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Transition Metal Nitrosyls as Nitrosylation Agents. IV.* ^{51}V NMR Characteristics of Dinitrosyl and Carbonylmononitrosyl Vanadium Complexes

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The action of $[Co(X)(NO)_2]_2$ *(X = Cl, Br, I) on* $[V(H)(CO)_{6-n}L_n]$ *(L = 1/n di- and tritertiary phosphine; n = 2, 3) in thf yields* $[V(CO)_{5-n}(NO)L_n]$ *and* $[V(NO)_2(thf)_4]X$ *as the two main products. Thf is easily replaced by other ligands L′, leading to the complexes* cis-$[V(NO)_2(thf)_{4-n}L'_n]X$*, where n = 1 to 4. In the case of L′ = CNR (R = Cy, iPr, tBu), the species* $[VX(NO)_2L'_3]$ *are formed. The presence of X in the first coordination sphere is established by the normal halogen dependence* $(Cl < Br < I)$ *of* ^{51}*V shielding.*

$\delta(^{51}V)$ *values have been obtained for the two series of complexes and compared with δ of other nitrosylvanadium species, including* $[VX(NO)L'_4]X$*. for* $[V(NO)_2L'_4]Br$*,* ^{51}*V shielding increases in the sequence* $\{O\} < \{S\} < NR_3 < NCMe < AsEt_3 < SbEt_3 < PEt_2Ph < P(OMe)_3 < CNR$*, reflecting a general increase of shielding as the polarizability of the ligand function increases and its electronegativity decreases. Superimposed effects arising from electronic influences* $(PEtPh_2 < PMe_3 < P(OMe)_3)$ *and steric conditions (chelate-4 ring < 7 ring < 6 ring < 5 ring) are also discussed. Steric factors are especially pronounced in the* $[V(CO)_3(NO)Ph_2P(CH_2)_mPPh_2]$ *series (m = 1–4). The thermo-labile parent compound,* $[V(CO)_5NO]$*, has been characterized by its* $\delta(^{51}V) = -1489$ *ppm at 245 K.*

Introduction

Nitrosylvanadium complexes $[V(CO)_n(NO)L_n]$ (n = 2–4) [1] and $V(NO)_2L'_nX$ (n = 4, 2) [2] have recently attained preparative interest; the variability within these two nitrosylvanadium series remained, however, restricted. We have now successfully extended our preparative route to nitrosyl complexes, based on cobaltdinitrosylhalides as NO transfer reagents [1, 3], to the synthesis of a variety of new complexes. In this report, we emphasise ^{51}V NMR spectroscopic characteristics which lead to (i) a new concept of the ligand arrangement in the coordination sphere of vanadium, and (*ii*), in the context of comparative studies concerned with metal shielding trends as the coordinating functions vary across the periods and down the groups of the Periodic Table, to a considerable increase of systematic data and a consolidation of current ideas on the factors influencing the paramagnetic deshielding contribution, given by

$$\sigma_{para} = \text{const}\cdot\overline{\Delta E^{-1}}\,\langle r^{-3}\rangle_{3d}\,C_{V(3d)}^{2}$$

$\overline{\Delta E}$ is the mean excitation energy, r the distance of the vanadium-3d electrons from the nucleus, and C the LCAO coefficient for the V-3d orbitals taking part in the electronic transitions. In this description, diamagnetic influences upon the overall shielding

$$\sigma' = \sigma_{para} + \sigma_{dia}^{l} + \sigma_{dia}^{nl}$$

are taken as constant (local diamagnetic term) or negligibly small (non-local σ_{dia}).

Results and Discussion

General

The dinitrosyl complexes are prepared as depicted in the following scheme by action of cobalt dinitrosylhalides upon carbonylhydridophosphine vanadium complexes to yield $[V(NO)_2(thf)_4]X$ and $[V(CO)_3(NO)dppe]$ in a dark reaction (dppe = $Ph_2PCH_2CH_2PPh_2$). After 48 h, the latter is completely

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*See Ref. 1. for communication III.

