42 © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *63*, *42—46 (1990)* [Vol. 63, No. 1

^{17}O NMR Study of Metal Carbonyl Cluster Compounds. IV.[1] The Substituent Effect on the ^{17}O NMR Chemical Shifts for a Series of Tri-Nuclear Metal Carbonyl Cluster Compounds

Satoru Onaka,* Sigeru Takagi, Hiroyuki Furuta, Yoshio Kato, and Atushi Mizuno
Department of Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

(Received June 27, 1989)

^{17}O NMR spectra have been measured for series of cobalt carbonyl cluster derivatives, $RCCo_3(CO)_{9-x}(PPh_3)_x$, $(RC_2R')Co_{3-x-y}Fe_xMo_y(CO)_{9-y}Cp_y$, and $R_{3-x}Sn[Co(CO)_4]_{x+1}$. The small ^{17}O-chemical shift differences due to the change of R and/or introduction of PPh_3 have been interpreted in terms of the electron buffer action of the Co_3 core for $RCCo_3(CO)_{9-x}(PPh_3)_x$. Good linear correlations between ^{17}O-chemical shifts and CO stretching frequencies have been observed for these derivatives. Some effect of the magnetic anisotropy resulted from the ring current along the metal-triangle on ^{17}O-chemical shifts has been suggested for metal-triangle clusters.

Proliferate studies on the metal carbonyl cluster derivatives has been made during past two decades for both syntheses[2,3] and theories on the shapes and/or electron count rules of metal cluster cores.[2,4,5] Although X-ray crystal structure analysis technique has played a crucial role for elucidating structures and bondings of these cluster compounds, NMR (^{1}H and ^{13}C) and IR (ν (CO) and ν (M–M) regions) spectroscopies have been appreciated as only a complementary means for structure analysis. Thus ^{17}O NMR spectroscopy has scarecely been employed as a structural probe.[6,7] This facet is surprising for us, because recent ^{17}O NMR studies on mixed metal carbonyl cluster compounds demonstrated that ^{17}O NMR spectrum is easily available for even naturally abundant level (0.037%) of the ^{17}O nucleus[1] and are obtained for CO groups which are coordinated to a metal atom with a large nuclear quadrupole moment without significant line-broadening of peaks as in the case of ^{13}C NMR. Another characteristic for ^{17}O NMR spectroscopy is that the ^{17}O-chemical shift of terminal carbonyls depends mainly on the metal atom to which the carbonyls of interest are coordinated[1] and the magnitude of the chemical shift of ^{17}O NMR is more prominent than that of ^{13}C NMR[8] for same CO groups; the latter feature indicates that ^{17}O NMR spectroscopy is more perceptive to the change of the electron distribution around the CO groups of interest. These lines of findings have prompted us to examine ^{17}O NMR data as an effective structural and bonding probe for higher nuclearity clusters which at least contain three metal carbonyl units. In this paper, we report the substituent effect on the ^{17}O NMR chemical shift for following trinuclear metal carbonyl clusters, $RCCo_3(CO)_{9-x}(PPh_3)_x$ and $(RC_2R')Co_{3-x-y}Fe_xMo_y(CO)_{9-y}Cp_y$ (x=0 or 1; y=0 or 1).

Experimental

Literature methods have been employed to obtain all the following samples: $RCCo_3(CO)_9$ (R=Me (**1a**), Ph (**1b**), Cl (**1c**), and H (**1d**)),[9,10] $RCCo_3(CO)_8PPh_3$ (R=Me (**2a**), Ph (**2b**), and Cl (**2c**)),[11] $(HPhC_2)Co_2(CO)_6$ (**3**),[12] $(Ph_2C_2)Co_2Fe$-

