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Isotope Effects and Coupling Constants in [CpV(CO)$_3$(^{1,2}H)]$^-$ and the ^{13}CO and C^{18}O Isotopomers of CpV(CO)$_4$ and [V(CO)$_6$]$^-$

MARTIN HOCH and DIETER REHDER*

Institut für Anorganische Chemie der Universität, D-2 Hamburg 13, F.R.G.

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The high-field (low-frequency) isotope shift of metal shielding on going from ML_n to $ML_{n-x}L'_x$, where L′ is the heavier isotopomeric ligand, is usually discussed in terms of a decrease of the vibronic ground states, leading to an increase of the average HOMO–LUMO splitting ΔE. An increase of ΔE decreases the paramagnetic deshielding contribution to the overall shielding [1, 2]. We have recently reported on the effects of ^{13}CO upon the pattern of the ^{51}V NMR spectra of [V(^{12}CO)$_{6-n}$(^{13}CO)$_n$]$^-$ [3]. In the present paper, we extend our studies to the effect of C^{18}O substitution, and to the isotopomers obtained by replacing CO in CpV(CO)$_4$ by ^{13}CO, C^{18}O, ^{1}H$^-$ and ^{2}H$^-$. Data are presented in Table I.

Replacement of ^{12}CO by ^{13}CO in CpV(CO)$_4$ can be achieved via the *in situ* generation of CpV(CO)$_3$-THF [4]. For this purpose, CpV(CO)$_4$ (100 mg) dissolved in THF (40 ml) is irradiated for 8 min at 240 K under ^{13}CO and, with occasional shaking, brought to room temperature within *ca.* 30 min. Repetition of this procedure in two more cycles yields a mixture of CpV(^{12}CO)$_{4-n}$(^{13}CO)$_n$ with a molar ratio of the different species for n = 0/1/2/3/4 of 25/40/25/10/1 (by simulation of the ^{51}V NMR). The ^{51}V NMR spectrum of this mixture (Fig. 1, a) shows the expected binominal multiplets for the various isotopomers. *cis-* and *trans-*[CpV(^{12}CO)$_2$(^{13}CO)$_2$] are not distinguished.

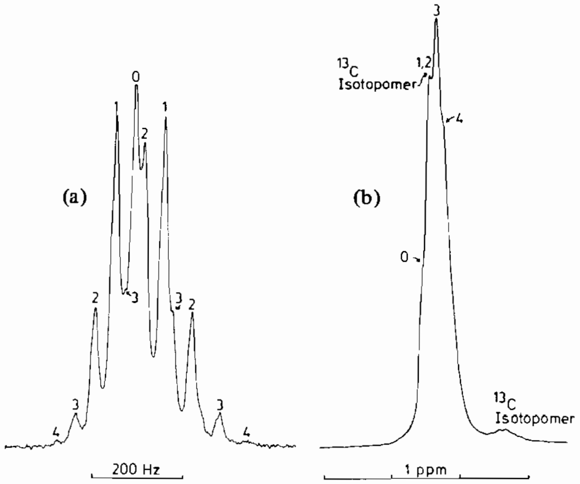

Fig. 1. ^{51}V NMR spectra of ^{13}CO (a) and C^{18}O enriched CpV(CO)$_4$ at a resolution of 1.27 (a) and 0.35 Hz/data point (b). The spectra have been obtained on Bruker spectrometers: (a) WH 90, 23.66 MHz, THF solution (acetone-d$_6$ as external lock); (b) AM 360, 94.61 MHz, CDCl$_3$ solution. The spectrum of the ^{13}CO enriched sample (31%) exhibits the binominal multiplets of the isotopomers CpV(^{12}CO)$_{4-n}$(^{13}CO)$_n$ with n = 0 to 4.

There is an eight-line pattern in the ^{13}C NMR (Fig. 2; the eight lines are due to the coupling of ^{13}C to the spin 7/2 nucleus ^{51}V), differing from the corresponding pattern for [V(^{12}CO)$_{6-n}$(^{13}CO)$_n$]$^-$ [3] in that the lines are much broader. The ^{13}C resonance of the Cp ring has a plateau-like shape due to coupling to ^{51}V; the overall width is 64 Hz. Hence, an upper limit for ^1J(^{51}V–^{13}Cp) is 9 Hz. The coupling constant ^1J(^{51}V–^{13}CO) is 107 Hz, which compares to ^1J(^{51}V–^{13}C) = 116 Hz for [V(CO)$_6$]$^-$ [3], ^1J(^{51}V–

