complexes where O-coordination is established (THF, OPh_2, $OCMe_2$). Further, ν(SO) is shifted to higher wavenumbers (1288 cm^{-1} in $[V(CO)_5Me_2SO]^-$) with respect to the unligated sulfoxide (1055 cm^{-1}). This is in accord with general considerations on S-coordinated sulfoxides[39] and with appropriate results for the isoelectronic $[Cr(CO)_5Me_2SO]$ (1221 cm^{-1}).[40]

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Table IV. IR and ^{51}V NMR Parameters of $[V(CO)_5L]^-$ Complexes[a]

L	coord. mode	$\delta(300)$[b]	B_1(calcd),[c] cm^{-1}	k_1[d] N m^{-1}	k_2[d], N m^{-1}	π,[e] N m^{-1}	σ,[f] N m^{-1}
CS_2	η^2-C,S	-1368	1890	1538	1501	163	-43
THF	0	-1367	1849	1253	1380	2	-1
4-CN-py	py-N	-1440	1855	1282	1389	19	-11
py	N	-1461	1849	1251	1380	-3	2
NEt_3[g]	N	-1456	1850	1255	1381	0	0
NEt_2Ph	N	-1481	1848	1251	1379	-2	0
NH_2Ph	N	-1483	1849	1261	1380	7	-8
$NHEt_2$	N	-1498	1843	1238	1371	-7	-3
2-NH_2-py	NH_2	-1494	1849	1254	1380	0	-1
SO_2	η^1-S	-1472	1930	1551	1504	173	-50
MeCN	η^1-N	-1601	1855	1308	1389	45	-37
PhCN	η^1-N	-1606	1858	1282	1394	14	-1
2-CN-py	η^1-NC	-1614	1859	1288	1394	20	-7
SPh_2	S	-1594	1867	1286	1407	5	21
SMePh	S	-1605	1856	1284	1391	19	-9
$SePh_2$	Se	-1635	1864	1297	1402	21	0
Me_2SO	η^1-S	-1657	1873	1370	1416	80	-45
Ph_2SO	η^1-S	-1657	1880	1384	1427	83	-37
1-hexyne	η^2-C,C	-1636	1861	1350	1398	78	-61
N_2	η^1-N	-1671	1857	1341	1391	76	-66
cyclopentene	η^2-C,C	-1731	1866	1320	1406	40	-15
1-pentene	η^2-C,C	-1788	1871	1327	1414	39	-6
$TePh_2$	Te	-1753	1863	1311	1401	36	-16
CN^-	η^1-C	-1864	1841	1248	1367	7	-21
CN-*t*-Bu	η^1-C	-1899	1860	1359	1396	89	-74
CN-*i*-Pr	η^1-C	-1902	1863	1363	1401	88	-68
CNCy	η^1-C	-1908	1861	1359	1398	87	-70
$CNCH_2CO_2Et$	η^1-C	-1908	1866	1370	1406	90	-75
$AsPh_2R$[h]	As	-1805	1874	1309	1418	17	20
$SbPh_2R$[h]	Sb	-1875	1875	1340	1419	47	-9
PF_3[i]	P	-1956	1904	1468	1463	131	-49
H^-[j]	H	-1969	1764	1196	1256	66	-191
$SnPh_3^-$[k]	Sn	-1994	1828	1254	1349	31	-63

[a] Calculated from the data contained in Table III and ref 16. [b] $\delta(^{51}V)$ extrapolated to 300 K with a temperature gradient of 0.25 ppm/deg. [c] Calculated according to ref 46. [d] k_1 and k_2 are the CO stretching force constants for the axial and equatorial CO groups, respectively. [e] Graham's π parameter. Increasing π indicate increasing π acceptor ability. [f] Graham's σ parameter. Increasing negative values indicate increasing σ donor ability. [g] Reference for the calculation[47] of π and σ. [h] R = CH_2EPh_2 (E = As, Sb); data from ref 6. [i] ν(CO) from ref 58, $\delta(^{51}V)$ from ref 20c and 20d. [j] Data from ref 26. [k] Data from ref 11 (ν(CO)) and 15 ($\delta(^{51}V)$).