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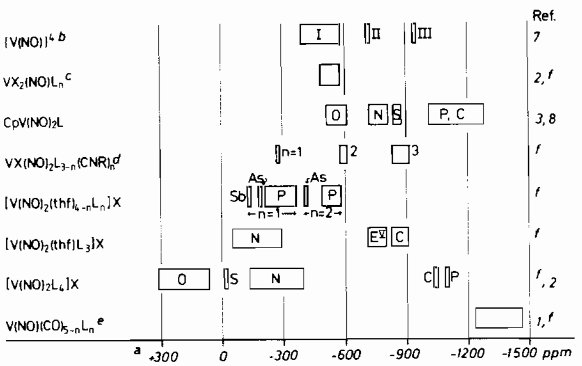
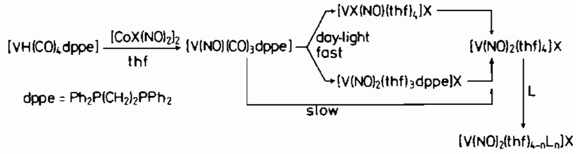


Fig. 1. ^{51}V Shift ranges of nitrosylvanadium complexes. ^{a}Shift values are given relative to VOCl$_3$ (neat); ^{51}V shielding increases from left to right. Ligand abbreviations: O = OCR$_2$, OR$_2$, OPR$_3$; S = SR$_2$; N = NR$_3$, NCR; P = PR$_3$ (including R = OMe); As, Sb = AsR$_3$, SbR$_3$; E^V = P, As, Sb; C = CNR, CO. X = Cl, Br (in most cases), I, PF$_6$. ^{b}I = [V(tha)(NO)L]$^-$; tha = nitrilotri(2-propanolato); L = OMe$_2$, OHEt, OH$_2$, O$_3$CH, CN. II = [V(dipic)NO(ONH$_2$)OH$_2$]$^-$; dipic = dipicolinato. III = [V(CN)$_4$NO(ONH$_2$)]$^{3-}$. ^{c}L = OC(iPr)$_2$, thf, NCMe. ^{d}L = thf, NCMe. ^{e}L = P, As, CO; n = 0–3 (*cf.* Table II). ^{f}This work.



converted to the dinitrosyl complex and may therefore be considered an intermediate. In the case of X = Cl, there is spectroscopic support for further intermediates, which we tentatively assign to [V(NO)(thf)$_4$Cl]Cl (δ(^{51}V) = –534) and [V(NO)$_2$(thf)$_3$dppe]X (–254 ppm). Cobalt is converted completely to [CoNO(CO)$_{3-n}$L$_n$] (n = 0–3). For the synthesis of carbonylhydridovanadium(I) from carbonylvanadates(–I) on silica gel see [4]. In the dinitrosyl compound, thf is easily replaced by other ligands L$'$ to form [V(NO)$_2$L$'_4$]X. The two NO groups occupy *cis* positions in the octahedral structure (IR evidence, see ref. 2). This route to dinitrosyl vanadium complexes appears to be more generally applicable than the reductive treatment of [VCl$_2$(NO)$_3$]$_n$ in acetonitrile in the presence of L$'$ [2], or the treatment of [V(CN)$_5$NO]$^{3-}$ with bidentate nitrogen ligands (L$'$ = ½ 1,10-phenanthroline; 2,2$'$-dipyridyl [6]).

The carbonylmononitrosyl complexes [V(CO)$_{5-n}$(NO)L$_n$] are prepared by the action of cobaltdinitrosylbromide on carbonylphosphinevanadates(–I), as described in [1]. For nL = Ph$_2$P(CH$_2$)$_m$PPh$_2$ (m = 1, 4), Ph$_2$As(CH$_2$)$_2$AsPh$_2$ and 1,2-C$_6$H$_4$(AsMe$_2$)$_2$, the complexes decompose above *ca.* 270 K; they can, however, be characterized by their ^{51}V NMR signals. The same is true for the thermally-labile parent compound [V(CO)$_5$NO], the preparation of which was recently described by Ellis [32], following one of the alternative routes proposed by us for the synthesis of phosphine derivatives (*i.e.* conversion of an apt carbonylvanadate by NO[BF$_4$] [1]). At 245 K, [V(CO)$_5$NO] shows a signal at –1489 ppm and a second, weak resonance at –2008 ppm (which might be due to its – hypothetical – precursor [V(CO)$_6$NO]).