Table 1. Spectral Data

Compound	^{17}O NMR chemical shift, δ/ppm[a]	ν(CO)/cm^{-1}
$RCCo_3(CO)_9$		
R=Me (**1a**)	368.3	2104, 2051, 2038, 2018[d]
R=Ph (**1b**)	368.9	2104, 2055, 2039, 2021[d]
R=Cl (**1c**)	370.4	2111, 2064, 2046, 2030[d]
R=H (**1d**)	371.4	2109, 2058, 2041, 2023[d]
$RCCo_3(CO)_8PPh_3$		
R=Me (**2a**)	367.5	2077, 2072, 2033, 2020, 2011, 1992, 1988, 1968[e]
R=Ph (**2b**)	366.4	2077, 2035, 2025, 2012, 1995, 1989, 1968[e]
R=Cl (**2c**)	366.2	2083, 2041, 2029, 2020, 1998, 1979[e]
$(HCCPh)Co_2(CO)_6$ (**3**)	364.3	2098, 2072, 2060, 2045, 2032, 2030, 2018, 1986[d]
$(PhCCPh)Co_2Fe(CO)_9$ (**4**)	362.8	2095, 2057, 2030, 2012[d]
$(HPhC_2)Co_2Fe(CO)_9$ (**5**)	368.3 (Fe), 374.1 (Co)	2104, 2060, 2050, 2042, 2025, 1982, 1977[f]
$(HPhC_2)CoFeMo(CO)_8Cp$ (**6**)	371.3 (Co, Fe), 398.8 (Mo)	2074, 2032, 2028, 2020, 1990, 1985, 1966, 1959, 1943, 1884[f]
Me_3Sn–$Co(CO)_4$ (**7**)	352.4[b]	2082, 2020, 1988[b]
$Me_2Sn[Co(CO)_4]_2$ (**8a**)	359.7[c]	2095, 2078, 2031, 2024, 2013, 2002, 1992[c]
$Ph_2Sn[Co(CO)_4]_2$ (**8b**)	357.4[c]	2095, 2080, 2033, 2029, 2018, 2009, 1995[c]
$Cl_2Sn[Co(Co)_4]_2$ (**8c**)	362.9[c]	2114, 2097, 2056, 2052, 2040, 2023, 2016[c]
$MeSn[Co(CO)_4]_3$ (**9**)	357.0[b]	2079, 2040, 2028, 2020, 2010, 1992, 1961[b]

a) $C_6H_6+C_6D_6$. b) Ref. 13. c) Ref. 1. d) Nujol mull. e) Ref. 11. f) Ref. 12.

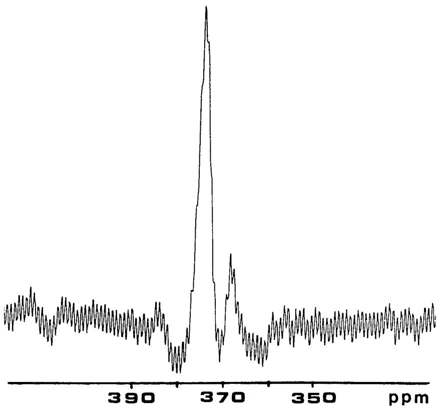
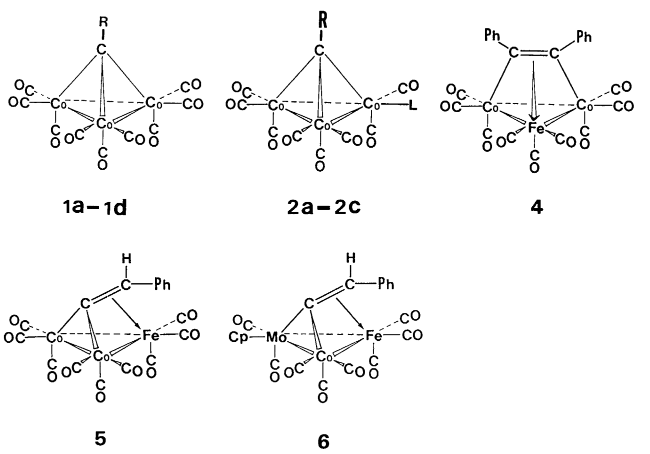


Fig. 1. ^{17}O NMR spectrum of $(HPhC_2)Co_2Fe(CO)_9$ in $C_6H_6+C_6D_6$ at room temperature.



Scheme 1.

