Preliminary communication

APPLICATION OF OXYGEN-17 NMR TO MANGANESE CARBONYL COMPOUNDS

ROBIN L. KUMP and LEE J. TODD

Department of Chemistry, Indiana University, Bloomington, Indiana 47405 (U.S.A.)

(Received March 26th, 1980)

Summary

^{17}O NMR spectroscopy has been found to give better resolution of the carbonyl resonances of manganese carbonyl complexes and their triphenylphosphine derivatives than ^{13}C NMR spectroscopy.

Although infrared spectroscopy is useful in elucidating the structures of some manganese carbonyl complexes the only conclusive method of determining the stereochemistry of manganese carbonyl complexes is X-ray crystallography. Due to the quadrupole moment of ^{55}Mn ($I = 5/2$), ^{13}C NMR carbonyl signals of these complexes are in many cases very broad and unresolved [1—5]. In some cases the ^{13}C resonances can be sharpened by thermal decoupling at lower temperatures [5]. We have found that oxygen-17 NMR provides a powerful alternative method for determining the structures of manganese carbonyl complexes. Since oxygen is not directly bonded to manganese in these complexes, ^{55}Mn—^{17}O coupling is small and not observed. This absence of coupling allows ^{17}O NMR spectra to be obtained at room temperature.

Thus the ^{17}O NMR spectra of $Mn_2(CO)_{10}$ and $CH_3Mn(CO)_5$ (see Fig. 1) clearly resolve the equatorial and axial carbonyl signals while the ^{13}C NMR carbonyl resonances are reported to be broad and not well resolved [1,2]. Since previously only one broad carbonyl resonance was observed for the ^{13}C NMR spectrum of $CH_3Mn(CO)_5$, it was not certain if at room temperature an intramolecular exchange of the ligands was occurring or if it was due to the ^{55}Mn—^{13}C spin—spin coupling [4]. The ^{17}O NMR unambigously shows that an intramolecular exchange is not occurring under these conditions. The ^{17}O NMR spectra of $Mn_2(CO)_9(PPh_3)$ [6] and $Mn_2(CO)_8(PPh_3)_2$ [7] (see Table 1) show clearly the triphenylphosphine ligand occupying the axial position in these two molecules. Comparison of the shielding trends for $Mn_2(CO)_{10}$ and its phosphine-substituted derivatives indicates that substitution causes an upfield shift of all the carbonyl signals relative to $Mn_2(CO)_{10}$. It is probable that the area four signal at 379.5 ppm of $Mn_2(CO)_9PPh_3$ is due to the equatorial carbonyls adjacent to triphenyl-
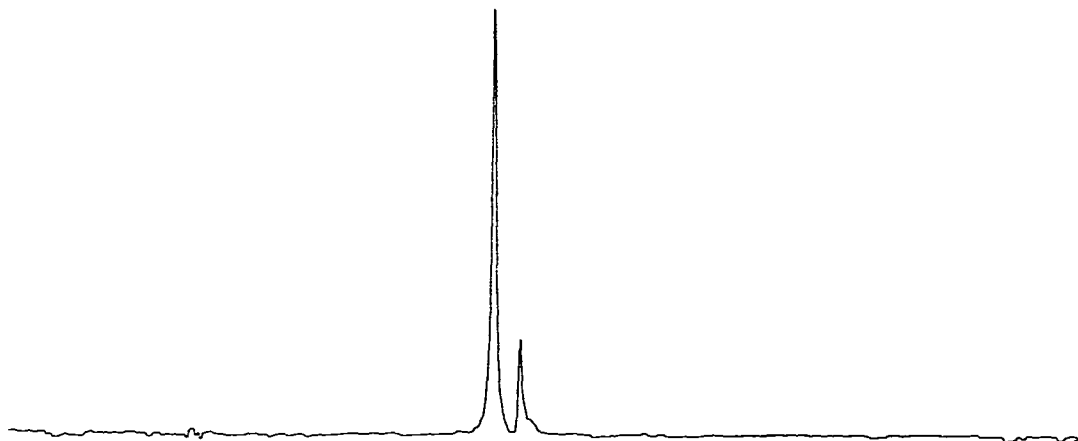
Fig. 1. The room temperature ^{17}O NMR spectrum of MeMn(CO)$_5$ at natural abundance.