^{51}V NMR chemical shifts of the two series are collated in Tables I and II. Figure 1 gives a comprehensive view of shift values (quoted relative to VOCl$_3$) of known nitrosylvanadium complexes. The wide shift range is especially noteworthy. Nitrosylvanadium complexes are placed between carbonylvanadates at the low-frequency (high-field) side, limited by [V(Cp)(SnPh$_3$)(CO)$_3$]$^-$ (δ = –2054 ppm [9]), and chalcogen or halogen complexes on the high-frequency (low-field) side such as [VS$_4$]$^{3-}$ (+1395 ppm [10]), [VOBr$_3$] (+434 ppm [11]) and [V(Cp)F(CO)$_3$]$^-$ (+417 ppm [33]).

Arrangement of the Vanadium Coordination Sphere; Halogen Dependence of δ(^{51}V)

The reaction products which Herberhold [2] obtained by the treatment of [VCl$_2$(NO$_3$]$_n$ [5] with acetonitrile, were two dinitrosyl species characterized by δ(^{51}V) = –223 and –272 ppm, and [VCl(NO)(NCMe)$_4$]Cl (δ = –517 ppm). Reduction of [VCl$_2$(NO)$_3$]$_n$ (Na/Hg; Zn) in MeCN and subsequent treatment with L$'$ yielded the dinitrosyl species only. The signal at –223 ppm was tentatively assigned to [VCl(NO)$_2$(NCMe)$_2$]$_x$ on the basis of IR and analytical data [2]. Accordingly, the complex formed by ligand displacement with methyl isonicotinate (δ = –209 ppm) was formulated as [VCl(NO)$_2$(NC$_5$H$_4$CO$_2$Me)]$_y$, while the complex with tert. butylisocyanide (δ = –1040 ppm) is mononuclear ([V(NO)$_2$(CNtBu)$_4$]$^+$).

The halogen, if coordinated directly to vanadium, should definitely influence the shielding of the metal nucleus. In the dinitrosyl complexes considered here ({V(NO)$_2$}^{10}, the formal oxidation state of vanadium is –I (NO$^+$) or +I (neutral NO). In any case, we have to deal with low-valent, open-shell (V-d^6 or V-d^4) complexes, and for these systems, a 'normal' halogen dependence of σ'(M) (Cl < Br < I) is to be expected [33], contrasting with the 'inverse' dependence (F > Cl > Br) observed in the closed-shell d^0 complexes VOX$_3$ [11].* The inverse halogen dependence reflects increasing participation of V-3d orbitals in the V–X bond (d^{3}s hybrids), as the ioni-

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*Although there is no reason for the halogen dependence in d^0 systems to be considered other than normal, we shall use the terminology introduced by Kidd [12].

TABLE I. ^{51}V Chemical Shifts ((ppm) Relative $VOCl_3$, at 305 K if not otherwise Indicated) of $[V(NO)_2(thf)_{4-n}(L')_n]X$.

$[V(NO)_2L'_4]X$	$\delta(^{51}V)$	$[V(NO)_2thf(L')_3]X$	$\delta(^{51}V)$	$[V(NO)_2(thf)_2L'_2]X$	$\delta(^{51}V)$	Remarks
$[V(NO)_2(dmpe)_2]Br$	-1100^a	$[V(NO)_2NCMe(dmpe)_2]Br$	$-894^{b,c}$			
$[V(NO)_2(CNiPr)_4]X$		$[VX(NO)_2(CNiPr)_3]$		$[VX(NO)_2thf(CNiPr)_2]$		
X = Cl	d	X = Cl	−847	X = Cl	−577	
Br	d	Br	−873	Br	d	
I	−1042	I	−922	I	−611	e
$[V(NO)_2(CNtBu)_4]X$		$[VX(NO)_2(CNtBu)_3]$				
X = PF_6	-1040^f	X =				
Cl	−1038	Cl	−831			
Br	d	Br	−875			
		$[VBr(NO)_2(CNCy)_3]$	−885			
		$[V(NO)_2thf(P(OMe)_3)_3]Br$	−816	$[V(NO)_2(thf)_2(P(OMe)_3)_2]Br$	−577	g
		$[V(NO)_2thf(PMe_3)_3]Br$	-795^h			
		$[V(NO)_2thf(diars)_2]Br$	-790^c			i
		$[V(NO)_2thf(PEt_2Ph)_3]Br$	−760	$[V(NO)_2(thf)_2(PEt_2Ph)_2]Br$	−544	
		$[V(NO)_2thf(SbEt_3)_3]Br$	−735			j
		$[V(NO)_2thf(AsEt_3)_3]Br$	−723	$[V(NO)_2(thf)_2(AsEt_3)_2]Br$	−397	k
		$[V(NO)_2thf(PEtPh_2)_3]X$		$[V(NO)_2(thf)_2(PEtPh_2)_2]Br$		
		X = Cl	−726	X = Cl	−483	
		Br	−730	Br	-479^l	
		I	ca. −745	I	-476^m	
		$[V(NO)_2thf\{Ph_2P(CH_2)_nPPh_2\}_2]Br^c$		$[V(NO)_2(thf)_2\{Ph_2P(CH_2)_nPPh_2\}]Br$		
		n = 1	−726	n = 1	−487	
		2	−731	2	−544	
		3	−734	3	d	
		4	−737	4	−486	n
$[V(NO)_2(phen)_2]Br$	−394	$[V(NO)_2CH_3CN(phen)_2]Br$	−308			
$[V(NO)_2(NCMe)_4]X$		$[VX(NO)_2(NCMe)_3]$				
X = Cl	-272^f	X = Cl	-223^o			
Br	−275					
I	−276					
$[V(NO)_2(n_4)]Br$	−176	$[V(NO)_2thf(n_4)]Br$	-63^c			p
$[V(NO)_2(py)_4]Br$	−174					
$[V(NO)_2(NH_2Ph)_4]Br$	−130					

