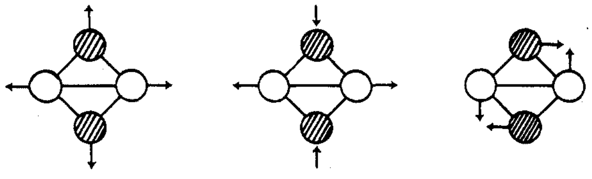
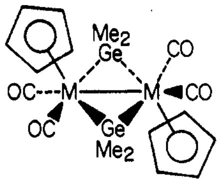
639 (w) (dp). Considering only the metal-metal vibrations, group theory predicts three Raman-active fundamentals, $2\ A_g + B_{1g}$.


1st A_g 2nd A_g B_{1g}

Accordingly, the two clearly polarized bands at 206 and 242 cm^{-1} are assigned to the two A_g modes and the 102-cm^{-1} band is assigned to the B_{1g} mode (overlap with the excitation line prevented accurate measurement of the depolarization ratio of this band). In the carbonyl stretching region, Raman bands were observed at 2076, 1980 (sh), 1970, and 1954 cm^{-1}. The low intensity of these bands precluded meaningful polarization studies; but the spectrum is consistent with the proposed D_{2h} structure which allows four Raman-active carbonyl stretches ($2\ A_g + B_{1g} + B_{3g}$). After submission of this article, the structure of $(Ph_2Si)_2Mn_2(CO)_8$ was reported and conforms to approximate D_{2h} symmetry.[26]

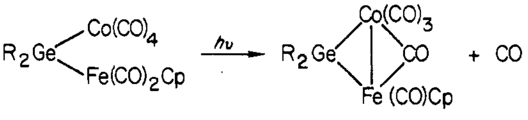
The chromium and molybdenum complexes $CpM(CO)_3$-$Ge(Cl)Me_2$ (**12** and **20**) decompose extensively upon photolysis. However, low yields of the bis(germylene) complexes, **13** and **21**, could be realized from the complex reaction mixtures. The spectral data for these compounds are consistent with trans-bridged structures.[27] It is interesting that the iron complexes **2** and **20** prefer the cis configuration while



13, M = Cr
21, M = Mo

the chromium and molybdenum complexes adopt the trans structure.

The methods described here for preparing germylene complexes would appear to be generally applicable to the other group IV elements, Si, Sn, and Pb.[13] It should also be possible to prepare heterocycles, *e.g.*, **22**, by the photolysis of mixed carbonyl derivatives (eq 12). These aspects of the



(12)

22

photolysis reaction are currently under investigation.

Acknowledgments. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The Raman and mass spectrometers were purchased with the aid of National Science Foundation Grants GP-87419 and GP-8345, respectively.

Registry No. **1**, 41517-29-7; **7**, 41538-92-5; **8**, 12705-84-9; **9**, 39382-82-6; **10**, 41538-93-6; **11**, 36116-50-4; **12**, 41517-28-6; **13**, 39382-83-7; **14**, 41538-95-8; **15**, 41517-08-2; **16**, 41538-96-9; **17**, 41550-24-7; **18**, 41517-30-0; **19**, 41517-31-1; **20**, 41517-32-2; **21**, 39382-84-8; $CpFe(CO)_2Na$, 41517-33-3; $NaMn(CO)_5$, 13859-41-1; $NaMo(CO)_3Cp$, 12107-35-6; $NaCr(CO)_3Cp$, 12203-12-2; dimethyldichlorogermane, 1529-48-2.

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[26] G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, **95**, 783 (1973).

[27] The data do not exclude a rapid (nmr time scale) cis-trans isomerization involving terminal Me_2Ge groups.

Contribution from the Department of Chemistry,
Carleton University, Ottawa, Canada

Studies on the Pentacarbonyltechnetium Radical

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Received February 2, 1973

A species believed to be the $\cdot{}^{99m}Tc(CO)_5$ radical is produced in high yield on the β decay of $^{99}Mo(CO)_6$ in the solid state. This species is found to be scavenged by rapid exchange with $IMn(CO)_5$ to give $ITc(CO)_5$ and is destroyed by nitric oxide. It reacts slowly with photochemically produced $\cdot Mn(CO)_5$ to produce a species probably $TcMn(CO)_{10}$. When still trapped in the $Mo(CO)_6$ lattice, it survives heating to 110°.

