304 © *1988 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***61***, *304—306 (1988)* [Vol. 61, No. 1

^{17}O NMR Study of Metal Carbonyl Cluster Compounds. III.[1)]
^{17}O NMR Spectra of Mixed Metal Carbonyl Cluster Compounds, $R_2Sn[M(CO)_x][M'(CO)_y]$, $R_2Sn[M(CO)_x][M'(CO)_yCp]$, and $ClSn[Mn(CO)_5][Fe(CO)_2Cp]_2$

Satoru Onaka* and Yoshio Kato
Department of Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

(Received July 6, 1987)

Synopsis. A series of mixed metal carbonyl cluster compounds of $R_2Sn[M(CO)_x][M'(CO)_y]$ and $R_2Sn[M(CO)_x][M'(CO)_yCp]$ were synthesized and their ^{17}O NMR spectra were measured to demonstrate how ^{17}O NMR spectroscopy is superior to IR spectroscopy to study the electronic nature of the oxygen atoms in CO groups. For these mixed metal clusters, ^{17}O NMR spectral assignments were easily made and the electron distribution around the O atoms was concluded to be only slightly changed compared with those of homo-dinuclear $R_2Sn[M(CO)_x]_2$ and $R_2Sn[M'(CO)_yCp]_2$.

In previous papers,[1)] we have demonstrated that ^{17}O NMR is an eligible alternative to ^{13}C NMR or IR (ν(CO) region) for elucidating the change of electron distribution and/or structures of metal carbonyl cluster derivatives. This trait of ^{17}O NMR spectroscopy is now applied to a series of $R_2Sn[M(CO)_x]_2$, $R_2Sn[M'(CO)_yCp]_2$, $R_2Sn[M(CO)_x][M'(CO)_y]$, and $R_2Sn[M(CO)_x][M'(CO)_yCp]$ type derivatives. The present paper reports the syntheses of a series of $R_2Sn[M(CO)_x][M'(CO)_y]$, $R_2Sn[M(CO)_x][M'(CO)_yCp]$ type compounds and $ClSn[Mn(CO)_5][Fe(CO)_2Cp]_2$ and the results of ^{17}O NMR measurements for a sereis of aforementioned homo-dinuclear and hetero-dinuclear or hetero-trinuclear metal carbonyl derivatives.

Experimental

All the manipulations were made under a purified nitrogen atmosphere. Solvents were distilled from benzophenone ketyl under N_2 before use. Literature methods were employed to obtain the following homo-dinuclear metal carbony derivatives, $Me_2Sn[Mn(CO)_5]_2$ (**1**),[2)] $Ph_2Sn[Mn(CO)_5]_2$ (**2**),[3)] $Me_2Sn[Re(CO)_5]_2$ (**3**),[3)] $Me_2Sn[Co(CO)_4]_2$ (**4**),[4)] $Ph_2Sn[Co(CO)_4]_2$ (**5**),[4)] $Cl_2Sn[Co(CO)_4]_2$ (**6**),[5)] $Me_2Sn[Mo(CO)_3Cp]_2$ (**7**),[6)] $Me_2Sn[Fe(CO)_2Cp]_2$ (**8**)[7)], and $Cl_2Sn[Fe(CO)_2Cp]_2$ (**9**).[7)]

Synthesis of $Me_2Sn[Mn(CO)_5][Re(CO)_5]$ (10). A 850 mg sample (2 mmol) of $BrMe_2SnMn(CO)_5$[8)] was allowed to react with an equimolar amount of $NaRe(CO)_5$ in THF at room temperature and the reaction mixture was stirred overnight. Then the solvent was vacuum-stripped from the yellow-orange solution to leave yellow solid. This solid was recrystallized from hexane to yield 620 mg of pale yellow sample (yield 46%). Found: C, 21.77; H, 0.95%. Calcd for $C_{12}H_6MnO_{10}ReSn$: C, 21.52; H, 0.90%. ν(CO) (ligroine solution): 2117 (w), 2095 (w), 2080 (m), 2077 (m, sh), 2010 (vs), and 1982 (s) cm^{-1}.