(continued overleaf)

TABLE I. *(continued)*

$[V(NO)_2L'_4]X$	$\delta(^{51}V)$	$[V(NO)_2thf(L')_3]X$	$\delta(^{51}V)$	$[V(NO)_2(thf)_2L'_2]X$	$\delta(^{51}V)$	Remarks
$[V(NO)_2(SC_4H_4)_4]Br$	−20					q
$[V(NO)_2(SMePh)_4]Br$	−23					
$[V(NO)_2(OPEt_3)_4]Br$	+71					
$[V(NO)_2(OCMe_2)_4]Br$	+142					
$[V(NO)_2\{OC(iPr)_2\}_4]Br$	+210					r
$[V(NO)_2(thf)_4]X$						
X = Cl	+280					s
Br	+296					t
I	+306					u
$[V(NO)_2(thf)_4]Br$						
T = 290 K	+276					
305 K	+296					
320 K	+313					

[a] Triplet of triplets, $^1J(^{51}V-^{31}P)$ = 250 Hz, 170 Hz. [b] Doublet of triplets, $^1J(^{51}V-^{31}P)$ = 270 Hz, 180 Hz. [c] Only three functions coordinated to vanadium. [d] Not observed. [e] $[VI(NO)_2(thf)_2CNiPr]$, $\delta(^{51}V)$ = −271 ppm. [f] From ref. 2. [g] $[V(NO)_2(thf)_3\{P(OMe)_3\}]Br$, $\delta(^{51}V)$ = −363 ppm; doublet, $^1J(^{51}V-^{31}P)$ = 460 Hz. [h] Doublet of triplets, $^1J(^{51}V-^{31}P)$ = 250 Hz, 180 Hz. [i] Additional signal at $\delta(^{51}V)$ = −722 ppm. [j] $[V(NO)_2(thf)_3SbEt_3]Br$, $\delta(^{51}V)$ = −132 ppm. [k] $[V(NO)_2(thf)_3AsEt_3]Br$, $\delta(^{51}V)$ = −192 ppm. [l] Triplet, $^1J(^{51}V-^{31}P)$ = 240 Hz. [m] Triplet, $^1J(^{51}V-^{31}P)$ = 260 Hz. [n] $[V(NO)_2(thf)_3Ph_2P(CH_2)_4PPh_2]Br$, $\delta(^{51}V)$ = −204 ppm. [o] From ref. 2, assigned $[VCl(NO)_2(NCMe)_2]_n$. [p] r_{14} = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. [q] SC_4H_4 = thiophene. [r] $[VBr(NO)\{OC(iPr)_2\}_4]Br$, $\delta(^{51}V)$ = −528 ppm. [s] Additional signals at $\delta(^{51}V)$ = +232, −239 and −552 ppm; the latter signal presumably is $[VCl(NO)(thf)_4]Cl$. [t] Additional signal at $\delta(^{51}V)$ = +213 ppm. [u] Additional signals at $\delta(^{51}V)$ = +258 and +210 ppm.

TABLE II. ^{51}V Chemical Shifts (relative to $VOCl_3$) of $[V(CO)_{5-n}(NO)L_n]$ Complexes.

