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Notes

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Carbon-13 Chemical Shift Anisotropies of the Carbonyl and Thiocarbonyl Ligands in (η-Benzene)tricarbonylchromium(0) and (η-Benzene)dicarbonyl(thiocarbonyl)chromium(0)

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Solution ^{13}C chemical shifts have been widely used in studies of metal–CO and metal–CS bonding, but few analogous solid-state NMR investigations have been reported for metal carbonyls[1-5] and no such data are available for metal thiocarbonyls. We report here the first measurement of the ^{13}C chemical shift tensor of a CS ligand in a complex, viz., (η-benzene)dicarbonyl(thiocarbonyl)chromium(0), (η-C_6H_6)Cr(CO)$_2$(CS). The ^{13}C chemical shift tensor of the CO groups in (η-benzene)tricarbonylchromium(0), (η-C_6H_6)Cr(CO)$_3$, was also determined for comparative purposes.

Experimental Section

Powdered samples of ^{13}C-enriched (η-C_6H_6)Cr(CO)$_2$(^{13}CO) and (η-C_6H_6)Cr(CO)$_2$(^{13}CS) were prepared by the literature methods.[6,7] The ^{13}C enrichment of both complexes was about 90%. The ^{13}C chemical shift tensors were obtained from the spectra of nonspinning samples by visual inspection of the edges and by graphical analysis[8] of the sideband intensities of the MAS spectra. The measurements were made at room temperature on a Chemagnetics CMX-300 solid-state NMR spectrometer operating at 75.36 MHz with cross-polarization and high-power proton decoupling. To generate undistorted static spectra, a phase-cycled Hahn echo pulse sequence was used.[9] The CP-MAS spectra were recorded for samples packed in a bullet-type zirconia rotor (7.5-mm diameter). Various spinning rates (3.5–6.4 kHz) were employed.

Results and Discussion

The experimentally determined principal components of the chemical shift tensors of the ^{13}C nuclei of the CO groups in (η-C_6H_6)Cr(CO)$_2$(^{13}CO) and the CS ligand and benzene ring in (η-C_6H_6)Cr(CO)$_2$(^{13}CS) are listed in Table I. A typical CP-MAS spectrum for (η-C_6H_6)Cr(CO)$_2$(^{13}CS) is shown in Figure 1.

The chemical shift anisotropy is characteristic of the electron distribution around a nucleus and can be described by the values and directions of three principal components, σ_{11}, σ_{22}, and σ_{33}. The convention $|\sigma_{33} - \delta_i| > |\sigma_{11} - \delta_i| > |\sigma_{22} - \delta_i|$ is followed here, where the isotropic chemical shift, δ_i, the anisotropy, $\Delta\sigma$, and the asymmetry parameter, η, are defined as follows: $\delta_i = {}^1/_3(\sigma_{11} + \sigma_{22} + \sigma_{33})$; $\Delta\delta = |\sigma_{33} - {}^1/_2(\sigma_{11} + \sigma_{22})|$; $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \delta_i)$. For axially symmetric anisotropy, $\sigma_\perp = \sigma_{11} = \sigma_{22}$ and $\sigma_\parallel = \sigma_{33}$, and the shielding anisotropy becomes $\Delta\sigma = |\sigma_\parallel - \sigma_\perp|$.

Shielding tensors can be treated as the sum of a diamagnetic (σ^d) and a paramagnetic term (σ^p);[1,10] i.e., $\sigma = \sigma^d + \sigma^p$. Although the diamagnetic contribution is usually quite large, it is relatively insensitive to changes in electronic structure for a series of related compounds. On the other hand, the σ^p term depends primarily on the valence electrons and, therefore, on the bonding interactions. Thus, only σ^p is used qualitatively to discuss the variations in the observed chemical shift tensors of different complexes. Pseudolinear behavior has been proposed for a metal-bound carbonyl, since complexation of a CO group to a metal does not significantly distort the symmetric distribution of the electron orbitals about the C–O axis from that in free CO. This argument is supported by the fact that the carbonyl chemical shift tensors reported thus far are axially symmetric, or very nearly so, i.e., having very small η values (less than 0.1), and the values of $\sigma_\parallel$ (or σ_{33}) are close to that of free CO.[1-5] For axial symmetry