TABLE I. NMR Data

Compound	$\delta(^{51}V)^a$ (ppm)	$\Delta\delta^b$ (ppm)	$\delta(L)^c$ (ppm)	$^1J(^{51}V-L)^c$ (Hz)
CpV(^{12}CO)$_4$	−1534			
CpV(^{12}CO)$_{4-n}$(^{13}CO)$_n$		−0.46(2)	+256.6^e	107
CpV(C^{16}O)$_{4-n}$(C^{18}O)$_n$		−0.1^d		
[CpV(CO)$_3$(^{1}H)]$^-$	−1730		−6.33	21.7
[CpV(CO)$_3$(^{2}H)]$^-$		−4.7(1)		f
[V(CO)$_6$]$^-$	−1952			
[V(^{12}CO)$_{6-n}$(^{13}CO)$_n$]$^-$		−0.27(3)	+225.3	116
[V(C^{16}O)$_{6-n}$(C^{18}O)$_n$]$^-$		−0.10(2)		

^{a}Relative to VOCl$_3$. ^{b}(Mean) isotope shift per heavier isotopomeric ligand. ^{c}L = ^{13}CO or ^{2}H. The ^{13}C and ^{1}H δ values are given relative to TMS. ^{d}Estimate (see text). ^{e}The ^{13}C resonance for the Cp ring is centered at +92.5 ppm (*cf.* also ref. 10); an upper estimate for the ^{51}V–^{13}C coupling constant is 9 Hz (see text). ^{f}Not resolved.

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*Author to whom correspondence should be addressed.

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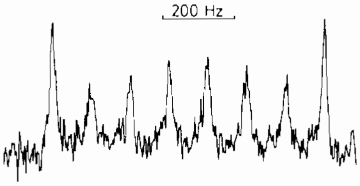

Fig. 2. CO pattern in the 20.115 MHz ^{13}C NMR of ^{13}CO enriched (31%) CpV(CO)$_4$ in acetone-d$_6$ at a resolution of 1.58 Hz/data point. Bruker WP 80, repetition time 20 s, pulse widths 4 μs, 2800 scans.

^{117,119}Sn) = 900 Hz for [CpV(CO)$_3$SnCl$_3$]$^-$ [4] and ^1J(^{93}Nb–^{13}CO) = 221 Hz for CpNb(CO)$_4$ [5].

The mean isotope shift per ^{13}CO, $\Delta\delta$(^{13}C), amounts to −0.46(2) ppm and is thus somewhat larger than the isotope shifts in the [V(^{12}CO)$_{6-n}$(^{13}CO)$_n$]$^-$ system (*vide infra*) [3]. The increase of ^{51}V shielding with the heavier isotope is linear within the limits of error. The partial replacement of ^{12}CO by ^{13}CO decreases the local symmetry as evidenced by the CO stretching pattern in the IR spectrum. Diminished local symmetry should lead to a low-field shift and a broadening of the ^{51}V resonance relative to CpV(^{12}CO)$_4$ [2, 5]. However, no such effects are observed (in fact, the $W_{1/2}$ are 20(2) Hz throughout); in the NMR experiment, the metal nucleus exhibits an effective local symmetry exclusively related to the electronic nature of the ligands. Similar effects, though less pronounced, have been noted for the partial replacement of CO by equally good π acceptor PF$_3$ [5].

[V(C^{16}O)$_{6-n}$(C^{18}O)$_n$]$^-$, prepared as described for the generation of the corresponding ^{12}CO/^{13}CO isotopomers [3], clearly exhibits, in the ^{51}V NMR spectrum, distinct signals for n = 0 to 5 (Fig. 3) with a molar ratio of 1/4/9/10/6/2 for n = 0/1/2/3/4/5, representing an overall C^{18}O content of 45%. The isotope shift, $\Delta\delta$(^{18}O), is −0.10(2) ppm; the increase with increasing substitution is again linear. The spectrum in Fig. 3 also shows the natural abundance ^{13}C satellite doublet. The fine structure of the two components (spaced by J(VC) = 116 Hz) reflects the [V(^{12}C$^{16/18}$O)$_5$(^{13}C^{16,18}O)]$^-$ isotopomers. $\Delta\delta$(^{18}O) is definitely smaller than $\Delta\delta$(^{13}C) (−0.27(3) ppm), showing that if a decrease of the vibronic ground level is responsible for the isotope shift, the ligand atom not directly bonded to the metal provides, not unexpectedly, a smaller contribution. Similar results have been reported for the ^{59}Co resonances of [Co(^{12}CN)$_{6-n}$(^{13}CN)$_n$]$^{3-}$ and [Co(C^{14}N)$_{6-n}$(C^{15}N)$_n$]$^{3-}$ [1].