Synthesis of $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$ (11). A similar method as the above was employed; a 960 mg (2 mmol) sample of $ClPh_2Sn-Co(CO)_4$[9)] was allowed to react with an equimolar amount of $NaMn(CO)_5$ in THF at room temperature. Similar treatment as the above and recrystallization from pentane to give 300 mg (yield 23%) of pale yellow crystals. Found: C, 39.53; H, 1.52%. Calcd for $C_{21}H_{10}CoMnO_9Sn$: C, 39.48; H, 1.56%. ν(CO) (Nujoll mull): 2105 (w), 2100 (w), 2080 (s), 2030 (m), 2018 (s), 2010 (vs), and 1985 (m) cm^{-1}.

Synthesis of $Me_2Sn[Mn(CO)_5][Mo(CO)_3Cp]$ (12). A 0.76 g (2 mmol) sample of $ClMe_2Sn-Mn(CO)_5$[10)] was treated with an equimolar amount of $NaMo(CO)_3Cp$ in THF as above described and recrystallization from petroleum ether gave 0.90 g sample of pure product (yield 76%). The purity of this sample was checked by spectroscopic data (IR, and ^{1}H NMR)[11)].

Synthesis of $ClSn[Mn(CO)_5][Fe(CO)_2Cp]_2$ (13). A 220 mg (0.55 mmol) sample of $Mn_2(CO)_{10}$ was dissolved into 50 ml of THF and the solution was stirred over 1% Na amalgam for 2 h. After filtration of this solution, a THF solution (50 ml) which contains a 400 mg (1.1 mmol) sample of $Cl_2Sn[Fe(CO)_2Cp]_2$ was added to this filtrate and the reaction mixture was stirred overnight at room temperature. From the resulting red solution, the solvent was vacuum-stripped and red-orange residue was extracted three times with each 20 ml of benzene. From the combined extracts, the solvent was partially vacuum-distilled off and 20 ml of petroleum ether was added. Storage of this solution in a refrigerator for a few days gave orange-red crystals (220 mg; yield 28%). So far analytically pure sample has not yet been obtained. However, several spectroscopic data suggest that this sample is spectroscopically pure. ν(CO) (CCl_4 solution): 2089 (s), 2060 (vw), 2025 (m, sh), 2010 (vs), 2000 (s), 1990 (s), and 1949 (m) cm^{-1}. ^{1}H NMR: δ=4.5 (C_5H_5).

Spectral Measurements. ^{17}O NMR spectra were recorded on a Varian XL-200 spectrometer operated at 27.12 MHz for ca 0.5 mol dm^{-3} THF, benzene, and/or chloroform solutions at 30 °C with Fourier transform mode for naturally abundant level (0.037%). The spectra were measured using a 10 mm o.d. sample tube with 0.01 s acquisition time and 90° pulse. Chemical shifts were measured in parts per million with reference to external $H_2{}^{17}O$ standard contained in a 1 mm capillary. IR spectra were recorded on a Jasco 701G spectrometer and proton NMR spectra were obtained with a Hitachi-Perkin-Elmer R-24A spectrometer (60 MHz). Absorption spectra were recorded on a Hitachi 220A double-beam spectrophotometer with a 1.0 mm quartz cell in cyclohexane. All the spectral results are tabulated in Table 1.