TABLE 1

OXYGEN-17 NMR DATA OF MANGANESE CARBONYL DERIVATIVES

Compound[a]	δ(^{17}O) (ppm)[b]		Relative areas[c]
Mn$_2$(CO)$_{10}$	387.8	368.2	4/1
Mn(CO)$_5$Cl[d]	386.7	378.7	1/4
Mn(CO)$_5$Br	386.5	380.8	1/4
MeMn(CO)$_5$	372.6	363.0	4/1
Mn(CO)$_4$(PPh$_3$)Br[d]	379.7 376.3	373.0	1/2/1
Mn(CO)$_3$(PMe$_2$Ph)$_2$Br	371.2	364.4	1/2
Mn$_2$(CO)$_9$(PPh$_3$)	384.7 379.5	359.7	4/4/1[e]
Mn$_2$(CO)$_8$(PPh$_3$)$_2$	377.9		
Mn$_2$(CO)$_8$Br$_2$[d]	392.3	381.3	1/1

[a]CH$_2$Cl$_2$ solvent. [b]Downfield positive relative to H$_2$O. [c]All carbonyl resonances show 10 Hz ≤ Δ$\nu_{\frac{1}{2}}$ ≤ Hz. [d]Enriched with C^{17}O. [e]Δ$\nu_{\frac{1}{2}}$ ≈ 110 Hz.

phosphine. This assignment is based on the fact that the resonance for the equatorial carbonyls adjacent to triphenylphosphine in Mn$_2$(CO)$_8$(PPh$_3$)$_2$ occurs at 377.9 ppm. An upfield ^{17}O carbonyl shift due to phosphine substitution has been observed in many [8,9] but not all cases [10]. The unique axial CO in Mn$_2$(CO)$_9$(PPh$_3$) has a much broader resonance (Δ$\nu_{\frac{1}{2}}$ ≃ 110 Hz) compared to the equatorial carbonyls (Δ$\nu_{\frac{1}{2}}$ ≃ 50 Hz). This difference in peak width may be explained in terms of anisotropic tumbling with the axial CO relaxing at a faster rate than the equatorial carbonyls. These two different types of peak shapes for the environmentally different carbonyls has also been observed for cis-Mo(CO)$_4$L$_2$ complexes [9].

To obtain an ^{17}O NMR spectrum at natural abundance with most metal carbonyls a 0.3 M or greater solution is required*. Where compound solubility

was too low, oxygen-17 enrichment was employed. Exchange of $Mn(CO)_5X$ (X = Cl or Br) with $C^{17}O$ (ca. 22% enriched) was accomplished at room temperature in chloroform [11]. Reflux of a heptane solution of $Mn(C^{17}O)_5Br$ formed ^{17}O-enriched $Mn_2(CO)_8Br_2$ [12]. The ^{17}O NMR spectrum of this halogen bridged dimer contains two carbonyl signals of equal area. Comparison with the shielding values of $Mn(CO)_5Br$ (see Table 1) suggest that the high field signal at 381.3 ppm is due to the carbonyl groups *cis* to both bridging bromine atoms. The carbonyl resonances of *cis*-$Mn(CO)_4(PPh_3)Br$ [13] and *fac*-$Mn(CO)_3(PMe_2Ph)_2Br$ [13,14] are all shielded relative to $Mn(CO)_5Br$. (The infrared spectrum easily distinguishes the facial and meridional isomers of $M(CO)_3L_2X$ complexes [14,15].) Substitution with two phosphine groups on $Mn(CO)_5Br$ shifts the carbonyl resonances further upfield than substitution with one phosphine. Comparison of the ^{17}O NMR data suggests that the lowest field signal at 379.7 ppm of *cis*-$Mn(CO)_4(PPh_3)(Br)$ is due to the carbonyl group *trans* to bromine.

References

1 L.J. Todd and J.R. Wilkinson, J. Organometal. Chem., 77 (1974) 1.
2 O.A. Gansow, A.R. Burke and G.N. LaMar, J. Chem. Soc. Chem. Commun., (1972) 456.
3 S. Aime, G. Gervasio, L. Milone and E. Rosenberg, Trans. Met. Chem., 1 (1976) 177.
4 S. Aime and L. Milone, Progress in NMR Spectroscopy, 11 (1977) 183.
5 L.J. Todd and J.R. Wilkinson, J. Organometal. Chem., 80 (1974) C31.
6 H. Wawersik and F. Basolo, Chem. Commun., (1966) 366.
7 M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 2065.
8 J.P. Hickey, J.R. Wilkinson and L.J. Todd, J. Organometal. Chem., 179 (1979) 159.
9 R.L. Kump and L.J. Todd, J. Chem. Soc., Chem. Commun., (1980) 292.
10 Y. Kawada, T. Sugawara and H. Iwamura, J. Chem. Soc. Chem. Commun., (1979) 291.
11 B.F.G. Johnson, J. Lewis, J.R. Miller, B.H. Robinson, P.W. Robinson and A. Wojcicki, J. Chem. Soc. A, (1968) 522.
12 E.W. Abel and G. Wilkinson, J. Chem. Soc., (1959) 1501.
13 R.J. Angelici and F. Basolo, J. Amer. Chem. Soc., 84 (1962) 2495.
14 R.J. Angelici, F. Basolo and A.J. Poe, J. Amer. Chem. Soc., 85 (1963) 2215.
15 A.M. Bond, F.R. Keene, N.W. Rumble, G.H. Searle and M.R. Snow, Inorg. Chem., 17 (1978) 2847.