C^{18}O substitution in CpV(CO)$_4$ is carried out as noted for ^{13}CO (*vide supra*) to yield CpV(C^{16}O)$_{4-n}$(C^{18}O)$_n$ (IR evidence; compare the appropriate IR analysis in ref. 6). The spectrum (Fig. 1, b) exhibits an asymmetric, partly split resonance accompanied by the high-field component of the ^{13}C (natural abundance) satellite doublet, which represents the non-resolved lines for the ^{13}C^{16,18}O isotopomers. The mean position of this doublet should be shifted relative to unsubstituted CpV(^{12}C^{16}O)$_4$ by −0.56 ppm. This value represents the joint effects of $\Delta\delta$(^{13}C) (−0.46) and $\Delta\delta$(^{18}O) (−0.1), assuming the same $\Delta\delta$(^{18}O) as measured for the hexacarbonylvanadate(1−). The low-field component of the satellite doublet partially overlaps the signals for CpV(C^{16}O)$_3$(C^{18}O) and CpV(C^{16}O)$_2$CpV(C^{18}O)$_2$.

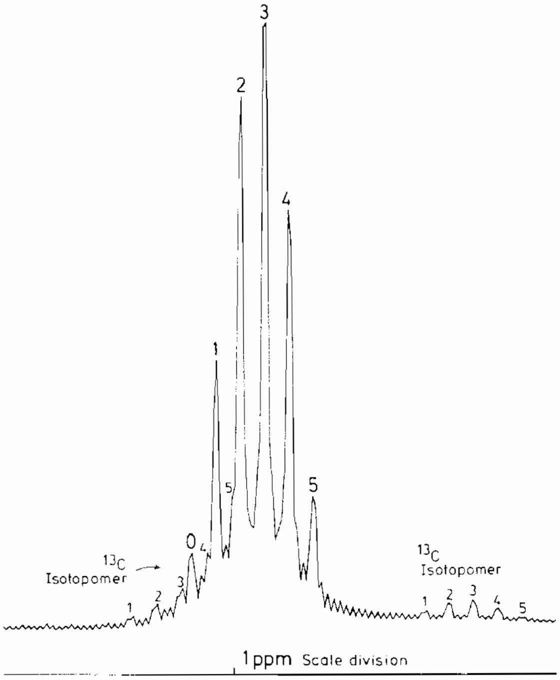

Fig. 3. 94.541 MHz (Bruker AM 360) ^{51}V NMR spectrum of ^{18}CO enriched (45%) [V(CO)$_6$]$^-$ in acetone-d$_6$ at a resolution of 1.22 Hz/data point. Assignments refer to the isotopomers [V(C^{16}O)$_{6-n}$(C^{18}O)$_n$]$^-$ with n = 0 to 5. A similar pattern arises for the ^{13}C (natural abundance) doublet (small numbering).

A sizable isotope effect of −4.7 ppm is observed on going from [CpV(CO)$_3$^{1}H]$^-$ to [CpV(CO)$_3$^{2}H]$^-$. A mixture of the hydrido and deuterido complexes (with the lighter isotopomer as the main component) is obtained [7, 8] when Na$_2$[CpV(CO)$_3$] (from CpV(CO)$_4$ and Na/Hg in THF) is dissolved in a 1/1 mixture of C(^{1}H)$_3$CN and C(^{2}H)$_3$CN. The isotope shift is similar in magnitude to that reported for [CpNb(CO)$_3$H]$^-$ (−6 ppm) [7] and CpW(CO)$_3$H (−10 ppm) [9]. While [CpV(CO)$_3$^{1}H]$^-$ shows a partly resolved doublet (peak-to-peak distance 16 Hz; ^1J(^{51}V–^{1}H) = 21.7 Hz) with an overall $W_{1/2}$ = 54 Hz, the coupling in [CpV(CO)$_3$^{2}H]$^-$, as expected from the small γ(^{2}D), is not observed. The signal for the deuterido complex is not significantly broadened with respect to the hydrido complex. The ^{1}H resonance of this compound is a broad plateau [8].

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