^{17}O NMR Spectral Results and Assignment

The manganese and rhenium carbonyl unit, $M(CO)_5$ (M=Mn and Re) has four equatorial and one axial carbonyls. Therefore, two peaks wth relative intensity of 4:1 are observed for compounds **1**—**3** (Fig. 1a). The cobalt carbonyl unit, $Co(CO)_4$, has three equatorial and one axial carbonyls. However, compounds **4**—**6** show unresolved ^{17}O NMR spectra. Molybdenum cyclopentadienyl derivative **7** has two carbonyl groups (Scheme) and therefore two peaks with relative intensity of 2:1 are observed (Fig. 1b). Two carbonyls in iron cyclopentadienyl derivatives **8** and **9** are equivalent and only one resonance is detected in ^{17}O NMR spectra of these derivatives. With all these assignments in mind for homodinuclear metal carbonyl derivatives, **1**—**9**, ^{17}O NMR spectral assignments are easily made for hetero-dinuclear or hetero-trinuclear metal carbonyl derivatives **10**—**13**; Me$_2$Sn[Mn(CO)$_5$][Re(CO)$_5$] (**10**) shows two intense and one weak resonances (Fig. 2a) and the most intense peak is assigned to the equatorial carbonyls in the Mn(CO)$_5$ moiety. The line width of the next intense peak at δ 366.8 is broader than that of the most intense peak at δ 382.1 and the chemical shift is quite close to the resonance of the axial carbonyls in Me$_2$Sn[Mn(CO)$_5$]$_2$ (**1**) at δ 365.9. Therefore, this peak is assigned to the equatorial carbonyls in the Re(CO)$_5$ moiety and the axial carbonyl in the Mn(CO)$_5$ moiety. The weak peak at 351.5 ppm is assigned to the axial carbonyl in the Re(CO)$_5$ moiety. Ph$_2$Sn[Mn(CO)$_5$][Co(CO)$_4$] shows three peaks at δ 383.0, 367.5, and 357.1 in THF (Fig. 2b). The most intense peak at δ 383.0 is assigned to the four equatorial carbonyls and the weakest peak at δ 367.5 is assigned to the axial carbonyl in the Mn(CO)$_5$ moiety. The medium intensity peak at δ 357.1 is assigned to the carbonyls in the Co(CO)$_4$ moiety. Here again the resonance due to the three equatorial carbonyls and the resonance due to the axial carbonyl in the Co(CO)$_4$ moiety are not resolved. Although the most complex

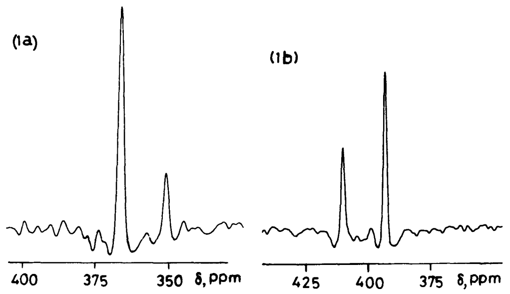


Fig. 1. ^{17}O NMR spectra of: (1a) Me$_2$Sn[Re(CO)$_5$]$_2$ and (1b) Me$_2$Sn[Mo(CO)$_3$Cp]$_2$.

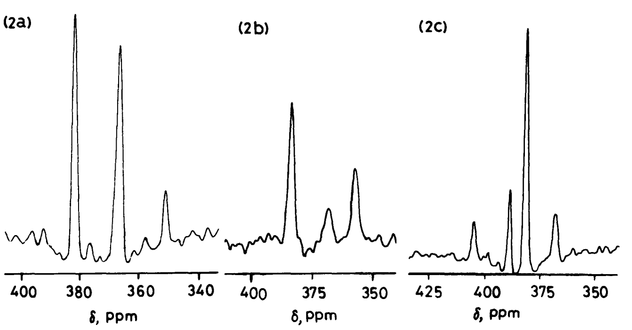
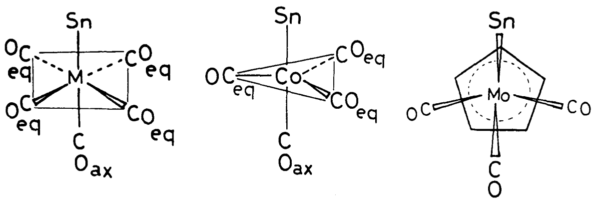


Fig. 2. ^{17}O NMR spectra of: (2a) Me$_2$Sn[Mn(CO)$_5$][Re(CO)$_5$], (2b) Ph$_2$Sn[Mn(CO)$_5$][Co(CO)$_4$], and (2c) Me$_2$Sn[Mn(CO)$_5$][Mo(CO)$_3$Cp].