Introduction

The radical species $\cdot Mn(CO)_5$ was first detected in neutron-irradiated $Mn_2(CO)_{10}$.[1,2] Recently, this radical has been prepared photochemically and studied more thoroughly by Hallock and Wojcicki.[3] Their simple method of preparation of this radical in solution has enabled us to study further reactions of $\cdot Mn(CO)_5$ and, in particular, to look at reactions of the homologous $\cdot Tc(CO)_5$.

The compounds $Tc_2(CO)_{10}$ and $ITc(CO)_5$ have been prepared[4] and characterized, but we did not have these available to us. As far as we are aware, no mention has been made of intermediate species or radicals of the type $\cdot Tc(CO)_x$.

As is shown in eq 1, the starting point of our experiments is $^{99}Mo(CO)_6$, carefully purified following neutron irradia-

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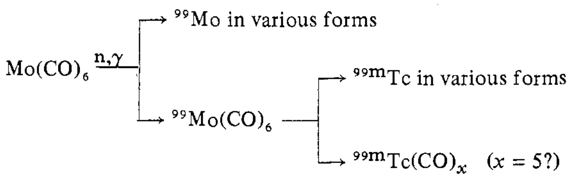
[1] I. G. de Jong and D. R. Wiles, *Chem. Commun.*, 519 (1968).

[2] I. G. de Jong, S. C. Srinivasan, and D. R. Wiles, *Can. J. Chem.*, **47**, 1327 (1969).

[3] A. Wojcicki, personal communication, June 1972; S. A. Hallock and A. Wojcicki, *J. Organometal. Chem.*, in press.

[4] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 2953 (1961).

tion of pure normal $Mo(CO)_6$. It is found[5-8] that some 60-75% of the ^{99}Mo remains as the hexacarbonyl after the nuclear activation; the remainder has not been chemically identified. Bulk decomposition is negligible. ^{99}Mo decays



(1)

by β^- emission (half-life 67 hr), with a transition energy of 1.23 MeV, to give 6.0-hr ^{99m}Tc. The ^{99m}Tc so prepared was expected, on the basis of earlier experiments[9-11] of Baumgartner and others, to yield a large fraction of the technetium atoms still in essentially the same chemical form as the parent molecule. It was our objective both to learn whether this is indeed the case and, if so, to study the properties of the technetium carbonyl species found.

It must be emphasized that these radioactive atoms are produced in the $Mo(CO)_6$ matrix in extremely small concentrations: about 10^5 Tc atoms/mg of $Mo(CO)_6$. This means that no conventional means of study will be applicable. Moreover, it is important to note that reactions involving two Tc atoms are thus not to be expected. Thus, the reaction

$$2(\cdot Tc(CO)_5) \rightarrow Tc_2(CO)_{10} \qquad (2)$$

would not be prominent.

It was found earlier[2,12] that the species $\cdot Mn(CO)_5$ exchanges rapidly with $IMn(CO)_5$[13]

$$^*Mn(CO)_5 + IMn(CO)_5 \rightleftarrows I^*Mn(CO)_5 + \cdot Mn(CO)_5 \qquad (3)$$

Thus, in the presence of macro quantities of $IMn(CO)_5$, the $^*Mn$ will be essentially all as $I^*Mn(CO)_5$, so that $IMn(CO)_5$ can be used as a scavenger and carrier for $\cdot^*Mn(CO)_5$. It was therefore apparent that the analogous reaction

$$\cdot Tc(CO)_5 + IMn(CO)_5 \rightleftarrows ITc(CO)_5 + \cdot Mn(CO)_5 \qquad (4)$$

could possibly be used to detect and study the expected $\cdot Tc(CO)_5$ radical. For similar reasons, the reaction

$$\cdot Tc(CO)_5 + \cdot Mn(CO)_5 \rightarrow TcMn(CO)_{10} \qquad (5)$$

was expected to be a useful process to scavenge $\cdot Tc(CO)_5$.