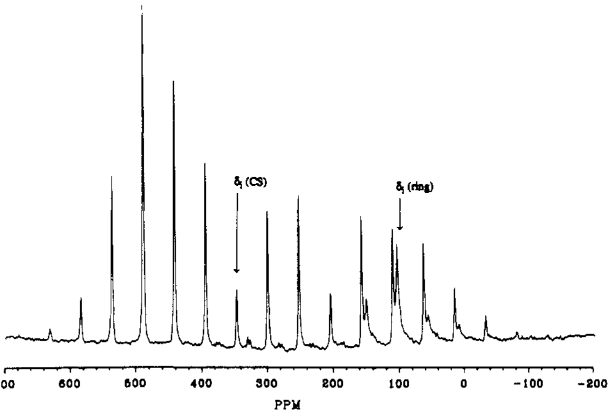

Figure 1. CP-MAS carbon-13 NMR spectrum of solid (η-C_6H_6)Cr(CO)$_2$(CS), rotating at 3.6 kHz.

$$\sigma_\parallel{}^p = (e^2/2mc)\sum_k (E_0 - E_k)^{-1}\langle 0|\sum_i L_{zi}|K\rangle\langle K|\sum_i L_{zi} r_i^{-3}|0\rangle \qquad (1)$$

$$\sigma_\perp{}^p = (e^2/2mc)\sum_k (E_0 - E_k)^{-1}\langle 0|\sum_i L_{\perp i}|K\rangle\langle K|\sum_i L_{\perp i} r_i^{-3}|0\rangle \qquad (2)$$

where e, m, and c are the electron charge, electron mass, and speed of the light, respectively, r_i is the length of the vector (x_i, y_i, z_i) between the electron and gauge origin, L_{zi} and $L_{\perp i}$ are the electron orbital angular momenta about and orthogonal to the unique z axis, and $|0\rangle$ and $|K\rangle$ are the ground and excited states of the molecule with energies, E_0 and E_k, respectively.

The ^{13}C chemical shift tensor of the ^{13}CO group in (η-C_6H_6)Cr(CO)$_2$(^{13}CO) is axially symmetric. The powder pattern is not averaged by intramolecular motion because the very large shielding anisotropy ($\Delta\sigma$ = 450 ppm) is consistent with the values found for terminal CO groups in rigid molecules, typically 350–450 ppm. Also, crystal packing prohibits the Cr(CO)$_3$ moiety from rotating in the solid state, whereas the benzene ring reorients with a relatively low barrier.[11,12] Axial symmetry is not required by the C_s molecular symmetry, but is consistent with the C_{3v} local symmetry of the Cr(CO)$_3$ moiety. Clearly, the benzene substituent does not affect the cylindrical electron density distribution around the C–O internuclear axis. The Cr(CO)$_3$ group has a larger $\sigma_\perp$ value (382 ppm) than is found for other metal carbonyls, which is to be expected, since the magnitude of $\sigma_\perp$ decreases with increasing atomic number on going across and down the transition metals.[2] The $\sigma_\perp$ component for (η-C_6H_6)Cr(CO)$_3$ is about 30 ppm greater than that for Cr(CO)$_6$ (353 ppm). The fact that the π-back-bonding between Cr and the CO groups is stronger than

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Table I. Principal Components, Isotropic Values, and Anisotropies of the ^{13}C Shielding Tensors for $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$ and $(\eta\text{-}C_6H_6)Cr(CO)_3{}^{a,b}$

species		σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	δ_i	η
$(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$	CS^c	533	517	−5	530	350	0.05
	CS^d	532	500	0	521	347	0.09
	ring^d	161	145	4	149	103	0.16
$(\eta\text{-}C_6H_6)Cr(CO)_3$	CO^c	382	382	−68	450	239	0
	CO^d	382	382	−63	445	234	0
	ring^e	152	138	7	138	99	0.15
$CS_2{}^f$		333	333	−92	425	121	0
OCS^g		275	275	−90	365	153	0
$NCS^{-\,h}$		240	240	−81	321	133	0

[a] Values of principal elements are in ppm, relative to external TMS. [b] Uncertainties are ±10 and ±15 ppm for the data obtained from static and CP-MAS spectra, respectively. [c] Obtained from static spectra. [d] Obtained from CP-MAS spectra. [e] From ref 23. [f] From ref 15. [g] From ref 16. [h] From ref 17.

it is in $Cr(CO)_6$[13] may account for this difference, since the additional π-back-bonding may either slightly reduce the excitation energy (ΔE) or increase the population on the CO π^* orbitals,[14] resulting in the downfield shift of $\sigma_\perp{}^p$.