$(CO)_9$ (**4**),[12] $(HPhC_2)Co_2Fe(CO)_9$ (**5**),[12] $(HPhC_2)CoFeMo(CO)_8Cp$ (**6**),[12] $Me_3Sn-Co(CO)_4$ (**7**),[13] $R_2Sn[Co(CO)_4]_2$ (R= Me (**8a**), Ph (**8b**), and Cl (**8c**)),[1] and $MeSn[Co(CO)_4]_3$ (**9**).[13] The purity of the samples was checked by IR (ν (CO) region) and ^1H NMR. Solvents were distilled from benzophenone ketyl (benzene and THF) or calcium chloride (CH_2Cl_2 and $CHCl_3$) before use. ^{17}O NMR sample solutions were prepared by the use of the vacuum-line technique; solvents were completely deaerated by three freeze-thaw cycles, distilled into a 10 mm o.d. NMR tube, and the tube was sealed off under vacuum. ^{17}O NMR spectra were obtained with the same procedure (90° pulse and 0.01 s acquisition time) as was described elsewhere for natural abundant level of ^{17}O by use of a Varian XL-200 spectrometer operated at 27.12 MHz.[1] Chemical shifts were measured in parts per million with reference to $H_2{}^{17}O$ frequency. Spectral data are listed in Table 1 and Fig. 1 displays the ^{17}O NMR spectrum of $(HPhC_2)Co_2Fe(CO)_9$ (**5**) as a typical example.

Spectral Results and Assignments

Before we deal with the results of ^{17}O NMR measurements, it seems appropriate to see the structures of the compounds subjected to the present ^{17}O NMR study. Scheme 1 depicts the structures of these compounds determined by X-ray analyses.[12,14–16]

$RCCo_3(CO)_9$ and $RCCo_3(CO)_8PPh_3$. For a series of $RCCo_3(CO)_9$ compouds, there are two kinds of CO groups, that is equatorial carbonyls and axial carbonyls. However ^{17}O NMR spectra for **1a**—**1d** have shown only one peak; ^{13}C NMR spectra also showed only one CO peak for these compounds.[17–19] Although CO scrambling is very often responsible for the coincidence of the two resonances,[20] such CO exchange among the equatorial and axial carbonyls has not yet been reported for **1a**—**1d** to our knowledge. Therefore, it seems reasonable to conclude that the axial CO and equatorial CO resonances are in accidental coincidence for some electronic reason. This issue is discussed later. Substitution of triphenylphosphine for one equatorial carbonyl in **1a** affords **2a**[15] and this makes all the remaining carbonyls nonequivalent. As IR spectra of **2b** and **2c** in ν (CO) region are quite similar to that of **2a**, **2b** and **2c** should have same structure as that of **2a**. Nevertheless, only one ^{17}O NMR peak is detected for **2a**—**2c** at room temperature. For these compounds, rapid CO scrambling should be responsible for the detection of only one ^{17}O NMR peak at ambient temperature, since Matheson et al. demonstrated a rapid CO scrambling process in solutions by measuring temperature-dependent IR and ^{13}C NMR spectra for $MeCCo_3(CO)_8P(C_6H_{11})_3$ which has a similar solid structure to that of **2a**;[21] this makes all carbonyls equivalent.

$(Ph_2C_2)Co_2Fe(CO)_9$ (4), $(HPhC_2)Co_2Fe(CO)_9$ (5), and $(HPhC_2)CoFeMo(CO)_8Cp$ (6). According to X-ray structure analyses,[12,16] five peaks are expected for **4**, six peaks for **5**, and eight peaks for **6**. However, **4** displays only one peak, **5** shows two distinct resonances at 374.1 and 368.3 ppm, and **6** shows one strong and broad multiplet centered at 371.3 ppm, and a weak peak at 398.8 ppm.