The NMR argument is only a good one if the nature of the ligands compared is similar with respect to their strengths (π acceptor powers) and their polarizabilities. Apparently, this is not the case with the pairs SO_2/Me_2SO or SO_2/SPh_2. The IR pattern of the SO_2 complex deviates largely from that of all of the other complexes in that the bands are notably shifted to higher wavenumbers, and the positions of E and A_1^{trans} are interconverted (a similar observation holds for $[V(CO)_5CS_2]^-$ [16]). In our sample, the ν(SO) region is obscured by bands belonging to THF and excess SO_2, and therefore, the S–O stretch cannot be employed as a tool to assign one of the known coordination modes of SO_2 which, together with the potential bonding orbitals,[41] are illustrated in Figure 3. On the basis of bonding considerations involving suitable metal and SO_2 orbitals, it has been noted[41] that, in d^6 complexes, η^1-pyramidal σ-(S) bonding can be excluded. Also, O-coordination is not likely to occur, since the π acceptor power—as evidenced by the IR parameters (cf. Table IV)—is extremely good and cannot be satisfied by O bonding, the π accepting $2b_1$ orbital being mainly localized on S. Among the two remaining coordination modes, η^1-(S)-planar and η^2-(O,S), η^1-(S) coordination is favored by IR and NMR criteria. (i) Variations in the IR spectra for the complexes $[V(CO)_5L]^-$ (L = SO_2, ^{13}CO, SR_2, Me_2SO) are very analogous to the trends observed for the corresponding $[M(CO)_5L]$ complexes (M = Cr, Mo, W)[40] for which the η^1-planar coordination via S has been verified.[42] The respective A_1^{cis} are 2018, 2008, 1963, and 1977 cm^{-1} for $[V(CO)_5L]^-$ and 2105, 2100, 2067, and 2082 cm^{-1} for $[Cr(CO)_5L]$. (ii) $\delta(^{51}V)$ (−1496 ppm) is between the δ values for S- and O-bonded ligands. However, η^2-coordination relative to η^1-coordination gives rise, as has been demonstrated for η^2-CS_2, η^2-alkyne,[16] and η^2-acyl,[43] to an additional deshielding contribution of at least 200 ppm. Hence, the resonance for a complex with η^2-SO_2 should be at a lower field than those of complexes with oxygen ligands. The deshielding produced by η^1-SO_2 relative to SR_2 is then a consequence of the greater electronegativity (diminished polarizability) of sp^2 as compared to sp^3-hybridized sulfur.

In the 207-K ^{51}V NMR spectrum of $[V(CO)_5OCMe_2]^-$, apart from the signal at −1423 ppm assigned to η^1-O-bound acetone, a second resonance arises at −546 ppm which might be associated with η^2-(C,O) coordination. This coordination mode has been noted for hexafluoroacetone.[44] The quotient of the polarizabilities of acetone parallel and perpendicular to the C–O axis is 0.38.[45] If the shift value for the η^1-$OCMe_2$ complex is multiplied with this factor, a $\delta(^{51}V)$ of −536 for a possible η^2-$OCMe_2$ complex is obtained.

Correlations. Table IV contains $\delta(^{51}V)$ values extrapolated (where necessary) to 300 K and ligand parameters

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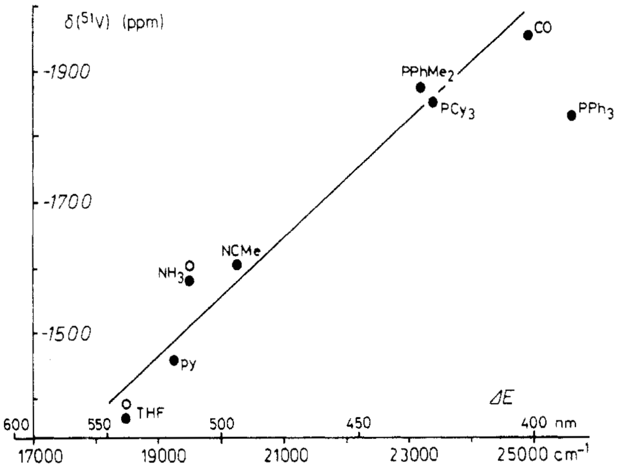

Figure 4. Plot of $\delta(^{51}V)$ vs. the lowest d–d transition ΔE in the electron absorption spectra of $[V(CO)_5L]^-$ complexes. Open circles are $\delta(^{51}V)$ at ca. 210 K; others are $\delta(300)$ values.

calculated from the CO stretching frequencies. Data from other sources have been included. The π and (mostly negative) σ parameters are used as a measure of the π delocalizing power and the σ donor ability (which increases with increasing $|\sigma|$). Reference is $[V(CO)_5NEt_3]^-$ (π, σ = 0).