Experimental Section

Reagents. $Mn_2(CO)_{10}$ and $Mo(CO)_6$ were obtained from various suppliers and were purified before use by silica gel chromatography with petroleum ether. $IMn(CO)_5$ was prepared from $Mn_2(CO)_{10}$ by a modification of the method of Abel and Wilkinson[14] and purified by silica gel chromatography. The $\cdot Mn(CO)_5$ radical was prepared by uv photolysis of $Mn_2(CO)_{10}$ in freshly distilled tetrahydrofuran (THF) according to the procedure reported by Wojcicki,[3] who reported that $\cdot Mn(CO)_5$ in THF solution lasts 1 hr or so before reverting back to $Mn_2(CO)_{10}$. A Rayonet photochemical reactor (3500-Å lamps) was used, with provision made for keeping the samples cooled to room temperature. We did not concern ourselves with the concentration dependence of this reaction and kept all conditions constant: 80 mg of $Mn_2(CO)_{10}$ in 4 ml of THF, under an atmosphere of carbon monoxide, irradiated for 30 min with 16 lamps. This solution was used immediately (<5 min). Neutron irradiations were done in the "Slowpoke" reactor of Atomic Energy of Canada, Ltd., Ottawa. Freshly purified $Mo(CO)_6$ was irradiated for 3 min with a neutron flux of 2.5×10^{11} n cm^{-2} sec^{-1} to produce ^{99}Mo. Of this, some 60-75% is known to be recoverable as the original parent compound, after correction for chemical and mechanical losses, while the rest is in various as yet unknown forms which are removed by the column chromatography. It was also found that a considerable amount of tungsten radioactivity was produced, regardless of the source of supply of the $Mo(CO)_6$. This did not interfere with our experiments, however.

Experiments. The experiments basically all involved the following steps: (1) preparation and purification of $^*Mo(CO)_6$; (2) growth of ^{99m}Tc by decay of ^{99}Mo (for 1-4 days) while the sample of crystalline $^*Mo(CO)_6$ was kept in the dark; (3) thermal treatment of the $^*Mo(CO)_6$, if desired; (4) dissolution of the $^*Mo(CO)_6$ either (a) in a solution of $IMn(CO)_5$ to scavenge the $\cdot Tc(CO)_5$ by reaction 4, (b) in petroleum ether or THF, to which $IMn(CO)_5$ is added after a certain delay time, or (c) in a solution of $\cdot Mn(CO)_5$ to scavenge $\cdot Tc(CO)_5$ by reaction 5 followed, after a delay time, by addition of $IMn(CO)_5$ to complete the scavenging; (5) separation and purification of $I(Mn,Tc)(CO)_5$ and the $(Mn,Tc)_2(CO)_{10}$ and measurement of their radioactivity. Steps 4 and 5 were carried out using solvents thoroughly purged with nitrogen. Air was carefully excluded and subdued (incandescent) light was used to avoid photolysis.

Radioactivity measurements were made using a 3-in. × 3-in. NaI scintillation crystal with a multichannel pulse height analyzer to measure the 142-keV γ ray from the transition $^{99m}Tc \rightarrow {}^{99}Tc$. The only likely interference with this measurement is the 130-keV γ ray from ^{99}Mo. The separation procedure was found to remove molybdenum completely, and occasional half-life measurements never revealed any contamination of the ^{99m}Tc (6.0 hr) with ^{99}Mo (67 hr). The measured counting rates were corrected for radioactive decay and for chemical recovery of the carrier and were compared with the radioactivity of a reference sample of $^*Mo(CO)_6$ to obtain the radiochemical yield.