Temperature-dependent ^{13}C NMR study by Milone et al. for $(Et_2C_2)Co_2Fe(CO)_9$, which has the same skeletal structure as that of **4**, has demonstrated only one peak at room temperature. This is due to the total CO scrambling associated with the alkyne ligand motion on the Co_2Fe metal triangle.[16] The similar CO scrambling should have caused the coalescence of the ^{17}O NMR peaks at room temperature for **4**. As for **5**, the peak at higher field with weak intensity is assigned to carbonyls on Fe and the peak at lower field with strong intensity to carbonyls on Co_2. Detection of two ^{17}O NMR peaks suggests that the alkyne group in *5* coordinates more strongly to the Co_2Fe triangle than in **4** and the alkyne motion on the Co_2Fe core seems to be frozen to some extent at ambient temperature. As for **6**, the weak peak at 398.8 ppm is due to carbonyls on the molybdenum atom[1] and the multiplet at 371.3 ppm is due to carbonyls on the cobalt and iron atoms. As the noise level is so significant, ^{17}O-enrich experiment is necessary to analyze the multiplet for **6**.

Discussion

For ^{17}O NMR signals of $RCCo_3(CO)_9$ (**1a**—**1d**), the substitution of R from Me (**1a**) to H (**1d**) causes only small low-field shift (ca. 3 ppm). The magnitude of the low-field shift with the change of R group is smaller than those of a series of $R_2Sn[Co(CO)_4]_2$; shift of 5.5 ppm between $Cl_2Sn[Co(CO)_4]_2$ and $Ph_2Sn[Co(CO)_4]_2$.[1)] $RCCo_3(CO)_8PPh_3$ (**2a**—**2c**) shows a slight high-field shift compared with the corresponding parent compounds (**1a**—**1c**); the up-field shift is maximum (4.2 ppm) for the chloro derivative and minimum (0.8 ppm) for methyl derivative.[22)] Another interesting finding is the decrease in ^{17}O-chemical shift dfifference between methyl and chloro derivative by introducing PPh_3 on the Co_3 core, from 2.1 ppm for **1a** and **1c** to 1.4 ppm for **2a** and **2c**. In order to understand ^{17}O-chemical shift in terms of the electronic function of CCo_3 core, it seems appropriate to peruse previous studies on $RCCo_3(CO)_9$ derivatives such as ^{59}Co NQR study by Brill et al.,[23)] PE(photo-electron) investigation by Granozzi et al.,[24)] and MO study by Fehlner et al.[25)] NQR study suggested that significant delocalization of electron density in the region of apical carbon atom occurs and is responsible for transmission of electron density between the cobalt atoms and the R group through a π-resonance mechanism. We have attempted to correlate ^{17}O-chemical shift and ^{59}Co nuclear quadrupole coupling constant; good linear correlation holds for **1b**, **1c**, and **1d** except **1a**; deviation of **1a** from the line may be due to the use of an averaged coupling constant which is obtained for solid sample. The correlation indicates that π-resonance mechanism works over the terminal oxygen atoms in CO groups. PE investigation has substantiated such π-resonance type mechanism to be operative for the interaction between the Co_3 triangle and the apical RC group, and also the $CCo_3(CO)_9$ fragment to be a good electron reservoir.[24)] Fehlner et al. have shown for **1a** that calculated Mulliken atomic charges around the oxygen atoms of the equatorial and axial carbonyls are quite close and also demonstrated the presence of the 3d orbitals overlapping along the Co–Co bond in the orbital contour diagrams.[25)] All of these results support the idea that the CCo_3 core is a good electron reservoir and that the electronic effect caused by the substitution of the R group or CO group by PPh_3 is well buffered by an effective function of the CCo_3 core as an electron reservoir. Small ^{17}O shift with the change of the apical substituent R and/or core substituent PPh_3 is thus best interpreted in terms of the electron buffer action of the CCo_3 core.