The theory of metal shielding for heavier nuclei predicts that there is a dependency of the overall shielding, σ', upon the molecular parameters ΔE, $\langle r^{-3}\rangle$, and C^2, which can be associated with the integral ligand strength, the nephelauxetic effect (or closely related quantities such as the polarizability α, the electronegativity χ, or the Pearson basicity of the ligand), and the covalency (or ionicity) of the metal–ligand bond.[19,47,48a] In the average energy approximation,[48b] this relation, in a simplified form adapted to our special problem of $[V(CO)_5L]^-$ (C_{4v}) complexes, can be written in the form

$$\sigma' = \sigma^{\text{dia}} + \text{const}\ \overline{\Delta E}^{-1}\langle r^{-3}\rangle_{3d}\bar{C}_{3d}^{\,2}$$

where σ^{dia} is the (practically constant) diamagnetic contribution and the second term refers to the paramagnetic deshielding σ^{para} which soley is responsible for variations in σ' (and δ). $\overline{\Delta E}$ is a weighted average for the three symmetry-allowed transitions from the occupied V 3d levels b_2 (xy) and e (xz, yz) to the empty a_1 (z^2) and b_1 ($x^2 - y^2$), and the $\bar{C}_i$ are the appropriate V 3d LCAO coefficients. The factor $\langle r^{-3}\rangle C^2$ (r is the distance of the V 3d electrons from the ^{51}V nucleus) is especially sensitive to variations in α_L or χ_L, and this is shown by the general trends (increase of shielding in the sequences O < S < Se < Te, N < P, and O < N < C) which, however, also reflect contributions arising from the ligand strengths. The latter may be dominant as evidenced by the ordering $AsR_3 < PR_3$ and $NR_3 <$ NCR.

There are several cases where the dominance of ΔE has been demonstrated from correlations between metal shielding and d–d transitions obtained from electron absorption spectra. A recent example are the complexes *cis*-$[Mo(CO)_4(PR_3)_2]$.[49] It has also been evidenced, for Co^{3+} complexes, that linear correlations cannot be expected within series of complexes with ligators of differing electronegativity.[47] For $[V(CO)_5L]^-$, data from electron absorption spectra have been reported for L = THF, py, NCMe,[9] NH_3, and PPh_3.[7] The visible absorption bands have been assigned to the $A_1(e^4b_2^{\,2}) \rightarrow E(e^3b_2^{\,2}a_1^{\,1})$ transition, which is the main component contributing to $\overline{\Delta E}$.[20c,d,50] These data, together with the appropriate transition for L = CO,[9,51,52] PCy_3, and PMe_2Ph (this work) are plotted against $\delta(^{51}V)$ in Figure 4. The approximate linearity of the $\delta(^{51}V)/\Delta E$ relation exhibited in Figure 4 should not be overestimated since, due to the limited number of points, it might well be accidential. E.g., PPh_3 does not fit the line.

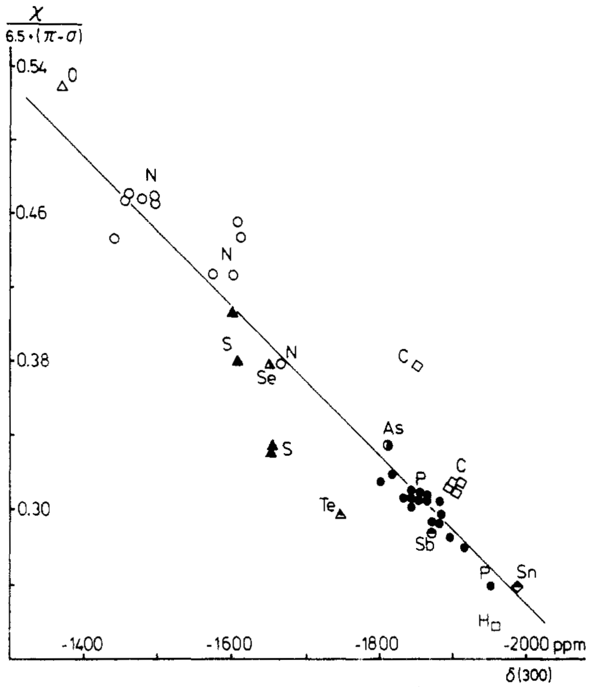

Figure 5. Plot of $\chi/(6.5 + (\pi - \sigma)$ against ^{51}V shielding $\delta(300)$ for the complexes $[V(CO)_5L]^-$ (η^1-bonded ligands only). χ is the Pauling electronegativity of the coordinating ligand atom; π and σ are the Graham parameters (here taken in mdyn/Å = 10^{-2} N/m). Data were taken from Table IV and (phosphines) ref 1: ◇, group 14, ○, group 15, △, group 16 ligands; open symbols, second period, full symbols, third period.

