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Normal Halogen Dependence of Vanadium-51 Shielding in $[V(\eta^5\text{-}C_5H_5)X(CO)_3]^-$; X = F, Cl, Br, I, CN

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Metal shielding in transition metal complexes containing halide ligands may increase in the order F < Cl < Br < I (normal halogen dependence, NHD), or follow the inverse order (inverse halogen dependence, IHD) [1]. NHD is observed with open-shell systems (such as d^4, d^6 and d^8), IHD with closed-shell d^0 systems. This differing behaviour is mainly a consequence of variations of the metal-nd coefficient, $C_{M(nd)}$, in the paramagnetic deshielding contribution $\delta_{para} \propto \overline{\Delta E}^{-1} \langle r^{-3} \rangle C^2$ of the overall shielding $\sigma' = \sigma_{dia} + \sigma_{para}$. Here σ_{dia} is the diamagnetic term which splits into a practically constant local and a (usually negligibly) small non-local part; r is the distance of the metal-nd electrons from the metal nucleus, and $\overline{\Delta E}$ is the main singlet excitation energy.

An IHD has been found for the complexes $[VOX_3]$ (X = F, $\delta(^{51}V) = -732$ ppm; X = Cl, 0 ppm; X = Br, +452 ppm [2]) and reflects increasing participation of vanadium-3d orbitals (d^3s hybrids) by $X(p_\pi) \rightarrow V(d_\pi)$ electron transfer as the electronegativity of X (the ionicity of the V–X bond) decreases. The increasing involvement of V-3d orbitals in bonding leads to an increase of C and σ_{para}, hence to a decrease of ^{51}V shielding in the order F > Cl > Br. There is an interesting parallel in the complex anions $[VE^{VI}]^{3-}$ both in the solid state (E^{VI} = S, Se, Te [3]) and in solution (E^{VI} = O, S [4]): shielding decreases in the order O > S > Se > Te.

The NHD is well established for complexes such as $[^{95}Mo(Cp)X(CO)_3]$ [5], $[^{55}MnX(CO)_5]$ [6], $[^{57}Fe(Cp)X(CO)_2]$ [7], $[^{59}CoX(NH_3)_5]^{2+}$ [8] and $[^{59}CoX(NO)_2]_2$ [9]. We have now obtained corresponding results for a vanadium system, namely $[V(Cp)X(CO)_3]^-$, where X = F, Cl, Br, I, and the pseudo-halogen CN. The compounds were prepared by UV irradiation (high-pressure mercury lamp, Duran filter) of CH_2Cl_2 solutions containing about equimolar amounts of $[VCp(CO)_4]$ and $[Et_4N]X$ (X = Cl, Br, CN) or $[Et_4P]I$. The fluoro complex is obtained from $[Et_4P][V(Cp)I(CO)_3]$ and NaF in CH_2Cl_2. They form green (X = Cl, Br, I) or yellow (X = CN) powders. Spectroscopic data are collected in the Table I.

The NHD of ^{51}V shielding in this series of d^4 complexes is clear. Here, metal-d electrons are formally available and hence originally involved in the vanadium–ligand bonds to a sizable extent. The increase of covalency on going from F to I in this case induces a decrease of C in the order F > Cl > Br > I. Simultaneously, r^{-3} decreases, and the overall effect is a decrease of σ_{para} and increase of σ'. Again, the NHD is paralleled by an analogous trend of ^{51}V shielding in low-valent vanadium complexes containing a $V\text{–}E^V$ or $V\text{–}E^{VI}$ bond ($[V(CO)_5E^VR_3]^-$: N < As, P < Sb [11b]; $[VCp(NO)_2E^{VI}R_2]$: O < S [14].

The NHD may be correlated with the polarizability of the ligating function. Then CN^- should occupy an extreme low-frequency position. Although this is in fact observed, this view rather simplifies the situation encountered with more complex ligands such as the cyanide ion, which should also interact with the metal center through π-electron withdrawal. Since π in back-bonding is of some importance in

TABLE I. Spectroscopic Data of $[V(Cp)L(CO)_3]$ Complexes.

L	$\nu(CO)$ (cm^{-1})			Phase, counter-ion	$\delta(^{51}V)$[a] (ppm)	$\Delta\nu_{1/2}$[b] (Hz)	Ref.
H^-	1889 s	1775 vs, br		CH_3CN, $[Et_4N]^+$	−1730 (d)	35[c]	10
CO	2027 w	1917 vs		thf	−1534	12	11
$P(OMe)_3$	1963 m	1882 s	1863 s	thf	−1496 (d)	50	11
CN^-[d]				CH_2Cl_2, $[Et_4N]^+$	−1394	125	f
I^-	1935 s	1835 vs	1805 sh	CH_2Cl_2, $[Et_4P]^+$	−742	167	f
Br^-[e]	1943 s	1840 vs	1800 sh	CH_2Cl_2, $[Et_4N]^+$	−578	208	f
Cl^-[e]	1948 s	1840 vs	1805 sh	CH_2Cl_2, $[Et_4N]^+$	−515	234	f
F^-	1967 s	1862 s	1815 vs	CH_2Cl_2, Na^+, $[Et_4P]^+$	+417	330	f

[a] In thf, except for L = CN^- (CH_2Cl_2), at 305 K; relative to $VOCl_3$; d = doublet. [b] Widths of the resonance signal at half height. [c] 60 Hz ^1H-decoupled. [d] Formerly prepared from $[V_2(Cp)_2(CO)_5]$ and CN^- [12a], $[VCp(CO)_4]$ and $K[N(SiMe_3)_2]$ [12b] or $[VCp(CO)_3PCy_3]$ and $[Et_4N]CN$ [12c]. [e] Formerly described by Bergman *et al.* [13]. [f] This work.

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low-valent transition metal complexes, ΔE is supposed to be largely affected. The low-frequency position of [VCp(CO)$_3$P(OMe)$_3$] ($\delta = -1496$ ppm), close to that of the cyano complex (−1394), demonstrates that good π accepting ligands (such as phosphites) will influence ^{51}V shielding predominantly via an increase of ΔE. In the wider context of shielding variations within the family of [VCp(CO)$_4$] derivatives, the halogens have then to be classified as 'very weak' ligands on a magneto-chemical scale.

Finally, it should be noted that the half-widths of the resonance signals increase smoothly as $\delta(^{51}V)$ decreases in the series of [VCp(CO)$_3$L] complexes, indicating an increasing nuclear field gradient with decreasing ligand strength/decreasing polarizability of the ligand coordinated to vanadium.

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