Then, we are tempted to investigate how the ^{17}O-chemical shift is influenced when the RC group is replaced with RC=RC group. For this purpose, comparison of the chemical shift among **1a**, **1b**, and **5** seems appropriate; compound **4** is not included, because the observed ^{17}O-shift datum is an "averaged" value among the carbonyls coordinated to the cobalt and iron atoms and the shift data for carbonyls coordinated to the cobalt atoms alone are not available at present. As was described in the spectral assignment section, carbonyls coordinated to the cobalt atoms in **5** resonate at lower field (ca. 5 ppm) than those in **1a** and **1b** and the amount of lower-field shift is larger than the shifts among **1a**—**1d**. Extended Hückel calculations for M_3L_9 and M_3L_9R (M=Co, Fe, Ru; $R=C_2H_4$, C_2H_2) by Hoffmann et al. showed that the incorporation of acyclic unsaturated ligands such as C_2H_4 and C_2H_2 through their π-electron affords significant change in the energy levels of related orbitals.[26)] However, neither E. H. calculations for mixed metal M_3L_9 nor mixed metal M_3L_9R where R binds to M_3 core through σ- and π-bonds has not yet been made to our knowledge. We just point out the factors which may induce the observed effect on ^{17}O-chemical shift. One factor is electronical change caused by the incorporation of the iron atom in the metal ring system. Another factor is the magnetic anisotropy effect from the C=C bond and such effect may depend on the relative orientation of the C=C bond to the Co–Co bond.

The CO stretching frequency, ν (CO), has been employed as a conventional measure or elucidating the change of the electron distribution around the oxygen atoms in metal carbonyls.[1,8,23)] In order to clarify what factors are operative for ^{17}O-chemical shift, ^{17}O-chemical shifts are plotted to CO stretching frequencies (total symmetric mode observed at highest frequency region for each compound)[27,28)] for two series of cobalt carbonyl derivatives, "open clusters" $R_{3-x}Sn[Co(CO)_4]_{x+1}$ and "triangle clusters" $RCCo_3(CO)_{9-x}(PPh_3)_x$ (Fig. 2). A good linear relationship holds for each cluster system; ^{17}O-chemical shifts move to a lower field with the increase of the CO stretching

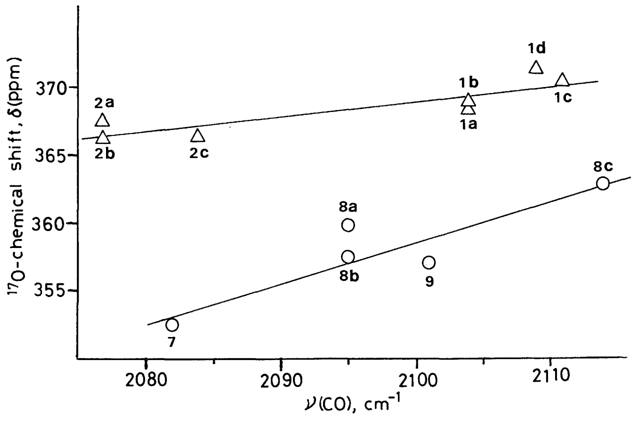


Fig. 2. Correlations between ^{17}O NMR chemical shifts and ν(CO) frequencies. ○—○ denotes plots for open clusters, $R_{3-x}Sn[Co(CO)_4]_{x+1}$ and △—△ denotes plots for triangle clusters, $RCCo_3(CO)_{9-x}(PPh_3)_x$.

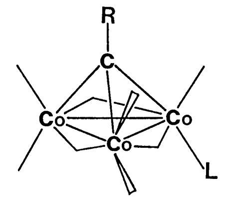
frequencies for each system. Interesting findings obtained from the plots are that the slope of the line drawn for open cluster system is steeper than that of the triangle cluster system and the ^{17}O-nuclei in triangle system resonate at lower field than those in open cluster system. As was shown in the previous papers,[23,29] the lower-field shift of ^{17}O-resonance occuring in accord with the increase of the CO stretching frequencies for increase of the $Co(CO)_4$ unit and/or for introduction of the electronegative group on the tin atom can be best interpreted in terms of the decrease of the electron density around the oxygen atoms of interest through σ- and π-interaction between the cobalt atom and CO groups for the series of open clusters, $R_2Sn[Co(CO)_4]_2$ and $R_{3-x}Sn[Co(CO)_4]_{x+1}$. A similar lower-field shift of ^{17}O-resonances in accord with the increase of CO stretching frequencies is observed for the series of triangle clusters when the electronegative group is introduced on the apical carbon atom. It is well-known that the electron density around the oxygen atoms increases when the CO group is replaced by weaker π-accepting ligand such as PPh_3 for $RM(CO)_n$ type compounds and the CO stretching frequencies shift to a lower energy region.[30] Thus, observed good correlation between ^{17}O-chemical shift and CO streching frequency for $RCCo_3(CO)_{9-x}(PPh_3)_x$ is reasonablly interpreted in terms of the electron density term, Q_{aa}, in paramagnetic shielding constant σ_p (Eq. 1).