For most of our carbonylvanadates, reliable data from electron absorption spectra have not been obtained. In this situation, an alternative parameter is desirable to test the limitations of the $\sigma'/\Delta E$ relation. We have shown, in the preceding paper,[1] that the quantity ($\pi - \sigma$) provides a suitable measure of the ligand strength and hence of ΔE in the series of phosphine complexes. For the wider range of ligands considered here, the problem is more complex and one must account for the following points. (i) Apart from ΔE, $\langle r^{-3}\rangle$ and C^2 influence changes in σ^{para}, and these influences become increasingly important as the electronegativities of the coordinating atoms vary substantially. An increase of χ will increase C^2 (through a decrease of the covalency of the V–L bond) and also increase $\langle r^{-3}\rangle$ (through a decrease of the ligand polarizability). This influence of χ can be taken into account by employing the quantity $\chi/(\pi - \sigma)$ in correlations with $\delta(^{51}V)$. (ii) π and σ for $[V(CO)_5NEt_3]^-$, by definition, are zero. Hence, a plot of δ vs. $(\pi - \sigma)^{-1}$ is a nonlinear function. Linearity can be regained either by choosing an exponential presentation (δ vs $\chi/e^{\pi-\sigma}$)[53] or by correcting the arbitrary assumption

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of NEt_3 having no σ donor ability through the introduction of a correction factor D, i.e., by plotting δ vs. $\chi/(D + (\pi - \sigma))$. A linear correlation line (correlation coefficient 0.95 for an empirically optimized $D = 6.5$) is obtained (Figure 5). The deviations for some of the ligands (NCPh, CN^-, $S(O)R_2$, $TePh_2$) should be a measure for the difference between the effective χ_L and the Pauling values of the ligating atoms.

Conclusion

It has been shown, for $[V(CO)_5L]^-$ complexes, that the IR and ^{51}V NMR spectroscopic series of ligand strengths can be matched if the ligand field splitting parameter $\Delta\bar{E}$ as one of the factors influencing the shielding constant is interchanged with the quantity $\chi/(6.5 + (\pi - \sigma))$, where π and σ are the Graham parameters calculated from the $\nu(CO)$. The electronegativity χ is a suitable measure for the contributions arising from the covalency of the V–L bond (C_{3d}^2) and the polarizability of L (or its nephelauxetic effect; $\langle r^{-3}\rangle$). A straight correlation is thus obtained for $\delta(^{51}V)$ as the parameter quantifying overall shielding.

The magnetochemical series of ligands as depicted by decreasing ^{51}V shielding are as follows: group 14 ligands, $SnPh_3^- > PbPh_3^- > CO > CNR > CN^- > \eta^2\text{-}C{=}C > \eta^2\text{-}C{\equiv}C$; group 15 ligands, $SbR_3 > PR_3 > AsR_3 > BiEt_3 > N_2 > NCR > NH_3 > NR_3$, NC_5H_4R, NO^+;[54] group 16 ligands, $TePh_2 > S(O)R_2 > SePh_2 > SR_2 > SO_2 > \{O\}$; second period, $\{C\} > \{N\} > \{O\}$; third period, $PR_3 > \{S\}$; fourth period, $AsR_3 > SePh_2$; fifth period, $SnPh_3^- > SbPh_3 > TePh_2$. Closely related trends have been reported for, inter alia, $\delta(^{51}V)$ of $[CpV(NO)_2L]$[55] and $[V(NO)_2L_4]X$[34,35] and $\delta(^{95}Mo)$ of $[Mo(CO)_5L]$.[56,57] The orderings represent counteracting effects arising from $\Delta\bar{E}$ (dominated by the $A_1(b_2{}^2e^4) \rightarrow E(b_2{}^2e^3a_1{}^1)$ transition) related to the strength of the ligand and the quantity $\langle r^{-3}\rangle_{3d}C_{3d}^2$. The importance of the ligand polarizability as a factor responsible for variations in metal shielding is evidenced by a comparison of η^1 and η^2 coordination, the additional deshielding contribution observed with side-on bonded ligands being a consequence of the low polarizability perpendicular to the backbone axis.