	$\delta(^{51}V)^b$ (ppm)	Temp. (K)	$\delta(^{51}V)_{corr}{}^c$ (ppm)
$[V(CO)_5NO]^a$	−1489	245	−1458
$[V(CO)_4NO(PMe_3)]$	−1460 [m]^d	305	−1460
$[V(CO)_3NO(L)_2]$			
L = PMe_3	−1332 [m]^d	305	−1332
2L = $Me_2P(CH_2)_2PMe_2$	−1480 [145]^d	305	−1480
$Et_2P(CH_2)_2PPh_2$	−1426	305	−1426
$Ph_2P(CH_2)_mPPh_2$			
m = 1	−1270	240	−1237
2	−1379 [180]^d	305	−1379
3	−1340^d	305	−1340
4	−1317	240	−1284
$PhHP(CH_2)_3PHPh$	−1395	305	−1395
$MeC(CH_2PPh_2)_3$	−1325	305	−1325
$1,2\text{-}C_6H_4(AsMe_2)_2{}^e$	−1415	240	−1388
$Ph_2As(CH_2)_2AsPh_2{}^e$	−1357	240	−1331
$[V(CO)_2NO(L)_3]^f$			
3L = $PhP(CH_2CH_2PPh_2)_2$	−1331 [m]	240	−1295
$MeC(CH_2PPh_2)_3$	−1238^d	305	−1238

[a] A second (weak) signal at −2008 ppm (245 K; −1978 ppm extrapolated to 305 K) is observed. [b] In brackets: $^1J(^{51}V-^{31}P)$ (Hz); m = multiplet. [c] Corrected for 305 K, assuming a temperature gradient of 0.5 ppm/deg (from the δ/T dependence of the $PhP(CH_2CH_2PPh_2)_2$ complex. [d] From ref. 1. [e] Signal assignments given in ref. 1 are in error; the δ values reported (−187 and −140 ppm) presumably correspond to $[V(NO)_2(thf)_3L_{0.5}]Br$. At T > 270 K, the complexes decompose *via* mononitrosyl intermediates to dinitrosyl complexes. [f] Preliminary assignment.

city decreases with decreasing electronegativity of X, $\chi(X)$, resulting in an increase of C_V (increase of σ_{para}, decrease of the overall shielding σ'). Where metal-d electrons were available originally (low-valent complexes), the increase of the nephelauxetic effect (decrease of $\langle r^{-3}\rangle$) and of the covalency of the V–X bond (decrease of C_V) induce a decrease of σ_{para} (increase of σ' and $|\delta|$) as $\chi(X)$ decreases down the halogen family. The normal halogen dependence has also been observed in *e.g.* $[MnX(CO)_5]$ [13], $[Mo(Cp)X(CO)_3]$ (Cp = $\eta^5\text{-}C_5H_5^-$) [14], $[MoX(CO)_5]^+$ [15], $[W(Cp)X(CO)_3]$ [16], $[CoX(NO)_2]_2$ and $[CoX(NO)_2PZ_3]$ [17], $[CoX(NH_3)_5]^{2+}$ [18, 19], and $[Fe(Cp)X(CO)_2]$ [20]; and in $[V(Cp)X(CO)_3]^-$ [33].

The reaction of $[V(H)(CO)_4Ph_2P(CH_2)_2PPh_2]$ with $[CoX(NO)_2]_2$ in thf (X = Cl, Br, I) yields tetrahydrofuranedinitrosyl complexes with very similar $\delta(^{51}V)$ values (*cf.* Table I), and this likeness of $\delta(^{51}V)$ is even more obvious for the products obtained when thf is exchanged by NCMe or $PEtPh_2$. Hence, these complexes in solution are not likely to contain a halogen ligand in the first coordination sphere and have a ligand arrangement similar to that proposed for $[V(NO)_2(CNtBu)_4][PF_6]$ [2] and $[V(NO)_2(LL)_2][ClO_4]$ (LL = phen, dipy [6]). We suggest that these formulations (four identical ligand functions bonded to V in addition to two NO groups in *cis* positions) also hold for $[V(NO)_2(dmpe)_2]Br$ ($\delta(^{51}V)$ = −1100 ppm), where the fine structure of the signal (triplet of triplets) indicates the presence of four phosphorus atoms in the coordination sphere.

