

OXYGEN-17 NUCLEAR MAGNETIC RESONANCE SPECTRA OF TRANSITION METAL CARBONYL COMPOUNDS *

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Summary

The natural abundance ^{17}O NMR shielding values observed by FTNMR in the present study on a representative variety of terminal transition metal carbonyl complexes are shown to range 400–300 ppm downfield from $^{17}\text{OH}_2$. The carbonyl ^{17}O chemical shift trends are generally opposite to those for the carbonyl ^{13}C chemical shifts and this is explained by metal π -backbonding to the carbonyl π^* orbitals. A metal triad effect is observed for ^{17}O chemical shifts. There is an upfield shift in the carbonyl oxygen shielding values on descending a given group in the periodic table. This is the same effect as observed previously for the ^{13}C shieldings of carbonyl groups.

Introduction

The ^{17}O nucleus has in the past been difficult to study by nuclear magnetic resonance spectroscopy. It has a natural abundance of only 0.037%, a spin of 5/2, a considerable quadrupole moment which gives rise to a broadening of ^{17}O resonance signals, and a low resonance frequency of 13.6 MHz at 23.5 kgauss. Recently, a review [1] on the utility of ^{17}O NMR spectroscopy as a structural probe demonstrated the sensitivity of the ^{17}O chemical shift to structural environments. The vast majority of compounds studied have been organic in nature, and until recently very little work has been done on inorganic or transition metal carbonyl complexes [2–3]. The work presented here was undertaken to determine the region of ^{17}O shielding values for the carbonyl oxygen atoms in a representative series of transition metal carbonyl complexes, and to compare wherever possible the ^{17}O and ^{13}C shielding trends [4] for the carbonyl groups in metal carbonyl complexes.

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Experimental

Instrumentation and ^{17}O NMR spectra were obtained with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 13.57 MHz. The instrument was equipped with a Transform Technology, Inc. pulse unit which delivers a 90° pulse in 20 μsec and a 36 K Nicolet Computer system with disk. The ^{17}O chemical shifts were measured in dry, degassed solvents relative to an external ^{17}O -enriched H_2O sample as standard with downfield values being positive. Sample concentrations of 0.1–0.5 g compound in 2.5–3.0 ml solvent were used to alleviate viscosity effects.

A spectral width of 10000 Hz was used. Owing to machine limitations, pulsing was done at the upfield end of the spectrum starting at the resonance frequency for $^{17}\text{OH}_2$, +500 Hz, causing complete reflection of the spectrum. This was corrected for by use of a "spectrum reverse" computer manipulation. Due to the quadrupolar properties of the ^{17}O nucleus, a pulse width of 25 μsec followed by a pulse interval of 0.11 sec was used for each scan. All spectra were observed at 30°C (unless otherwise noted) using natural abundance samples. An average of 65×10^3 transients per sample were required for an adequate signal-to-noise ratio. Digital resolution was 0.09 ppm (1.2 Hz)/data point. The chemical shifts reported here are considered accurate to ± 0.15 ppm (2.0 Hz), and all linewidths (peak width at half-height) are accurate to ± 2.5 Hz. The earlier data [2–3] were obtained with continuous wave instruments, and the limit of error was given as ± 8 ppm at best.

Materials

Most samples used in this investigation were prepared by literature methods (see references contained in ref. 4), and were checked for purity by a combination of ^{13}C NMR, and/or IR spectroscopy. Certain metal carbonyl derivatives were obtained from commercial sources and their purity was verified by measurement of their ^{13}C NMR spectra. A sample of $\text{W}(\text{CO})_4(\text{diphos})$ with the carbonyl oxygens enriched to 0.5–1.0% in ^{17}O was generously supplied by D.J. Darensbourg (Tulane University).

Results and discussion

General trends

The range of ^{17}O shielding values observed in the present study for the terminal transition metal carbonyl oxygen lies between 300 and 400 ppm downfield from $^{17}\text{OH}_2$ (see Table 1 for all ^{17}O and ^{13}C resonances). This range is more extensive than the 30 ppm range observed for the corresponding carbon resonances [4] but, with oxygen one bond further from the metal than carbon, the ^{17}O resonance exhibits a proportionately smaller response to changes in electron density at the metal center as well as to the intrinsic properties of the metal atom itself (as seen in Table 1). Photoelectron studies on transition metal carbonyl compounds have shown that the oxygen is less affected than carbon by complexation [5–7].