Chemical Separations. Column chromatography on silica gel was used as the separation method for the several components. $Mo(CO)_6$ samples were dissolved in petroleum ether or THF. Since the THF (required by Wojcicki's procedure) was found to interfere with the subsequent separation, it was removed under suction and the crystals were taken up in petroleum ether. After the dissolved samples were put on a silica gel column, the initial development was with pure petroleum ether (bp 35-45°) which removed the $Mo(CO)_6$. A second fraction was removed with 3% $CHCl_3$ in petroleum ether and contained the $(Mn,Tc)_2(CO)_{10}$. Radioactivity measurements showed that the two compounds $Mn_2(CO)_{10}$ and $TcMn(CO)_{10}$ come closely together. The chloroform concentration was gradually increased and the $I(Tc,Mn)(CO)_5$ was finally removed with pure $CHCl_3$. The technetium pentacarbonyl iodide was found to lag behind the corresponding manganese compound, and hence a considerable amount of eluate was collected after the color of $IMn(CO)_5$ had left the column. Chemical recoveries of $Mn_2(CO)_{10}$ and $IMn(CO)_5$ were, of course, directly measurable gravimetrically and were consistently about 70%. The losses were felt to be largely mechanical, and thus the measured recoveries of $Mn_2(CO)_{10}$ and $IMn(CO)_5$ were used to represent the radiochemical recoveries of $TcMn(CO)_{10}$ and $ITc(CO)_5$, respectively. There is no evidence to support this assumption other than reasonable consistency of the data.

Results and Discussion

Measurements done in which the $Mo(CO)_6$ was dissolved directly in an $IMn(CO)_5$ scavenging solution showed immediately the occurrence of a technetium species which was eluted along with (actually slightly after) the $IMn(CO)_5$.

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(5) G. Harbottle and U. Zahn, *Radiochim. Acta*, **8**, 114 (1967).

(6) E. Henrich and G. K. Wolf in "The Uses of Cyclotrons in Chemistry, Metallurgy and Biology," Butterworths, London, 1970, p 51.

(7) U. Zahn, C. H. Collins, and K. E. Collins, *Radiochim. Acta*, 11, 33 (1969).

(8) H. R. Groening and G. Harbottle, *Radiochim. Acta*, 14, 109 (1970).

(9) F. Baumgartner, E. O. Fischer, and U. Zahn, *Chem. Ber.*, 94, 2198 (1961).

(10) F. Baumgartner, E. O. Fischer, and U. Zahn, *Naturwissenschaften*, 48, 478 (1961).

(11) F. Baumgartner, E. O. Fischer, and U. Zahn, *Naturwissenschaften*, 49, 156 (1962).

(12) I. G. de Jong, S. C. Srinivasan, and D. R. Wiles, *J. Organometal. Chem.*, 26, 119 (1971).

(13) An asterisk will be used in this paper to denote that the following atom is radioactive, without implying chemical excitation. This is omitted for Tc, whose atoms here are all the radioactive ^{99m}Tc.

(14) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

This same species was produced when elemental iodine was used as scavenger and the carrier was added later.

Two experiments were done under an atmosphere of nitric oxide and showed very low yields, as is shown in Table I. The close parallel of this behavior to that of the radical $\cdot{}^*Mn(CO)_5$[2,12] convinces us that we are indeed dealing with the radical $\cdot Tc(CO)_5$. The strong scavenging action of nitric oxide, producing some species which does not reemerge in our chromatography, offers support to the conclusion that this species is a radical. This $\cdot Tc(CO)_5$ radical seems to be somewhat more stable (in THF) than is the $\cdot Mn(CO)_5$ (in petroleum ether), although the data are not strictly comparable, and a delay in the addition of the $IMn(CO)_5$ scavenger of up to 30 min reduced the $ITc(CO)_5$ yield by only one-third. As is seen in Table I, atmospheric oxygen gives a small but noticeable scavenging action, even in the short times of these experiments.

It was of interest to study the stability of the $\cdot Tc(CO)_5$ radical in the solid matrix, to see whether it more resembled that of $\cdot Mn(CO)_5$ in $Mn_2(CO)_{10}$ or that of $\cdot Mo(CO)_5$ in $Mo(CO)_6$. The $\cdot Mn(CO)_5$ radical has been found[2,12] to be stable at room temperatures for some hours when held in a $Mn_2(CO)_{10}$ matrix. Since, in our experiments, the average age of the technetium atoms is 8.7 hr (the maximum attainable) the high yields which we observe testify to the stability of the $\cdot Tc(CO)_5$ radical when trapped in $Mo(CO)_6$ at room temperature.