1—3 4—6 7

Scheme

Table 1. Spectral Data

Compound		^{17}O NMR chemical shift, δ/ppm	λ_{max}/nm (ε/M^{-1} cm^{-1})	ν(CO)/cm^{-1}
Me$_2$Sn[Mn(CO)$_5$]$_2$	(**1**)	381.5(eq), 365.9(ax)[a]	320(17000)	2099, 2074, 2019, 2004,[d] 2002, 1984, 1961
Ph$_2$Sn[Mn(CO)$_5$]$_2$	(**2**)	383.1(eq), 366.7(ax)[a]	328(20400)	2100, 2078, 2029, 2009,[d] 2006, 2002, 1986, 1961
Me$_2$Sn[Re(CO)$_5$]$_2$	(**3**)	365.9(eq), 350.8(ax)[a]	328(15600)	2114, 2092, 2070, 2044,[d] 2010, 2009, 1998, 1987
Me$_2$Sn[Co(CO)$_4$]$_2$	(**4**)	359.7[b]	310(sh)	2095, 2078, 2031, 2024,[e] 2013, 2002, 1992
Ph$_2$Sn[Co(CO)$_4$]$_2$	(**5**)	357.4[a]	320(13300)	2095, 2080, 2033, 2029,[e] 2018, 2009, 1995
Cl$_2$Sn[Co(CO)$_4$]$_2$	(**6**)	362.9[b]	355(2000)	2114, 2097, 2056, 2052,[f] 2040, 2023, 2016
Me$_2$Sn[Mo(CO)$_3$Cp]$_2$	(**7**)	410.3(tr), 393.1(cis)[c]	323(4000)	2004, 1988, 1937, 1925,[g] 1910, 1894
Me$_2$Sn[Fe(CO)$_2$Cp]$_2$	(**8**)	356.3[b]	332(10200)	2002, 1990, 1945, 1936[h]
Cl$_2$Sn[Fe(CO)$_2$Cp]$_2$	(**9**)	367.9[a]	355(2000)	2040, 2025, 1993[h]
Me$_2$Sn<Mn(CO)$_5$ Re(CO)$_5$	(**10**)	382.1(eq), 366.8(ax)[b] 366.8(eq), 351.5(ax)	322(16200)	2117, 2095, 2080,[i,j] 2077, 2010, 1982
Ph$_2$Sn<Mn(CO)$_5$ Co(CO)$_4$	(**11**)	383.0(eq), 367.5(ax)[a] 357.1	325(10200)	2105, 2100, 2080, 2030,[i,k] 2018, 2010, 1985
Me$_2$Sn<Mn(CO)$_5$ Mo(CO)$_3$Cp	(**12**)	381.7(eq), 367.8(ax)[c] 405.6(tr), 388.8(cis)	312(12200)	2092, 2088, 2076, 2020,[i,l] 2002, 1990, 1930, 1903
ClSn<Mn(CO)$_5$ [Fe(CO)$_2$Cp]$_2$	(**13**)	382.1(eq), 367.2(ax)[a] 367.2	340(15300)	2089, 2060, 2025, 2010,[i,m] 2000, 1990, 1949

a) THF solution. b) CHCl$_3$ solution. c) C$_6$H$_6$ solution. d) Ref. 3. e) Ref. 4. f) Ref. 5. g) Ref. 6. h) Ref. 7. i) This work. j) Ligroine solution. k) Nujoll mull. l) Cyclohexane solution. m) CCl$_4$ solution.

spectrum is displayed for $Me_2Sn[Mn(CO)_5][Mo(CO)_3Cp]$ (**12**) (Fig. 2c), spectral assignment is easily made with reference to the assignments of (**1**) and (**7**). The weak peak at δ 405.6 is assigned to the trans CO with respect to Sn and the medium intensity peak at δ 388.8 to the two cis CO with respect to Sn on the $Mo(CO)_3Cp$ moiety. The most intense peak at δ 381.7 is assigned to the equatorial four CO and the weak peak at δ 367.8 to the axial CO in the $Mn(CO)_5$ moiety. $ClSn[Mn(CO)_5][Fe(CO)_2Cp]_2$ (**13**) shows two intense peaks at δ 382.1 and δ 367.2. The peak at δ 382.1 is assigned to the four equatorial carbonyls in the $Mn(CO)_5$ moiety and the peak at δ 367.2 is assigned to the axial CO in the $Mn(CO)_5$ moiety and the four carbonyls in the two $Fe(CO)_2Cp$ units.

Discussion

As for absorption spectra, we have previously suggested that the absorption between 300 and 400 nm is assignable to $\sigma \rightarrow \sigma^*$ transition of the Sn–Mn bonds in $Me_2Sn[Mn(CO)_5]_2$ and $MeSn[Mn(CO)_5]_3$.[2] To supplement this suggestion, absorption spectral measurements are examined for a present series of derivatives, **1**—**13**. All these derivatives exhibit absorptions between 300 and 400 nm and these absorptions are assignable to $\sigma \rightarrow \sigma^*$ transition of the Sn–M bonds in the present series of derivatives.