The parent carbonyl complexes generally exhibited lower field resonances

TABLE 1
 ^{17}O NMR CHEMICAL SHIFT DATA FOR TRANSITION METAL CARBONYL COMPLEXES

Compound	$\delta(\text{CO})(\text{ppm})$				Solvent ^c
	$\delta(^{17}\text{O})^a$		$\delta(^{13}\text{C})^b$		
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	
<i>Chromium complexes</i>					
$\text{Cr}(\text{CO})_6$	376.2		212.2		A
	375.3		211.7		B
$\text{Cr}(\text{CO})_5\text{PPh}_3$	371.2	—	216.5	221.3	A
	372.6	—			C
$\text{Cr}(\text{CO})_5\text{P(OPh)}_3$	373.6	368.4	213.8	217.5	A
$\text{Cr}(\text{CO})_5\text{CS}^d$	373.0	—	211.5	208.4	A
$\text{Cr}(\text{CO})_5\text{CSe}^d$	373.4	385.3	210.4	206.8	A
<i>cis</i> - $\text{Cr}(\text{CO})_4(\text{SbPh}_3)_2$	372.5	—	222.1	227.8	A
	373.8	—			C
<i>cis</i> - $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_{11})_2$	360.6	—	218.1	221.1	A
$\text{Cr}(\text{CO})_4(\text{Norbormadiene})^e$	388.4	370.1	226.8	234.5	A
$(\eta^6\text{-o-C}_6\text{H}_4\text{Cl}_2\text{C}_6\text{H}_4)\text{Cr}(\text{CO})_3^d$	377.5		230.0		A
$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_3^d$	374.7		231.4		A
$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2\text{CS}^d$	376.1		229.5		A
$(\eta^6\text{-m-C}_6\text{H}_4(\text{Me})\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2\text{CS}^d$	376.4		229.9		A
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3^d$	370.7		233.4		A
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{CS}^d$	374.1		231.5		A
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{CSe}^d$	375.7		229.0		A
$(\eta^6\text{-p-C}_6\text{H}_4\text{Me}_2)\text{Cr}(\text{CO})_3^d$	370.7		234.3		A
$(\eta^6\text{-o-C}_6\text{H}_4\text{Me}_2)\text{Cr}(\text{CO})_3^d$	370.7		234.2		A
$(\eta^6\text{-o-C}_6\text{H}_4\text{Me}_2)\text{Cr}(\text{CO})_2\text{CS}^d$	374.8		232.2		A
$(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Cr}(\text{CO})_3^d$	370.0		233.7		A
$(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Cr}(\text{CO})_2\text{CS}^d$	372.0		231.7		A
$(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)\text{Cr}(\text{CO})_3^d$	368.2		234.5		A
$(\eta^6\text{-C}_6\text{Me}_6)\text{Cr}(\text{CO})_3$	334.0		236.3		A
$(\eta^6\text{-C}_6\text{H}_5\text{NH}_2)\text{Cr}(\text{CO})_3^d$	369.4		235.1		A
$(\eta^6\text{-o-C}_6\text{H}_4(\text{NH}_2)\text{Me})\text{Cr}(\text{CO})_3^d$	370.5		235.6		A
$(\eta^6\text{-1,2,6-C}_6\text{H}_3(\text{NH}_2)\text{Me}_2)\text{Cr}(\text{CO})_3^d$	371.6		235.4		A
$(\eta^6\text{-C}_6\text{H}_5\text{NMe}_2)\text{Cr}(\text{CO})_3^d$	372.1		235.4		A
<i>Molybdenum complexes</i>					
$\text{Mo}(\text{CO})_6$	364.9		202.0		A
	366.9		200.7		B
$\text{Mo}(\text{CO})_5(\text{CNC}_6\text{H}_{11})$	359.7	358.1	203.8	207.9	A
$\text{Mo}(\text{CO})_4(\text{Norbormadiene})^e$	381.9	369.2	215	218	A
<i>Tungsten complexes</i>					
$\text{W}(\text{CO})_6$	355.5		192.1		A
	357.4		191.4		B
$\text{W}(\text{CO})_5(\text{CNC}_6\text{H}_{11})$	349.9	—	193.8	196.0	A
$\text{W}(\text{CO})_5\text{CS}^d$	347.0	364.4	192.4	189.3	A
$\text{Et}_4\text{N}[\text{W}(\text{CO})_5\text{I}]$	348.5	348.5			D
$\text{W}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$	348.7	358.0	196.6	201.9	A
			204.9	—	A
			$(2J(^{31}\text{P}-^{13}\text{C})\ 9\ \text{Hz})$		
	349.6	360.9			C
$\text{W}(\text{CO})_4(\text{Norbormadiene})^e$	377.0	346.2	203.6	209.4	A
$(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{W}(\text{CO})_3$	345.9		210.1		A
<i>Iron compounds</i>					
$\text{Fe}(\text{CO})_5$	388 ± 8 ^f		211.9		E
	378.7		211.9		E
	379.8		210.8		A
$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	336.6		214.3		A
			$(2J(^{31}\text{P}-^{13}\text{C})\ 29.5\ \text{Hz})$		
	334.2				C