On being heated to higher temperatures, $\cdot Mn(CO)_5$ was found[2,12] to decompose abruptly (at 65°) without producing $Mn_2(CO)_{10}$ (hence presumably giving dissociation of the metal-carbonyl bond). This thermal behavior is not typical of most such radical species, which usually[15] add more carbonyls to any as yet incomplete species and thus increase the radiochemical yield of the final species. Similarly, warming of chemically or photochemically produced trapped $M(CO)_x$ radicals (M = Ni, Pd, or Ta) in various carbonyl-rich matrices has been shown[16-18] to cause formation of $M(CO)_{x+1}$

$$M(CO)_x + CO \rightarrow M(CO)_{x+1} \qquad (6)$$

We have therefore studied the thermal properties of the $\cdot Tc(CO)_5$ radical trapped in $Mo(CO)_6$ and have obtained the results given in Table II. These results show clearly that the $\cdot Tc(CO)_5$ radical is stable under these conditions for times up to 20 min and at temperatures up to 110°. $Mo(CO)_6$ is a compound which appears to have labile ligands in solution[19] and, to judge from radiochemical studies,[7,8] to have reactive CO molecules available in the solid as well. It appears, therefore, that the governing factor in eq 6 may be the availability of CO in the host matrix, rather than the reactivity of the metal atom.

Studies were done of the scavenging of $\cdot Tc(CO)_5$ by $\cdot Mn(CO)_5$ over various periods of time prior to the addition of the $IMn(CO)_5$. Aged pure $^*Mo(CO)_6$ was dissolved in THF under nitrogen and this solution was added to a solution of uv-irradiated $Mn_2(CO)_{10}$. After a delay time, Δt, $IMn(CO)_5$ was added to complete the scavenging. $IMn(CO)_5$ and $Mn_2(CO)_{10}$ were subsequently separated on a silica gel column, as was described above, and their radioactivities were compared. The results are shown in Figure 1 as a function of Δt. From these results it is clear that whatever reactions occur are completed within the first 15 min. It is evident from the rise in activity of the $TcMn(CO)_{10}$ fraction that the scavenging is effective and that reaction 5 does occur, albeit to a small extent. It is also clear that the increase in the $TcMn(CO)_{10}$ yield is very much smaller than the decrease in the $ITc(CO)_5$ yield. Thus, reactions 4 and 5 do not account for all of the $\cdot Tc(CO)_5$ and the decrease in $ITc(CO)_5$ yield must be due to the action of trace impurities in the solution—residual oxygen and others. It is noteworthy that the $ITc(CO)_5$ yield reaches a value below which it seems not to decrease further. This suggests that some other species is being formed, which exchanges rapidly with $IMn(CO)_5$ but which is not scavengeable as a radical. An obvious possibility is $HTc(CO)_5$ which, by analogy with $HMn(CO)_5$, must exchange rapidly with $IMn(CO)_5$[20] and should be moderately stable. Thus, the reactions

$$\cdot Tc(CO)_5 + THF \rightarrow HTc(CO)_5 + \ldots \qquad (7)$$

$$HTc(CO)_5 + IMn(CO)_5 \rightleftarrows ITc(CO)_5 + HMn(CO)_5 \qquad (8)$$

would account for the observations, if one were to find evidence for the occurrence of reaction 7. Evidence accumulated in this laboratory and elsewhere[3] shows that $\cdot Mn(CO)_5$ does not abstract hydrogen atoms very effectively. Unfortunately, we have not been able to carry this study fur-

Table I. Yields of $ITc(CO)_5$ from $Mo(CO)_6$ in Various Experiments

Atmosphere	Yield, %	Atmosphere	Yield, %
Nitrogen	73.5	Nitric oxide	0.44[a]
Air	69.0	Nitric oxide	0.09[b]

[a] Sample dissolved in $IMn(CO)_5$ solution. [b] Sample dissolved in petroleum ether; $IMn(CO)_5$ added 5 min later.

