CHEMISTRY LETTERS, pp. 665-668, 1990. © 1990 The Chemical Society of Japan

^{17}O NMR Evidence for Magnetic Anisotropy Due to Metal Cluster Cores[1)]

Satoru ONAKA,* Shigeru TAKAGI, and Hiroyuki FURUTA
Department of Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466

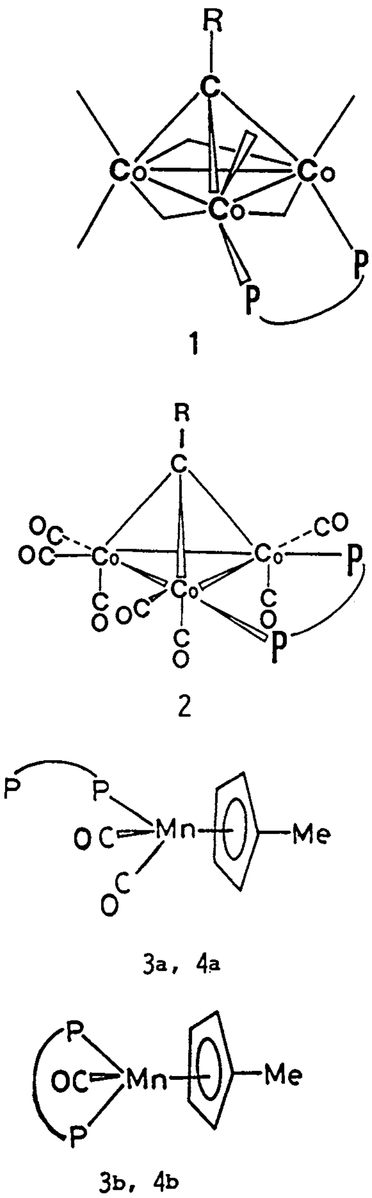
^{17}O NMR spectra have been measured for series of metal carbonyl derivatives and convincing evidence for magnetic anisotropy due to the metal cluster core has been obtained from the comparison of the ^{17}O chemical shift data for $RCCo_3(CO)_7$dppfe, $RCCo_3(CO)_7$dppm, MeCpMn-$(CO)_x$dppfe, and MeCpMn$(CO)_x$dppm.

It has been connoted recently that the ^{17}O NMR chemical shift is sensitive to the relative positions of CO groups to metal cluster core in the series of $RCCo_3(CO)_{9-x}L_x$ derivatives (L = PPh_3; x = 0 or 1).[2)] This finding suggests that the magnetic anisotropy originated from the metal ring current or metal-metal bond in the clusters should afford strong influence on the ^{17}O chemical shift. In order to obtain crucial evidence for this assertion, it is necessary to provide two types of compounds which show two different CO conformations and retain these CO conformations in solutions. Recently, we have synthesized $MeCCo_3(CO)_7$dppfe(**1a**)[3)] of which CO conformation is different from those of $MeCCo_3(CO)_7$dppm (**2a**)[4)] and $RCCo_3(CO)_9$[5)] (dppfe = 1,1'-bis(diphenylphosphino)ferrocene and dppm = bis(diphenylphosphino)-methane) in solid state. Comparison of ^{17}O NMR data for $RCCo_3(CO)_7$dppfe (R = Me(**1a**) and R = Ph(**1b**)[6)]) and $RCCo_3(CO)_7$dppm (R = Me(**2a**) and R = Ph(**2b**)) has provided convincing evidence on the magnetic anisotropy due to the CCo_3 core. The present paper reports the results on these ^{17}O NMR measurements.

Table 1. ^{17}O NMR Data

Compound	^{17}O NMR chemical shift, δ/ppm[a)]
$RCCo_3(CO)_7$dppfe	
R = Me (**1a**)	404.0
R = Ph (**1b**)	408.8
$RCCo_3(CO)_7$dppm	
R = Me (**2a**)	361.2
R = Ph (**2b**)	361.3
$RCCo_3(CO)_9$[b)]	
R = Me (**5a**)	368.3
R = Ph (**5b**)	368.9
$RCCo_3(CO)_8PPh_3$[b)]	
R = Me (**6a**)	367.5
R = Ph (**6b**)	366.4
$MeCpMn(CO)_x$dppfe	
x = 2 (**3a**)	364.3
x = 1 (**3b**)	not observed[c)]
$MeCpMn(CO)_x$dppm	
x = 2 (**4a**)	364.0
x = 1 (**4b**)	352.5
$MeCpMn(CO)_3$ (**7**)	371.4

a) Signals are all due to terminal carbonyls. b) Ref. 2. c) Not observed due to exchange between two conformers.[7)]



Scheme 1.