TABLE 1 (continued)

Compound	$\delta(\text{CO})(\text{ppm})$				Solvent ^c
	$\delta(^{17}\text{O})$ ^a		$\delta(^{13}\text{C})$ ^b		
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	
$\text{Fe}(\text{CO})_3(\text{PhC}_2\text{Ph})_2$	365.8		213.9		A
$\text{Fe}(\text{CO})_3(\text{PhC}_2\text{Ph})_2\text{CO}$	371.6		208.3		A
	(org. CO 556.0)(org. CO 169.8)				
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$	380.5		213.3		A
$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$	379.2		213.6		A
$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-}(\text{cyclohexene})]\text{PF}_6$	387.3		209.7		A
<i>Manganese complexes</i>					
$\text{Mn}_2(\text{CO})_{10}$	387.8	368.2	212.9	223.1	A
	(broad resonances)				
	355 ± 8 ^f				B
$\text{Mn}(\text{CO})_5\text{Br}$	318.7	387.4	199.2	191.5	A
	(-60°C)				
$(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_3$	374.3		224.5		E
	372.8		225.4		A
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$	377.1				F
	375.5				G
	374.3		225.7		A
	374.1				H
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{PPh}_3$	366.0		223.3		A
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{CS}^d$	376.8		224.5		A
<i>Rhenium compounds</i>					
$\text{Re}_2(\text{CO})_{10}$	372.8	—			C
	371.6	—			A
			192.7	183.7	H
$\text{Re}(\text{CO})_5\text{Br}$	335.4	—	177.8	176.3	A
<i>Cobalt compounds</i>					
$\text{Co}_2(\text{CO})_8$	391.2		202.5		A
			(-20°)		
$\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})_2$	365.1		198.6		F
	364.6				G
	363.2		198.2		A
			(-67°)		
	363.1				H
$\text{PhC-CO}_3(\text{CO})_9$	370.7		199.7		A
$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$	357.5		206.1		A
<i>Rhodium compounds</i>					
$\text{Rh}_2(\text{CO})_4\text{Cl}_2$	342.0				A
			181.3		I
			$(^1J(^{103}\text{Rh}-^{13}\text{C}) 71.9 \text{ Hz})$		
					C
$\text{Rh}_2(\text{CO})_4\text{Cl}_2$	340.2		177.8		G
			$(^1J(^{101}\text{Rh}-^{13}\text{C}) 77.5 \text{ Hz})$		
<i>Nickel compounds</i>					
$\text{Ni}(\text{CO})_4$	349.6		191.2		E
	362 ± 8 ^f				E
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2$	512.1		225.2		A

^a Spectra recorded in degassed solvents, relative to external $^{17}\text{OH}_2$. ^b See ref. 4, except where noted.