As is shown in the Table 1, all the derivatives which are employed for the present study show very complex IR spectra in the ν(CO) region. On the other hand ^{17}O NMR spectra for these derivatives are generally simpler than the corresponding ν(CO) spectra and the ^{17}O NMR spectral assignments are easily achieved as is mentioned in the previous section. The investigation for the change of electron distribution around the oxygen atom(s) of interest are easily made in terms of the ^{17}O chemical shift, whereas normal coordinate treatments by use of a computer are necessary in order to make similar investigation in terms of force constants for IR spectroscopy in the ν(CO) region.[12] In this sense, the superiority of ^{17}O NMR spectroscopy to IR spectroscopy is again demonstrated for present more complex systems than those simpler systems which were demonstrated in the previous studies.[1]

Then, ^{17}O NMR spectroscopy is applied to investigate the effect of substitution of one of the $M(CO)_x$ or $M'(CO)_yCp$ unit in the homo-dinuclear $R_2Sn[M(CO)_x]_2$ or $R_2Sn[M'(CO)_yCp]_2$ system with other metal carbonyl unit, $M'(CO)_y$ on the electron distribution around the O atom(s) of interest; that is, ^{17}O-chemical shifts for **10**—**13** are compared with those for **1**—**3**, **5**, **7**, and **9**. The substitution, however, causes only slight changes of the chemical shifts except for $Me_2Sn[Mo(CO)_3Cp]_2$ (**7**); several ppm shifts are observed for the $Mo(CO)_3Cp$ moiety by substitution of one of the $Mo(CO)_3Cp$ unit with a $Mn(CO)_5$ unit. The fact that the substituent is on the third atom from the O atoms of interest explains this range of small shift. Todd et al. reported a larger down-field shift, that is, 14.4 ppm, in the substitution of bromine atoms for triphenylphosphines in $Mn_2(CO)_8(PPh_3)_2$;[13] in this system, the substituent is on the second atom from the O atoms of interest. The effect of the substituents, R, on the ^{17}O-chemical shift is also studied for a series of $R_2Sn[Co(CO)_4]_2$ (R=Me, Ph, and Cl) (**4**—**6**) and $R_2Sn[Fe(CO)_2Cp]_2$ (**8**, **9**) (R=Me and Cl). For a series of Co derivatives, 5.5 ppm lower-field shift is observed by substitution of Ph with Cl and 11.6 ppm lower-field shift is observed by substitution of Me with Cl for a series of Fe derivatives. Here again, the substituent is on the third atom from the O atoms of interest and only slight lower-field shifts are observed. These lines of evidence suggest that ^{17}O-chemical shift of CO groups is sensitive to the metal atom to which the CO groups are coordinated and the effect of the substituent on the ^{17}O-chemical shift, that is, on the electron distribution around the oxygen atom(s), is small, if any, in the case that the substitution is made on the third atom from the O atoms of interest. We are now applying this trait of ^{17}O NMR spectroscopy for higher nuclearity mixed metal carbonyl clusters.

We would like to express our gratitude to professor Kensuke Takahashi of this Institute for his kind help to get ^{17}O NMR spectra.

References

1) Part 1: S. Onaka, T. Sugawara, Y. Kawada, and H. Iwamura, *J. Chem. Soc., Dalton Trans.*, **1982**, 257. Part 2: S. Onaka, T. Sugawara, Y. Kawada, Y. Yokoyama, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **59**, 3079 (1986).

2) S. Onaka, Y. Kondo, N. Furuichi, K. Toriumi, and T. Ito, *Bull. Chem. Soc. Jpn.*, **56**, 87 (1983).

3) J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1365 (1967).

4) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

5) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

6) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

7) F. Bonati and G. Wilkinson, *J. Chem. Soc. A*, **1964**, 179.

8) S. Onaka, T. Miyamoto, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **44**, 1851 (1971).

9) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **7**, 771 (1968).

10) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

11) H. R. H. Patil and W. A. G. Graham, *J. Am. Chem. Soc.*, **87**, 673 (1965).

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

13) R. L. Kump and L. J. Todd, *J. Organomet. Chem.*, **194**, C43, (1980).