For $PEtPh_2$ and $Ph_2P(CH_2)_mPPh_2$ (m = 1–4), two groups of signals are observed in the ^{51}V NMR spectrum. The high-frequency resonance (around −480 ppm) is a resolved triplet, if X = Br or I, indicating that there are only two phosphine ligands bonded to vanadium, leaving (if coordinated X is again excluded) two thf molecules ligated, *i.e.* $[V(NO)_2(thf)_2L_2]X$. The low-frequency resonance (around −730 ppm), which is broad and unresolved, very likely corresponds to a species where three thf molecules are substituted, hence $[V(NO)_2(thf)L_3]X$. This view is strongly supported by the corresponding PMe_3 complex, for which a resolved ^{51}V NMR signal (δ = −795 ppm) with the coupling pattern expected for $[V(NO)_2(thf)(PMe_3)_3]Br$ (doublet of triplets) is observed.

Signals appearing at higher frequency (lower magnetic field) may then represent species with only partially exchanged thf (as demonstrated for the $PEtPh_2$ derivatives) and/or compounds with the halide ligand at the coordination center. There is strong support for this latter assumption if L′ = CNiPr (Table I). Only for X = I is a resonance related to that of $[V(NO)_2(CNiPr)_4]^+$ (−1042 ppm) observed. In addition, a strong signal at −922 ppm arises and, for X = Br (δ = −873) and Cl (δ = −847), these lower-field signals are the only strong resonances in the ^{51}V NMR spectrum. There is a distinct shift trend on going from Cl to I in the direction expected for the normal halogen dependence, indicative of X participating in the coordination. The complexes presumably have to be formulated $[V(X)(NO)_2L'_3]$, if we again assume that in solution mononuclear complexes of octahedral geometry prevail. The additional signals for X = I (−611 and −271 ppm) can be assigned $[VX(NO)_2(thf)_{3-n}L_n']$ (n = 2, 1).

It is also noteworthy that in $[V(NO)_2(thf)_4]Br$ there is an unusually large temperature dependence of the ^{51}V resonance (−1.2 ppm/deg; Table I), exceeding that of other vanadium complexes by a factor of 2 to 3 [21], suggesting exchange contributions to the temperature effect.

Chalcogen and Pnictogen Dependence of $\delta(^{51}V)$

As observed for the halogeno complexes, shielding of the vanadium nucleus increases with increasing polarizability (decreasing electronegativity) of the coordination function, *i.e.* in the order O < S, N < P and As < Sb. The ordering P > As, paralleling a decrease of $\langle r^{-3}\rangle C^2$, reflects counter acting influences arising from the splitting between the highest occupied and the lowest unoccupied orbitals, ΔE, with decreasing ligand strength. For mono-dentate nitrogen ligands, the ordering $NR_3 < NCR$ indicates the greater π-acceptor strength of nitriles. The same argument is valid for $PEt_2Ph < P(OMe)_3$ and $-AsPh_2 < -AsMe_2$. The trends observed here are very much the same as in $[V(CO)_5L]^-$ [22] and $[V(Cp)(NO)_2L]$ [8], and have also been reported for molybdenum(0) [15, 23–26], tungsten(0) [16, 24] and manganese(I) complexes [27, 28]. An increasing number of NO ligands in pseudo-octahedral vanadium complexes leads to an increasing high-frequency shift of the $\delta(^{51}V)$ signal: shielding decreases in the sequence $[V(CO)_5L]^- > [V(CO)_{5-n}(NO)L_n] > [VX(NO)L_4]^+ > [V(NO)_2L_4]^+$ for the same ligand L throughout; *cf.* also Fig. 1; which places NO with other nitrogen ligands such as NCR, and thus in the medium π-acceptor category. A similar observation has been reported for nitrosylmolybdenum complexes [26].

Shielding Trends Across the Periods

If there is a correlation between metal shielding and the electronegativity (and polarizability) of the ligand functions, as exemplified by the shielding trends within the groups, this should also show across the periods. In fact, the expected normal trends* (O < N < C, S < P) are observed, contrasting again with the inverse ordering in d^0 VOL_3 [11], but paralleling findings for $[V(CO)_5L]^-$ [22], $[Mn(NO)_3L]$ [29], $[Mn(CO)_4L_2]$ [28] and $[CoL_6]^q$ [12, 30], all of which are open-shell systems.