^c Solvent key: A = CH_2Cl_2 ; B = CHCl_3 ; C = $\text{CH}_3\text{C}_6\text{H}_5$; D = $(\text{CH}_3)_2\text{CO}$; E = neat; F = C_6H_{12} ; G = C_6H_6 ; H = THF; I = CH_3CN . ^d $(\eta^6\text{-C}_6\text{H}_6\text{-}n\text{R}_n)\text{Cr}(\text{CO})_2\text{CX}$, ref. 8; $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{CS}$ and $\text{M}(\text{CO})_5\text{CX}$, ref. 9.

^e ^{17}O assignment tentative, see text. ^f See ref. 2, 3.

than their respective derivatives. In $\text{Co}_2(\text{CO})_8$ the observed resonance is probably a result of intramolecular fluxionality.

The carbonyl oxygen ^{17}O shielding value is directly affected by electron density shifts in the molecule. In general, replacement of carbonyl ligands by Lewis bases (e.g. phosphines, stibines, isocyanides) and arenes will result in a shift of the remaining carbonyl ligand ^{17}O resonances to higher field, contrary to that found for the corresponding ^{13}C resonances [4]. Increasingly electronegative substituents cause the carbonyl ^{17}O resonances to shift downfield and the carbonyl ^{13}C resonances upfield. With the exception of the aniline derivatives, for the series $(\eta^6\text{-C}_6\text{H}_{6-n}\text{R}_n)\text{Cr}(\text{CO})_2(\text{CX})$ as R becomes more electron withdrawing, the carbonyl oxygen ^{17}O resonance shifts downfield while the corresponding carbonyl carbon ^{13}C resonance shifts upfield. And, as X is changed from O to S to Se, the carbonyl ^{17}O resonance shifts downfield as the ^{13}C resonance shifts upfield [8]. The same effects were also observed for $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CS})$ [9]. Whereas, the carbonyl ^{13}C resonances show an excellent linear correlation with the approximate CO stretching force constant $k(\text{CO})$, the ^{17}O resonances show a poor correlation, and in the opposite direction; the ^{17}O and ^{13}C resonances also show a poor correlation with each other [8]. The carbonyl oxygens may be affected by throughspace interactions with the ring substituent(s), especially for the aniline derivatives. In these aniline derivatives, the direct interaction of the nitrogen electron pair with the carbonyl orbitals may be responsible for the carbonyl ^{17}O and ^{13}C shielding value trends being closely parallel with increasing methyl substitution, not opposite as otherwise observed in this work. The ^{17}O NMR chemical shifts also correlate with $k(\text{CO})$ in the same direction as their analogous ^{13}C chemical shifts [8]. An examination of the ^{17}O and ^{13}C shielding values in Table 1 indicates an interaction with an electron-rich center (vide infra). Inspection of molecular models and the crystal structure of $(o\text{-C}_6\text{H}_4\text{NH}_2\text{CH}_3)\text{Cr}(\text{CO})_3$ [10] shows the nitrogen to be well within contact distance of the carbonyl ligand orbitals; the crystal structure shows that in the static structure of the *o*-toluidine derivative (and, by extrapolation, in all of the aniline derivatives) the nitrogen is situated directly over one carbonyl ligand. Also, contrary to that found in the ^{13}C spectra, the ^{17}O resonances for carbonyl ligands *trans* to a substituent in octahedral complexes occur upfield from the *cis* carbonyl oxygen ^{17}O resonances because the *trans* ligand is more affected by the inductive effects of the ligand. The Lewis bases CS and CSe cause the opposite trend for both ^{17}O and ^{13}C nuclei [9]. For the thio- and seleno-carbonyl derivatives $\text{M}(\text{CO})_5\text{CX}$ ($\text{M} = \text{W}$, $\text{X} = \text{S}$; $\text{M} = \text{Cr}$, $\text{X} = \text{Se}$) the CX ligands cause the *cis* ^{17}O resonance to occur upfield of the *trans* ^{17}O resonance; the ^{13}C NMR spectra show the reverse pattern. The better σ -donor and π -acceptor character of the CS and CSe ligands [11] as compared to CO and other Lewis base ligands affects the carbonyl oxygen to a lesser extent than the carbonyl carbon.