$$\sigma_p = -\frac{e^2\hbar^2}{2mc^2}\cdot\frac{<r^{-3}>}{<\Delta E>}\cdot(Q_{aa}+\Sigma Q_{ab}) \tag{1}$$

However, the observed difference in the slopes of the two lines and the lower-field ^{17}O-resonances of the triangle system may require additional factor other than the electron density term, Q_{aa}, which also affect the shielding constant σ. The shielding constant σ is expressed in the form of Eq. 2 and it is well-known that the σ_{para} term is operative for ^{17}O-resonance.[29]

$$\sigma = \sigma_{dia} + \sigma_{para} + \sigma_{oth} \tag{2}$$

In the previous paper, we have pointed out that the contribution from the metal–metal bond anisotropy effect to σ_{oth} should not be overlooked.[29] In addition, we believe the ring current effect should be included in σ_{oth} term for cobalt triangle clusters based on the following reasons; first, the orbital contour map drawn by Fehlner et al. showed the presence of the 3d orbitals overlapping along the Co–Co triangle[25] together with π-resonance mechanism working over the Co_3 triangle and the apical RC group. Second, **3** which is a kind of "open cluster" shows a higher-field resonance (364.3 ppm) than those for **1a**—**1d**. In order to appreciate the ring current effect on the ^{17}O-chemical shift, it seems reasonable to see the magnetic effect due to the ring current in the cyclopropane system; in the cyclopropane system, it has been suggested that the ring current produces two regions, magnetically shielded and deshielded regions, and the ring protons which are located in the magnetically shielded region resonate at higher field.[31–33] In the present cobalt cluster system, the equatorial carbonyls are located in the deshielded region and the axial carbonyls are located in the shielded region if similar ring current effect is conceivable. However, rapid CO scrambling for **2a**—**2c** at room temperature poses problems for evaluating the ^{17}O-chemical shift difference among the equatorial and axial carbonyls;[21] CO scrambling occurs among the carbonyls in two structural isomers, nonbridged isomer (**2a**—**2c** in Scheme 1) and bridged isomer (Scheme 2), which coexist in equilibrium in solutions at room temperature. In the bridged isomer, the terminal carbonyls shift to intermediate positions between axial and equatorial carbonyls and/or equatorial carbonyls and the apical carbon atom. Thus, obtained ^{17}O-chemical shift values for **2a**—**2c** are "averaged" one among the terminal carbonyls for two isomers. Another problem we should be aware of for interpreting the ^{17}O-chemical shift data is whether the intermediate position in the bridged-isomer is located in the magnetically shielded region or in the magnetically deshielded region. Although the magnetic shielding–deshielding cone angle of CCo_3 ring current system has not yet been evaluated, we presume that terminal carbonyls of the bridged isomer is located in the magnetically deshielded region based on the aforementioned trends on the ^{17}O-chemical shifts for triangle clusters. The trends are best interpreted in terms of the lower-field resonance of the terminal carbonyls of the bridged isomer. Thus "averaged ^{17}O-signal" due to CO scrambling is observed at somewhat lower-field region than that of the "pure" ^{17}O-signal due to axial and equatorial carbonyls.



Scheme 2.

Matheson et al. have also shown that the ^{13}CO resonance is deshielded by the introduction of the phosphine ligand.[21] All of these discussions together with the discussion on the function of the M_3 core as an electron reservoir indicate that ^{17}O NMR shielding is determined by the intricate balance between the local paramagnetic contribution due to the changes in charge density and the ring current effect along the metal–metal triangle. We would like to open our conclusion for future ^{17}O NMR study on metal carbonyl derivatives which are composed from metal ring systems.

