Oxygen-17 N.M.R. Studies of ^{17}O-Enriched Transition Metal Carbonyl Complexes

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Summary Oxygen-17 n.m.r. spectra of enriched, lower solubility metal carbonyl compounds are very useful in obtaining variable temperature, tumbling and acid-base data for these compounds.

RECENTLY a number of reports have appeared concerning ^{17}O n.m.r. studies of metal carbonyl compounds obtained at natural abundance (0·037%).[1] These studies indicate clearly that ^{17}O n.m.r. spectroscopy will be quite useful for enhancing the understanding of donor–acceptor properties of ligands L in $LM(CO)_n$ compounds. To date the natural-abundance n.m.r. samples have had to be at least 0·3 M in order to obtain a useful signal even after accumulation of a large number of transients. We report here an n.m.r. study of some ^{17}O-enriched metal carbonyl compounds which greatly enhances the usefulness of this method.

Treatment of $Mo(CO)_6$ with $H_2{}^{17}O$, an appropriate ligand L (PPh_3, $AsPh_3$, *etc.*), and a catalytic amount of sodium hydroxide formed[2] *cis*-$Mo(C^{17}O)_4L_2$ and the ^{17}O n.m.r. data for these complexes are in Table 1.

TABLE 1. ^{17}O N.m.r. data of *cis*-$Mo(CO)_4L_2$ complexes

L	$\delta(^{17}O)$/p.p.m.[a]	
PPh_3	359·9br	357·2sh
$AsPh_3$	362·4br	358·8sh
$SbPh_3$	365·3br	362·6sh
$PPhMe_2$	358·3sh	356·6sh

[a] br = broad, sh = sharp, CH_2Cl_2 solvent, shifts downfield from $H_2{}^{17}O$ are positive.

Each complex shows two equal-area peaks, which could not be resolved with a Varian XL-100-15 spectrometer operating at 13·57 MHz using natural-abundance samples. With the less bulky phosphine ligands in *cis*-$Mo(CO)_4(PMe_2Ph)_2$ the two signals are sharp, whereas one of the peaks is broad with the other complexes. The carbonyl groups *cis* to the more bulky group 5A ligands in these samples give sharper signals probably owing to anisotropic tumbling which affects nuclear relaxation at certain ^{17}O sites more than others.

TABLE 2. ^{17}O N.m.r. data of $[(C_5H_5)Fe(CO)_2]_2$ and $Ru_3(CO)_{12}$

Compound	Temp./°C	$\delta(^{17}O)$/p.p.m.
$[C_5H_5Fe(CO)_2]_2$	55[a]	461·5
	−46[b]	555·7, 359·7 (*cis*-isomer) 458·8 (*trans*-isomer)
$[C_5H_5Fe(CO)_2]_2\cdot 2AlPr^i{}_3$	28[c]	371·2
$Ru_3(CO)_{12}$	28[b]	375·3

[a] C_6H_6 solvent. [b] CH_2Cl_2 solvent. [c] $MePh\text{-}AlPr^i{}_3$ solvent.

The ^{17}O n.m.r. data for $[(C_5H_5)Fe(CO)_2]_2$ and $Ru_3(CO)_{12}$ by exchange with *ca.* 7% enriched $C^{17}O$ are given in Table 2. The $C^{17}O$ was produced by gas-phase photolysis of enriched cyclohexanone. Both polynuclear compounds have one carbonyl oxygen signal at room temperature, and the ^{13}C n.m.r. spectra of these compounds also show one carbonyl carbon signal.[3,4] The ^{17}O spectrum for $Ru_3(CO)_{12}$ is the first reported for a trinuclear metal carbonyl complex. The relatively large molecular weight does not substantially affect the linewidth ($\Delta\nu_{\frac{1}{2}}$ *ca.* 22 Hz).

At −46 °C three signals are observed in the ^{17}O spectrum of $[(C_5H_5)Fe(CO)_2]_2$ indicating that the carbonyl exchange process is slower than the n.m.r. time-scale for the *cis*-isomer but not for the *trans*-isomer. Similar results were obtained at low temperatures by ^{13}C n.m.r. spectroscopy.[4] The 359·7 p.p.m. peak is relatively sharp and is assigned to the terminal carbonyls of the *cis*-isomer. The lowest-field peak is quite broad (270 Hz at half height) and is assigned to the bridging carbonyls of the *cis*-isomer. Some organic ketones also experience similar line-broadening.[5] The ^{17}O spectrum of the bis(tri-isopropylaluminium) adduct of the iron complex contains one sharp peak at 371·2 p.p.m. in the terminal CO region. A previous ^1H n.m.r. study[6] showed that the aluminium alkyl co-ordination to the two bridging carbonyl oxygen atoms slows down the carbonyl exchange process so that it is static on the n.m.r. time-scale at 28 °C. The bridging carbonyl oxygen signal is not observed owing to increased quadrupolar broadening.

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