The ^{17}O resonances for cationic complexes (e.g. $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{cyclohexene})]\text{PF}_6$) were observed downfield from those of neutral molecules, and for anionic complexes the ^{17}O signals (e.g. for $\text{Et}_4\text{N}[\text{W}(\text{CO})_5\text{I}]$) are upfield, again contrary to the trend observed for the carbonyl carbon ^{13}C resonances.

It should be noted here that in the organic nitriles, the ^{14}N resonances observed for a series of organic nitrile nitrogens [12] can be compared with the

nitrile carbon ^{13}C resonance [13]. Electron donor substituents cause a downfield shift in the ^{13}C NMR data, while the ^{14}N NMR data show an upfield shift. Although the mechanisms for transmission of shielding effects may be quite different for both organic nitriles and transition metal carbonyls, the point being made is that in $\text{C}\equiv\text{X}$ derivatives, the observed ^{13}C resonance trend is opposite that seen for the X resonances where $\text{X} = \text{O}$ or N .

Two other situations were observed where the ^{17}O and ^{13}C resonances showed parallel trends. For cases where analogs of a whole group were studied [$\text{M}(\text{CO})_6$ and $\text{M}(\text{CO})_4$ (norbornadiene) where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{M}(\text{CO})_5\text{Br}$ where $\text{M} = \text{Mn}, \text{Re}$], a "metal triad effect" was observed [14,15]. As the nuclear size increases on going down a group, the carbonyl ^{17}O and ^{13}C resonances exhibit a uniform upfield shift per metal; the ^{17}O resonance shifts were proportionately smaller than the ^{13}C shift (vide supra). The $(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)\text{W}(\text{CO})_3$ ^{17}O carbonyl resonance shows an upfield shift from its chromium analog value of the same amount as that shown for the carbonyl carbon ^{13}C resonance. This metal triad effect has yet to be fully understood, although it has been suggested that the diamagnetic shielding influence of the metal nucleus is an important factor. There is an $\langle r^{-1} \rangle$ dependence in the increased diamagnetic shielding term arising from increased nuclear size, the increased distance from the metal to the oxygen compared to the carbon lessens this shielding effect. Braterman [15] has also proposed that paramagnetic currents, dependent on $d-d$ transitions of the metal may have a direct effect on the carbonyl carbon ^{13}C shielding values.

The second situation where ^{17}O and ^{13}C resonances show parallel trends lies in the observation that bridging carbonyl ^{17}O and ^{13}C [4] nuclei are substantially deshielded compared to terminal CO resonances. The ^{17}O shielding value for the bridging carbonyl oxygens in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2]$ had the substantially deshielded value of 512 ppm which is in the organic ketone region [1].

Carbonyl ^{17}O chemical shift theory

Investigations into the theory of the chemical shift in general [16] and ^{17}O [17] and ^{13}C [18] shielding values in particular have shown that both ^{17}O and ^{13}C chemical shifts are dominated by the paramagnetic contributions to the total screening tensor. Pople [10] has described the paramagnetic contribution σ_p by the following equation

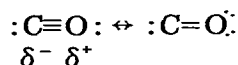
$$\sigma_p = -(\text{constant}) \langle r_{2p}^{-3} \rangle \frac{1}{\Delta E} \sum_{A,B} (Q_{AA} - Q_{AB})$$

where r_{2p} is the radius of the carbon $2p$ orbital, ΔE the average excitation energy, and the Q_{AA} and Q_{AB} terms are dependent on the bond order and charge density matrix of the ground state molecule.

To date, there does not exist in the literature a coherent working hypothesis to explain both the observed trends for the ^{17}O shielding values of carbonyl oxygen atoms and why these ^{17}O shielding constant trends are opposite to those observed [4] for the carbonyl carbons. Braterman has suggested that the ΔE term may be the dominant factor leading to the observed ^{13}C NMR shielding trends for transition metal carbonyl compounds [15]. Assuming a valence bond model for the metal-carbonyl bonding scheme, Klemperer [1] proposed that variations in the ^{17}O chemical shifts observed [2,3] for the five metal carbonyl

complexes studied prior to this investigation may be interpreted as reflecting relative magnitudes of π -backbonding interactions between the metal d and the carbonyl π^* antibonding orbitals. In previous studies [20,21] we have proposed that an increase in metal-to-carbonyl ligand π -backbonding best explains transition metal carbonyl carbon ^{13}C chemical shift trends. We propose here a possible rationalization for ^{17}O and ^{13}C carbonyl chemical shift trends and their general relative opposition to one another, which expands both on Klemperer's valence bond explanation and our earlier hypothesis.