Table II. Yields of $ITc(CO)_5$ Following the Annealing of $Mo(CO)_6$[a]

Temp, °C	Yield, %	Temp, °C	Yield, %	Temp, °C	Yield, %
None	73.5	60	70.7	90	60.0
40	72.0	70	61.6	100	68.2
50	69.0	80	69.1	110	65.8

[a] Annealing was done for 20 min, immediately prior to dissolution in $IMn(CO)_5$ solution.

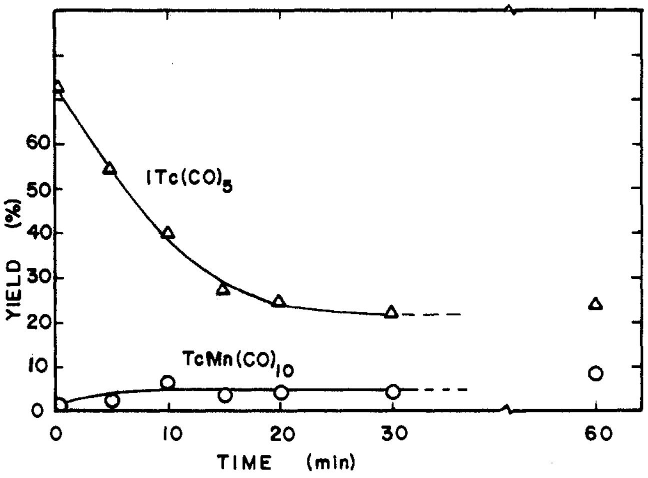

Figure 1. Radiochemical yields of $ITc(CO)_5$ and $TcMn(CO)_{10}$ as functions of the delay time, Δt, before addition of the scavenger $IMn(CO)_5$.

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(15) D. R. Wiles, *Advan. Organometal. Chem.*, 11, 207 (1973).

(16) A. J. Rest and J. J. Turner, *Chem. Commun.*, 1026 (1969).

(17) R. L. DeKock, *Inorg. Chem.*, 10, 1205 (1971).

(18) P. E. Kundig, M. Moskovits, and G. A. Ozin, *Can. J. Chem.*, 50, 3587 (1972).

(19) R. J. Angelici and J. R. Graham, *J. Amer. Chem. Soc.*, 88, 3658 (1966).

(20) H. Jakubinek, S. C. Srinivasan, and D. R. Wiles, *Can. J. Chem.*, 49, 2175 (1971).

ther, since our methods do not distinguish between $H(Tc,Mn)(CO)_5$ and $\cdot(Tc,Mn)(CO)_5$.

Summary

It has been shown that the $\cdot Tc(CO)_5$ radical is formed by the β decay of $Mo(CO)_6$ and that this radical displays several of the properties which would be expected of it. Its stability in the solid $Mo(CO)_6$ matrix is greater than that of the analogous $\cdot Mn(CO)_5$ in $Mn_2(CO)_{10}$. It seems to be rapidly destroyed by NO gas present during the early stages of the chemical workup and to be somewhat sensitive to atmospheric oxygen. The $\cdot Tc(CO)_5$ radical reacts slowly with $\cdot Mn(CO)_5$ to produce a species which is likely $TcMn(CO)_{10}$ and reacts rapidly with $IMn(CO)_5$ to produce $ITc(CO)_5$. The results suggest that some species such as $HTc(CO)_5$ may also be involved.

Acknowledgments. The impetus for parts of this work arose from a discussion with Professor A. Wojcicki, during which he very kindly gave us experimental information on his recently discovered photochemical preparation of $\cdot Mn(CO)_5$. The financial support of the National Research Council of Canada is gratefully acknowledged.

Registry No. $\cdot Tc(CO)_5$, 41375-71-7; $Mo(CO)_6$, 14040-11-0; $\cdot Mn(CO)_5$, 15651-51-1; $TcMn(CO)_{10}$, 41375-72-8; $IMn(CO)_5$, 14879-42-6; $ITc(CO)_5$, 41375-73-9; $Mn_2(CO)_{10}$, 10170-69-1.