The scheme shows schematic drawings on the structures of the metal carbonyl derivatives[8)] employed in the present study and ^{17}O NMR chemical shift data are tabulated in the Table 1.[9)] As is seen from the Table 1, the substitution of dppm for two CO groups in $RCCo_3(CO)_9$ affords such a normal high-field shift of ^{17}O resonance as is observed in the case of triphenylphosphine substitution for one CO group.[2] However, the substitution of dppfe for two CO groups causes a significant lower-field shift. It is suspected that the electronic effect difference between dppfe and dppm affords such an opposite influence on ^{17}O chemical shifts. To examine this query, ^{17}O NMR data for mononuclear manganese carbonyl derivatives, (MeCp)Mn$(CO)_x$dppfe (**3a** for x = 2 and **3b** for x = 1) and (MeCp)Mn$(CO)_x$dppm (**4a** for x = 2 and **4b** for x = 1) are compared. However, these compounds show similar high-field shifts by replacement of CO group(s) with these $\widehat{P\ \ P}$ type ligands. Therefore, other factors than the electronic effect should be responsible for observed change of ^{17}O chemical shifts among **1** and **2**. As is shown in the scheme, $RCCo_3(CO)_7$dppfe(**1**) possesses four terminal and three bridging carbonyls, whereas all seven carbonyls in $RCCo_3(CO)_7$dppm (**2**) are in terminal positions,[4] similar to those of parent $RCCo_3(CO)_9$.[5] In order to check the CO scrambling among terminal and bridging carbonyls of **1** in a solution, ^{17}O NMR spectra are also measured at -50 °C for **1a** in toluene-d^8. However, no significant change from that measured at room temperature to suggest such an exchange has so far been detected. Thus, a plausible explanation that the observed ^{17}O resonance at low-field for **1a** and **1b** is an ''averaged peak'' among the terminal and bridging carbonyls is untenable.[10] The observed low-field shifts of ^{17}O resonances in **1a** and **1b** compared with the high-field shifts for **2a** and **2b** are, therefore, best accounted for in terms of the magnetic anisotropy effect originated from the ring current of the CCo_3 core. Terminal carbonyls in **1a** and **1b** should be located in the deshielded magnetic field, and those in **2a** and **2b** should be located in the shielded magnetic field, although exact knowledge on the shielding-deshielding cone angle of the CCo_3 core should wait for future calculation on the shielding cone angles for CCo_3 core.[11]

The present work was financially supported by a Grant-in-Aid for Science Research No. 63540482 from the Ministry of Education, Science, and Culture.

References

1) This is Part V of ^{17}O NMR Study of Metal Carbonyl Cluster Compounds. Part IV: Ref. 2.
2) S. Onaka, S. Takagi, H. Furuta, Y. Kato, and A. Mizuno, Bull. Chem. Soc. Jpn., **63**, 42 (1990).
3) S. Onaka, A. Mizuno, and S. Takagi, Chem. Lett., **1989**, 2037.
4) G. Balavoine, J. Collin, J. J. Bonnet, and G. Lavigne, J. Organomet. Chem., **280**, 429 (1985).
5) P. W. Sutton and L. F. Dahl, J. Am. Chem. Soc., **89**, 261 (1975).
6) **1b** is synthesized by the same procedure to that of **1a**.[3] As IR spectra of **1b** is quite similar to that of **1a**, **1b** should have the same CO conformation to that of **1a**; ν(CO)(Nujol mull) : 2040(s), 2012(s), 1989(s), 1974(vs), 1874(m), 1845(m), 1820(s).
7) S. Onaka, Bull. Chem. Soc. Jpn., **59**, 2359 (1986).
8) IR(CO stretching region) and ^{1}H-NMR measurements are employed to make the characterization of the new compounds and to check the purities of all the compounds.
9) ^{17}O NMR data are obtained for natural abundant level (0.037%) of ^{17}O with same procedures described in the previous paper.[2]
10) Although the fact that the two protons of the methylene group in **2a** are inequivalent in ^{1}H-NMR spectrum at room temperature[4] seems to suggest that the total scrambling including the puckering of dppm is not the case for **2a** and **2b** at room temperature, it is suspected that the exchange among axial and equatorial carbonyls is not frozen at room temperature for **2a** and **2b** as in the case of $RCCo_3(CO)_9$ and $RCCo_3(CO)_8PPh_3$.[12] MAS-NMR measurements for **2a** and **5a** are now planned in this laboratory.
11) We stand in the view that the magnetic fields which two kinds of terminal carbonyls in **1a** and **1b** feel are quite similar because two kinds of terminal carbonyls are in the same shielding cone angle and thus two signals are not resolved. In addition, we notice the possibility that the charge densities of two kinds of terminal oxygen atoms are quite similar due to the nature of the CCo_3 core as a good electron reservoir.[2] MO calculation is necessary to ascertain this idea.
12) T. W. Matheson and B. H. Robinson, J. Organomet. Chem., **88**, 367 (1975).

(Received January 10, 1990)