The free carbonyl ligand has a resonance structure described by



I II

but I is the predominant form by force constant calculations. Complexation to a metal causes a change in charge distribution and a decrease in bond order for the carbonyl due to the interaction of the transition metal d orbitals with the π^* orbitals as shown in Fig. 1. The result is a subsequent disruption of one of the π -bonds in I. Since oxygen has donated one of its lone pairs to form the highest energy π -bond in I as this π -bond is disrupted the oxygen will regain this pair.

Backdonation by the metal into the π^* orbitals of the carbonyl group will affect both ^{17}O and ^{13}C nuclei, but in opposing ways as seen by the shielding values (Table 1). An electron donating ligand *trans* to the carbonyl ligand will allow the metal to transfer electron density to the CO ligand π^* orbital. This disrupts one of the π bonds in the carbonyl ligand, concurrently lowering the electron density on carbon and raising the electron density on oxygen. For carbon, as the effective nuclear charge increases, the $2p$ orbital contracts ($\langle r_{2p}^{-3} \rangle$ term increases) and σ_p shows a shift to lower field for the ^{13}C shielding value. In like manner, the increase in electron density on oxygen expands the $2p$ orbital ($\langle r_{2p}^{-3} \rangle$ term decreases) and σ_p shows a shift to higher field. Conversely, an electron-withdrawing ligand (e.g. CS and CSe) *trans* to the carbonyl ligand will cause the ^{13}C shielding value to be at higher field and the ^{17}O chemical shift to be at lower field due to the decrease in π -backdonation from the metal into the carbonyl π^* orbital, strengthening the $\text{C}\equiv\text{O}$ triple bond.

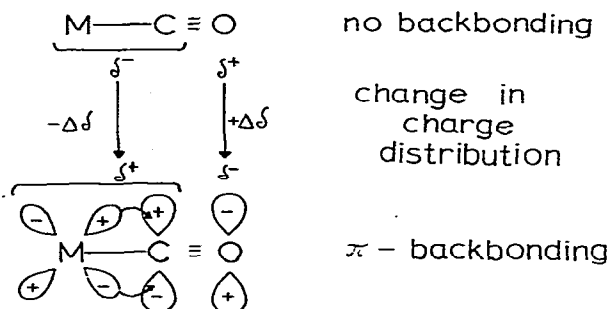


Fig. 1. Change in charge distribution for the carbonyl ligand due to interaction of a transition metal d orbital with a carbonyl π^* orbital.