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) Part III, S. Onaka and Y. Kato, *Bull. Chem. Soc. Jpn.*, **61**, 304 (1988).

2) "Transition Metal Clusters," ed. by B. F. G. Johnson, J. Wiley (1980) and references therein.

3) a) J. S. Bradley, *Adv. Organomet. Chem.*, **23**, 1 (1983); b) H. Vahrenkamp, *Adv. Organomet. Chem.*, **22**, 169 (1983).

4) B. K. Teo, *Inorg. Chem.*, **24**, 4545 (1985).

5) R. L. Johonson and M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, **1987**, 1445.

6) S. Aime, M. Botta, R. Gobetto, and D. Osella, *J. Chem. Soc., Dalton Trans.*, **1988**, 791.

7) S. Aime, D. Osella, L. Milone, G. E. Hawkes, and E. W. Randall, *J. Am. Chem. Soc.*, **103**, 5920 (1981).

8) Y. Kawada, T. Sugawara, and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, **1979**, 291.

9) G. Bor, L. Marko, and B. Marko, *Chem. Ber.*, **95**, 3333 (1962).

10) W. T. Dent, L. A. Dunconson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc. London*, **1961**, 169.

11) T. W. Matheson, B. H. Robinson, and W. S. Tham, *J. Chem. Soc. A*, **1971**, 1457.

12) T. Albiez, W. Bernhardt, C. Schnering, E. Roland, H. Bantel, and H. Vahrenkamp, *Chem. Ber.*, **120**, 141 (1987).

13) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 2222 (1966), **6**, 981 (1967).

14) P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 261 (1967).

15) M. D. Brice, B. P. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, **9**, 362 (1970).

16) S. Aime, L. Milone, D. Osella, A. Tiripicchio, and A. M. M. Lanfredi, *Inorg. Chem.*, **21**, 501 (1982).

17) S. Aime, L. Milone, and M. Valle, *Inorg. Chim. Acta*, **18**, 9 (1976).

18) D. C. Miller and T. B. Brill, *Inorg. Chem.*, **17**, 240 (1978).

19) D. Seyferth, G. H. Williams, C. S. Eschbach, M. O. Nestle, J. S. Merola, and J. E. Hallgren, *J. Am. Chem. Soc.*, **101**, 4867 (1979).

20) "Dynamic Nuclear Magnetic Resonance Spectroscopy," ed. by L. M. Jackman and F. A. Cotton (1975), and references therein.

21) T. W. Matheson and B. H. Robinson, *J. Organomet. Chem.*, **88**, 367 (1975).

22) Similar high-field shift was reported previously for a series of $Me_3Sn-Mn(CO)_{5-x}[P(OPh)_3]_x$.[23]

23) S. Onaka, T. Sugawara, Y. Kawada, Y. Yokoyama, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **59**, 3079 (1986).

24) G. Granozzi, E. Tondello, D. Ajo, M. Casarin, S. Aime, and D. Osella, *Inorg. Chem.*, **21**, 1081 (1982).

25) R. L. DeKock, K. S. Wong, and T. P. Fehlner, *Inorg. Chem.*, **21**, 3203 (1982); calculated Mulliken atomic charges for equatorial O atoms are 0.048 and those for axial O atoms are 0.044.

26) B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, **101**, 3456 (1979).

27) S. Onaka, *Bull. Chem. Soc. Jpn.*, **44**, 2135 (1971); S. Onaka, *ibid.*, **46**, 2444 (1973).

28) M. W. Howard, S. F. Kettle, I. A. Oxton. D. B. Powell, N. Sheppard, and P. Skinner, *J. Chem. Soc., Faraday Trans. 2*, **77**, 397 (1981).

29) S. Onaka, T. Sugawara, Y. Kawada, and H. Iwamura, *J. Chem. Soc., Dalton Trans.*, **1982**, 257.

30) S. Onaka and H. Sano, *Bull. Chem. Soc. Jpn.*, **48**, 258 (1975).

31) S. Forsen and T. Norin, *Tetrahedron Lett.*, **1964**, 2845.

32) D. J. Paatel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

33) K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965).