Oxygen-17 N.M.R. Shifts of Some Tungsten Carbonyl Complexes. A Sensitive Measure of the σ-Donor/π-acceptor Ratio of Ligands

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Summary Natural abundance ^{17}O n.m.r. shifts have been determined for ten tungsten carbonyls $L_nW(CO)_{6-n}$ and shown to vary widely depending on the σ-donor/π-acceptor ratios of the ligands L.

THE σ-donor and/or π-acceptor strength of ligands in metal carbonyl complexes has been investigated so far by analysing CO stretching frequencies and/or intensities and by determining the metal-to-CO and metal-to-ligand bond lengths.[1] More recently ^{13}C and ^{31}P n.m.r. spectroscopy has been used with moderate success.[2] We now report that ^{17}O n.m.r. spectroscopy serves as a more general and sensitive structural probe for metal carbonyls.[3]

The n.m.r. measurements were made with the ^{17}O in natural abundance (0·037%) on a Varian FT-80A spectrometer at 10·782 MHz. A 200—300 mg sample of the tungsten carbonyl was dissolved in 1·5 ml of $CDCl_3$ which also provided the deuterium signal for the internal lock. *Ca.* 5 × 10^5 transients were accumulated with a 90° pulse and an acquisition time of 0·03—0·04 s. Chemical shifts were measured as frequency shifts from the synthesizer frequency (8·532000 MHz) and expressed in p.p.m. relative to the oxygen of water which resonated at 8·53312 MHz when measured in a concentrically placed capillary tube.

The ^{17}O n.m.r. resonances of these complexes have reasonably sharp peaks (half-band widths of 25—30 Hz) compared to that (100—300 Hz) in organic compounds of similar molecular weight.[4] This is presumably due to the more or less spherical structure of the metal complexes and the resultant slow relaxation rate which is dominated by the interaction between the quadrupole moment of ^{17}O and the electric field gradient. Spin–lattice relaxation times are still short enough to allow short acquisition times which enable us to accumulate a large number of transients in a limited time.†

TABLE. ^{17}O Shifts and one-bond W–C coupling constants for some tungsten carbonyls.[a]

Carbonyl	$\delta(^{17}O)$/p.p.m. *cis*	$\delta(^{17}O)$/p.p.m. *trans*	$^1J(^{183}W-^{13}C)$/Hz *cis*	$^1J(^{183}W-^{13}C)$/Hz *trans*
$W(CO)_6$	356·8		124·5[b]	
$W(CO)_5CPh_2$	364·7	452·6	127·0	102·5[b]
$W(CO)_5C(OMe)Ph$	357·1	388·9	127·0	115·2
$W(CO)_5C(NH_2)Ph$	352·0	372·5	126·9	124·8
$W(CO)_5\overline{CCBu^t{=}C}Bu^t$	350·6	367·6	125·7	133·0[c]
$W(CO)_5P(OMe)_3$	353·7	359·0	125·1	139·1[d]
$W(CO)_5PPh_3$	353·6	⩾353·6[e]		
$W(CO)_5PBu^n_3$	354·1	354·1	124·4	142·1[d]
$W(CO)_4(PPh_2CH_2)_2$	349·4	358·1		
$W(CO)_5I^-Bu^n_4N^+$	349·0	349·0	127·0	175·8[f]

[a] Chemical shifts are accurate to ± 1 p.p.m. and tungsten–carbon coupling constants to ± 1 Hz. [b] F. H. Kohler, H. J. Kalder, and E. O. Fischer, *J. Organometallic Chem.*, 1976, **113**, 11. [c] Y. Kawada and W. M. Jones, to be published elsewhere. [d] P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1027. [e] Shoulder on the high-frequency side of the *cis*-carbonyl signal. [f] Coupling data on the tetramethylammonium compound in footnote b.

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† This is in contrast to ^{13}C n.m.r. spectra of metal carbonyls for which relaxation reagents are often employed to reduce the long spin–lattice relaxation time of the carbonyl carbons.

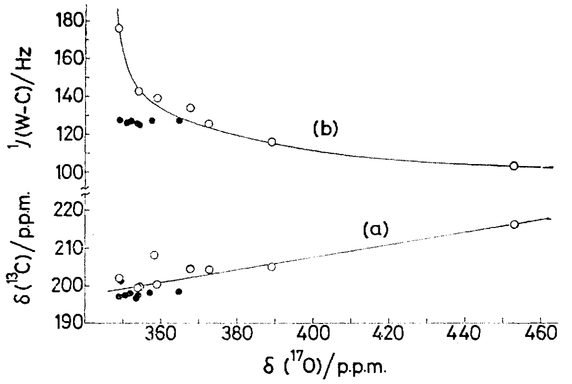

FIGURE. Plots of (a) ^{13}C n.m.r. shifts and (b) tungsten-to-carbon coupling constants *vs.* ^{17}O n.m.r. shifts of the carbonyls $L_nW(CO)_{6-n}$. ○, *trans*-CO; ●, *cis*-CO.

The results are summarized in the Table together with the one-bond coupling constants $^1J(^{183}W-^{13}C)$ between the tungsten and carbonyl carbons. In six examples resonances for the *cis-* and *trans*-carbonyl oxygens were observed as separate signals. Carbonyl groups *trans* to carbene and phosphine ligands have a range of shifts as large as 100 p.p.m. and *cis*-carbonyls have a range of 16 p.p.m. An approximately linear correlation was found between these ^{17}O shifts and the ^{13}C shielding which has been shown to be influenced by the interaction of metal *d*-orbitals with carbonyl π^* orbitals[2] (Figure 1a). The slope of the plots shows that the ^{17}O shielding is about six times more sensitive to changes in ligands than the corresponding ^{13}C of the carbonyl carbons. The carbonyl oxygens *trans* to carbene ligands are considerably more deshielded on changing from a cyclopropenylidene to a diphenylcarbene ligand. Since the downfield shifts are accompanied by a decrease in $^1J(^{183}W-^{13}C)$ (Figure 1b), it is suggested that this is also the order of decreasing σ-donor/π-acceptor ratio of these ligands including phosphines and an iodide as well as carbenes.

We conclude that natural abundance ^{17}O n.m.r. resonances are not only easily measured but also will be highly useful in elucidating the bonding in metal carbonyls.

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[2] L. T. Todd and J. R. Wilkinson, *J. Organometallic Chem.*, 1974, **77**, 1; F. H. Kohler, H. J. Kalder, and E. O. Fischer, *ibid.*, 1976, **113**, 11; S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 1967, **89**, 5573.

[3] ^{17}O N.m.r. data for metal carbonyls were first reported by R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, 1962, **58**, 1893. However, shift differences were not detected between non-equivalent ^{17}O atoms within a molecule, nor was a large shift range recognized.

[4] W. G. Klemperer, *Angew. Chem. Internat. Edn.*, 1978, **17**, 246; T. Sugawara, Y. Kawada, and H. Iwamura, *Chemistry Letters*, 1978, 1371.