Assignment difficulties and anomalies

The *cis* and *trans* resonances in the ^{17}O NMR spectra of those compounds where two resonances of equal area were observed [$\text{M}(\text{CO})_4(\text{norbornadiene})$ and $\text{W}(\text{CO})_4(\text{diphos})$] were tentatively assigned based on (a) the observation in Table 1 that the ^{17}O pattern is opposite the ^{13}C pattern (vide infra), and (b) by comparison to other $\text{M}(\text{CO})_5\text{L}$ ^{17}O and ^{13}C NMR spectra [4] which exhibit *cis* and *trans* resonances. As presently assigned, the *cis* resonance is downfield from the *trans* resonance in the ^{17}O NMR spectra of $\text{M}(\text{CO})_4(\text{norbornadiene})$, which is opposite to the trend seen for the carbonyl carbon ^{13}C resonances. An anomalously low field shift for the carbonyl ^{17}O resonances may be due to a long-range deshielding interaction of the *cis* carbonyl oxygen with the norbornadiene ligand. A similar interaction is proposed for the (aniline) $\text{Cr}(\text{CO})_3$ derivatives (vide supra). In a ^1H NMR study of these $\text{M}(\text{CO})_4(\text{norbornadiene})$ derivatives as well as the free ligand [22], Bennett et al. have proposed that a change in the shielding field of the olefin π -electrons by utilizing of these π -electrons for an olefin-metal bond is responsible for a shift to higher field for the olefinic proton resonance. A "long-range shielding" interaction of these protons with the carbonyl ligand was not considered to be a significant interaction. However, infrared studies [23-25] of $\text{M}(\text{CO})_4(\text{norbornadiene})$ where $\text{M} = \text{Cr}$ and Mo have demonstrated a lowering of $70-80\text{ cm}^{-1}$ from the corresponding stretching frequencies found for the free ligand, while $\nu(\text{=C-H})$ remains unchanged during complexation. It was proposed [24,25] that a change in the olefin π -electron distribution on complexation is responsible for the lowering of the respective stretching frequencies. The large (200 cm^{-1}) difference between the *cis* and *trans* $\nu(\text{M-CO})$ stretching frequencies was explained as being due either to a substantial dynamic interaction of the two types of M-CO bonds or to a difference in the force constants of the *cis* and *trans* M-CO bonds. Additional experimental evidence for the importance of ligand-carbonyl long-range interaction is found in studies by Dobson of the infrared spectra of $\text{Mn}(\text{CO})_5\text{X}$ derivatives [26], by Fenske and DeKock of the electronic structure and bonding of $\text{Mn}(\text{CO})_5\text{X}$ derivatives [27] and by Hall and Fenske of the force constants and electronic structure of d^6 transition metal carbonyl halides and dihalides [28].

Effect of metal quadrupole

With the carbonyl oxygen two bonds away from the metal center, the quadrupolar broadening observed [4,29] at room temperature in the ^{13}C NMR spectra of many cobalt, manganese and rhenium complexes is not a problem in the ^{17}O NMR spectra of these compounds. The ^{17}O NMR spectra of $\text{Co}_2(\text{CO})_8$, $\text{Co}_2(\text{CO})_6(\text{PhC}\equiv\text{CPh})$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ were each recorded as a sharp singlet at $+30^\circ\text{C}$. The ^{13}C NMR data were recorded at -60°C . The ^{13}C NMR data recorded for $\text{Mn}_2(\text{CO})_{10}$ at -20°C showed two broad resonances [4], but the ^{17}O NMR spectrum at $+30^\circ\text{C}$ showed two sharp signals which could be assigned as *cis* and *trans* by intensity. The $+30^\circ\text{C}$ ^{17}O NMR spectrum of $\text{Mn}(\text{CO})_5\text{Br}$ showed both *cis* and *trans* resonances, *cis* upfield of *trans*. This is opposite to the ^{13}C NMR data, recorded at -60°C . The rhenium derivatives $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{Br}$ each showed sharp singlets at $+30^\circ\text{C}$ in their ^{17}O NMR spectra. The $\text{Re}_2(\text{CO})_{10}$ ^{17}O singlet could not be resolved into *cis* and

trans resonances up to 100°C in toluene. The ^{13}C NMR spectra of $\text{Re}_2(\text{CO})_{10}$ and $\text{Re}(\text{CO})_5\text{Br}$ showed slightly broadened *cis* and *trans* resonances at room temperature.

Solvent studies

Solvent studies on $\text{Co}_2(\text{CO})_6(\text{PhC}_2\text{Ph})$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (Table 1) show that metal-carbonyl ^{17}O resonances are solvent dependent, generally shifting to higher field with increasing solvent polarity.

Difficulties

Owing to a natural abundance of 0.037%, spin of 5/2, electric quadrupolar broadening and low molecular symmetries, low solubilities caused restrictions on the compounds which gave satisfactory spectra. Enrichment studies are in progress to counteract the low solubility and potential asymmetric tumbling problems. If the sample is too viscous, the molecules may not tumble fast enough to provide for a quadrupole relaxation time short enough or the line-width may be too broad for observation of the resonance in the ^{17}O spectrum. Dilution or heating of the sample will reduce viscosity, but natural abundance problems necessitate high concentrations. Facile enrichment is a necessity.

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