The three components of the ^{13}C shift tensor of the thiocarbonyl group in $(\eta\text{-}C_6H_6)Cr(CO)_2(^{13}CS)$ are nondegenerate, but the powder pattern is still very close to axial symmetry ($\eta = 0.05$). The shift anisotropy is much larger than that for carbonyls. The ^{13}C chemical shift tensor of the free CS molecule is not known, but the elements of the chemical shift tensors for several linear molecules containing C═S double bonds have been reported (Table I).[15–17] The $\sigma_\parallel$ values for these compounds are about −90 ppm, while the σ_{33} value for the CS ligand in $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$ is 0 ppm. This large difference may indicate a breakdown in the pseudolinear approximation (vide infra) for metal-bound CS, possibly because of interactions between the CS ligand and the neighboring CO groups.

Since the ^{13}C signal for $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$ has a very small asymmetry parameter, its shift tensor can be considered (in order to make a comparison with the CO analogue) as having axial symmetry with σ_{11} equal to $\sigma_\perp$. The chief difference in the chemical shift tensors of the CS and CO groups is that the $\sigma_\perp$ component for thiocarbonyl is much more deshielded. The magnitudes of the perpendicular components (533 ppm) and anisotropy (530 ppm) observed for the CS group in $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$ are the largest values yet reported for a ^{13}C nucleus. The large $\sigma_\perp$ component can be explained by the paramagnetic term, eq 2, where the difference in excitation energies between the CS and CO ligands is the dominant term. The ΔE term can be associated with the 5s → 2p transition of CO. Molecular orbital calculations[18,19] have shown that, in the CS molecule, the carbon "lone-pair" 7s orbital is higher in energy than the corresponding 5s orbital in CO, due to the lower stability of sulfur atomic functions. On the other hand, the interaction between the carbon and sulfur p orbitals is also reduced, with the result that the π^* (3p) orbitals are lower in energy compared to the corresponding π^* (2p) orbitals in CO. Therefore, the 7s → 3p excitation transition energy in CS is smaller than the 5s → 2p transition energy in CO. Molecular orbital calculations for $(\eta\text{-}C_6H_6)Cr(CO)_2(CS)$ have established that this is also true when the CS and CO ligands coordinate to a metal, and this result has been used to interpret ^{13}C chemical shift data in solution.[20] It has also been suggested[2] that when CO is complexed to a metal, the metal d orbitals stabilize the excited state formed from the 5s → 2p transition and lower the excitation energy, which results in an increase in the paramagnetic contribution. This effect will increase with increasing d-orbital energy. It is known that, for CS, in addition to the expected $\sigma + \pi$ synergistic interaction, there is an interaction between the filled π-bonding orbitals of CS and the filled metal d orbitals.[19,21] This interaction increases the energy of the antibonding combination, which is mainly metal d in character.[21] Overall, these properties lead to a smaller ΔE term for CS than for CO, thus accounting for the large $\sigma_\perp$ value. Although ΔE is the predominant term in eq 2, there are other factors to be considered.[22] The much better π-acceptor ability of the CS group increases the electron density perpendicular to the CS-bond axis, and this may also contribute to $\sigma_\perp{}^p$.

The chemical shift tensor of the aromatic carbons in the thiocarbonyl complex was measured from the spinning sideband intensities (Table I). The shift anisotropy of the ring carbons in the related tricarbonyl complex has been reported,[23] and the effect of coordinating benzene to the metal, such as changing the directions of the principal components, has been discussed. The three components for both complexes are almost identical, within experimental error, indicating that substitution of CS for CO has little effect on the ring carbon chemical shift anisotropy.

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$[(t\text{-}Bu)_3P]_2Rh(CO)Cl$: A Simple Rhodium(I) Complex Which Is Not Square-Planar?

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Introduction

When Schumann, Heisler, and Pickardt[1] (hereafter SHP) originally determined the structure of the title compound, they noted that the coordination geometry was unusual. In particular, the four coordinating atoms adopted a flattened-tetrahedral

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