Effect of Chelate-Ring Size

The dependence of metal shielding upon the chelate-ring size is a very common feature in metal NMR spectroscopy (ref. 31 and references therein). The pattern usually observed is 4-ring < 7-ring < 6-ring < 5-ring. This sequence reflects the influence of strains in the metalla-cycle and hence the extent to which a complex is energetically stabilized (or destabilized) on coordination of a chelating ligand, relative to a complex containing two monodentate ligands comparable to the chelate functions, such as the pairs $PEtPh_2/Ph_2P(CH_2)_nPPh_2$.

$[V(NO)_2(thf)_2(PEtPh_2)_2]Br$ (δ = −483 ppm) is subject to practically the same shielding conditions as encountered with $[V(NO)_2(thf)_2Ph_2PCH_2PPh_2]Br$ (δ = −487 ppm). In both complexes there are steric strains (steric hindrance between the comparatively bulky $PEtPh_2$ ligands; ring strains in the four-membered system). Six-membered and seven-membered rings are torsionally strained, leading to almost the same shift values, while shielding is substantially greater in the five-ring structure (δ = −544 ppm), where strains are minimized. The overall steric situation appears to be equilibrated in $[V(NO)_2thf\{Ph_2P(CH_2)_mPPh_2\}_2]Br$ (m = 1–4). The coordination of three diphenylphosphino groups induces enhanced V–P bond lengths and hence decreased V–P overlap, which is not susceptible to changes in the chelate-ring size (δ = −731 ± 6 ppm). A stabilizing effect on chelation is again observed for the pairs $[V(NO)_2thf(AsEt_3)_3]Br/[V(NO)_2thf(diars)_2]Br$ and $[V(NO)_2(py)_4]Br/[V(NO)_2(phen)_2]Br$ (see Table I). The stabilization (larger shielding) observed as phenyl is substituted by methyl ($Ph_2PCH_2CH_2PPh_2/Me_2PCH_2CH_2PMe_2$) and is effected by both steric and electronic factors.

The $\delta(^{51}V)$/ring size dependence is more pronounced in the complexes $[V(CO)_3(NO)Ph_2P(CH_2)_mPPh_2]$ (Table II): shielding increases in the sequence m = 1 < 4 < 3 < 2, *i.e.* in the expected and well established [21, 27, 31] manner. An electronic effect for chelate-rings of the same ring size is also observed: $Ph_2P(CH_2)_2PPh_2$ < $Et_2P(CH_2)_2PPh_2$;

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*Extending Kidd's concept for the halogen dependence [12], we refer to a normal trend whenever metal shielding increases with increasing size of the atom coordinated to the metal.

$Ph_2As(CH_2)_2AsPh_2$ < $Ph_2P(CH_2)_2PPh_2$; $Ph_2As(CH_2)_2AsPh_2$ < 1,2-$C_6H_4(AsMe_2)_2$; $Ph_2P(CH_2)_3PPh_2$ < $PhHP(CH_2)_3PHPh$.

Experimental

Starting materials ($[V(H)(CO)_{6-n}L_n]$, $[CoX(NO)_2]_2$) were prepared according to literature procedures [4, 17], the complexes $[V(CO)_{5-n}(NO)L_n]$ being as described in ref. 1. For the preparation of $[V(NO)_2L'_4]Br$ and related complexes (Table I), $[V(H)(CO)_4Ph_2P(CH_2)_2PPh_2]$ was employed; preparative details along with IR, ^{13}C and ^{31}P NMR spectroscopic results will be subject of further report. Cobalt is recovered in the form of $[Co(CO)_3NO]$ and $[Co(CO)(NO)Ph_2P(CH_2)_2PPh_2]$.

^{51}V NMR spectra were scanned either on a Bruker WH 90 PFT NMR spectrometer at 23.66 MHz in 7.5 mm diameter vials, or on a Bruker SWL 3-100 wide-line spectrometer at 16.0 MHz and a central magnetic field of 1.432 T in 14 mm vials, using an adapted Varian 4230 B (8-16 MHz) probe-head. The complexes were measured in thf or ($[V(CO)_3(NO)diarsine]$) CH_3CN solution (overall vanadium concentration *ca.* 0.1 *M*) at 305 K where not indicated otherwise. Standard used was neat $VOCl_3$ (external). The maximum absolute error generally is ±3 ppm; for L′ = thiophene, NH_2Ph, PEt_2Ph, acetone and isopropyl ketone ±10 ppm.

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