Registry No. $[V(CO)_5py]^-$, 82887-76-1; $[V(CO)_5CN]^{2-}$, 45047-39-0; $[V(CO)_5(2\text{-}CN\text{-}py)]^-$, 96427-93-9; $[V(CO)_5(4\text{-}CN\text{-}py)]^-$, 86638-29-1; $[V(CO)_5(2\text{-}NH_2\text{-}py)]^-$, 86638-26-8; $[V(CO)_5THF]^-$, 86638-25-7; $[V(CO)_5(2\text{-}Me\text{-}THF)]^-$, 34089-14-0; $[V(CO)_5(Te(P\text{-}t\text{-}Bu_2)_2)]^-$, 96427-94-0; $[V(CO)_5S(O)Me_2]^-$, 96427-95-1; $[V(CO)_5CS_2]^-$, 96427-96-2; $[V(CO)_5(1\text{-hexyne})]^-$, 95974-55-3; $[V(CO)_5N_2]^-$, 95974-51-9; $[V(CO)_5(\text{cyclopentene})]^-$, 95974-61-1; $[V(CO)_5(1\text{-pentene})]^-$, 95974-59-7; $[Et_4N][V(CO)_6]$, 13985-78-9; $[Et_4N][V(CO)_5CN\text{-}i\text{-}Pr]$, 96427-67-7; $[Et_4N][V(CO)_5CN\text{-}t\text{-}Bu]$, 78954-02-6; $[Et_4N][V(CO)_5CNCy]$, 78954-04-8; $[Et_4N][V(CO)_5CNCH_2CO_2Et]$, 96427-69-9; $[Et_4N][V(CO)_5NCMe]$, 96444-39-2; $[Et_4N][V(CO)_5NCPh]$, 96427-70-2; $[Et_4N][V(CO)_5OCMe_2]$, 95974-68-8; $[Et_4N][V(CO)_5OPh_2]$, 96427-72-4; $[Et_4N][V(CO)_5SPh_2]$, 96427-74-6; $[Et_4N][V(CO)_5SMePh]$, 96427-76-8; $[Et_4N][V(CO)_5SePh_2]$, 96427-78-0; $[Et_4N][V(CO)_5TePh_2]$, 96427-80-4; $[Et_4N][V(CO)_5SO_2]$, 95998-43-9; $[Et_4N][V(CO)_5X(O)Ph_2]$, 96427-82-6; $[Et_4N][V(CO)_5NEt_3]$, 96427-84-8; $[Et_4N][V(CO)_5NHEt_2]$, 96427-86-0; $[Et_4N][V(CO)_5NH_2Ph]$, 96427-88-2; $[Et_4N][V(CO)_5NHPh_2]$, 96427-90-6; $[Et_4N][V(CO)_5NEt_2Ph]$, 96427-92-8.

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(59) More recent investigations in our group have shown that the temperature gradient (tg) of $\delta(^{51}V)$ increases with decreasing metal shielding. This effect amounts to ca. 6×10^{-4} ppm/ppm. The tg/δ correlation is roughly linear (M. Hoch and D. Rehder, unpublished).

Kinetic Investigation of the Mixed-Metal Bimolecular Reductive Eliminations in the Reactions of $EtOC(O)CH_2M(CO)_n$ or $EtOC(O)M(CO)_n$ ($M = Co$, $n = 4$; $M = Mn$, $n = 5$) with $HCo(CO)_4$ or $HMn(CO)_5$

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The alkyl- and acylmetal carbonyls $EtOC(O)CH_2M(CO)_n$ and $EtOC(O)M(CO)_n$ ($M = Co$, $n = 4$; $M = Mn$, $n = 5$) react with $HCo(CO)_4$ or $HMn(CO)_5$ to yield ethyl acetate or ethyl formate and the corresponding binuclear metal carbonyl. Kinetic experiments support a mechanism according to which the reaction between a coordinatively unsaturated alkyl- or acylmetal carbonyl (formed by CO loss) and the metal carbonyl hydride is rate determining. The rate of this bimolecular reductive elimination step varies strongly and unexpectedly in the mixed-metal systems.

Introduction

High activities and selectivities with homogeneous mixed-metal catalysts have been reported for aminomethylation,[1] carbonylation,[2] glycol formation from synthesis gas,[3] hydrogenation,[4] hydroformylation,[5] methanol homologation[6] and water gas shift reaction.[7] Very little

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