Contribution from the Departments of Chemistry, Northwestern University, Evanston, Illinois 60201, and State University of New York at Albany, Albany, New York 12222

Tin-119m Mossbauer and X-Ray Photoelectron (ESCA) Studies of Tin Oxidation State and Bonding in Base-Dialkyltin Pentacarbonylchromium and Tetracarbonyliron Complexes

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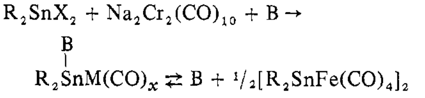
Received February 6, 1973

^{119m}Sn Mossbauer, $^{119}Sn-^1H$ three-bond nmr coupling constants, and Sn $3d_{5/2}$ ESCA electron binding energy data for the compounds $(t\text{-}C_4H_9)_2SnM(CO)_x\cdot B$, where for M = Fe, $x = 4$ and B = DMSO and pyridine and for M = Cr, $x = 5$ and B = THF, DMSO, and pyridine, favor a tin(IV) formulation. The Mossbauer QS values for M = Cr compounds (3.4–4.1 mm/sec) are the largest thus far recorded for four-coordinated organotin compounds. Explanations based upon ylide structures are proposed.

Introduction

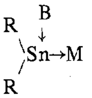
Recent attempts at synthesizing the analogs of metal carbonyl "carbene" complexes[2] from dialkyltin dihalides and $Na_2Cr_2(CO)_{10}$[3] have resulted in products shown to have structure I, which are also obtained from homolytic cleavage of the tin-iron bonds in the cyclic $[R_2SnFe(CO)_4]_2$ dimer by base[4,5] (eq 1). X-Ray crystal structure determination of $(t\text{-}C_4H_9)_2SnCr(CO)_5\cdot C_5H_5N$ shows the base molecule bonded to the tin atom in good accord with this formulation.[6] Compounds I bear an obvious conceptual relationship to the desired, three-coordinated "stannylene" complexes by simple removal of the neutral base molecule, but experimentally such a process in the iron case results in reconversion to the dimer,[5] and in the chromium case the syntheses of I do not proceed in noncoordinating solvents, nor has it been possible to remove the base from any of the known examples without decomposition.[3,4,6a] A number of electronic configurations can be drawn to represent the bonding of I, *i.e.*



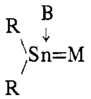
$$R_2SnX_2 + Na_2Cr_2(CO)_{10} + B \rightarrow \overset{B}{\overset{|}{R_2SnM(CO)_x}} \rightleftarrows B + {}^1/_2[R_2SnFe(CO)_4]_2 \qquad (1)$$

I

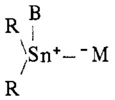
M = Cr, $x = 5$
M = Fe, $x = 4$
B = THF, DMSO, py



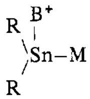
Ia



Ib



Ic



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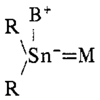

Ie

where M is a transition metal carbonyl. Structure Ia represents both base and "stannylene" molecules acting as Lewis bases (σ donors); structure Ib includes back-donation from the filled d orbitals of the transition metal. In Ia and Ib the tin atom is in a subvalent, tin(II) oxidation state. Structure Ic represents tin as making four formal covalent bonds in an ylide form; in structure Id the positive charge is delocalized onto the base molecule, and in structure Ie back-donation from the filled d orbitals of the transition metal is shown. In structures Ic–Ie the tin atom is viewed as in a formal oxidation state of 4. The relatively small magnitudes of $J(^{117,119}Sn\text{-}C\text{-}^1H)$ for compounds I where R = CH_3 [for M = Cr and

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(1) (a) Northwestern University. (b) State University of New York at Albany.

(2) (a) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 16, 487 (1972); (b) E. O. Fischer, *Pure Appl. Chem.*, 30, 353 (1972); (c) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 545 (1972).

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(6a) Note Added in Proof. By the use of bulky R groups and a different synthetic route, it recently has been reported possible to prepare $R_2SnCr(CO)_5$ compounds: P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 317 (1973).