for this mechanism (assuming that the reactions go to completion) will be given by $k_{\text{obsd}} = k_1 + k_2$. However, when the decomposition of *trans*-Mn(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$Br was studied in the presence of C^{18}O, the substrate ir band at 1951 cm^{-1} was observed to disappear qualitatively at a much faster rate than normal and a band due to a C^{18}O-substituted species rapidly appeared at approximately 1930 cm^{-1}. These observations suggest that the rate of CO substitution is significantly faster than the rate of decomposition and therefore we favor our proposed mechanism over that indicated by the referee.

$$trans\text{-Mn(CO)}_3[\text{P(C}_6\text{H}_5)_3]_2\text{X} \xrightarrow{k_1} \text{Mn(CO)}_3[\text{P(C}_6\text{H}_5)_3]\text{X} + \text{P(C}_6\text{H}_5)_3 \tag{5}$$

$$trans\text{-Mn(CO)}_3[\text{P(C}_6\text{H}_5)_3]_2\text{X} \xrightarrow{k_2} \text{Mn(CO)}_2[\text{P(C}_6\text{H}_5)_3]_2\text{X(?)} + \text{CO} \tag{6}$$

$$\text{Mn(CO)}_3[\text{P(C}_6\text{H}_5)_3]\text{X} + \text{CO} \xrightarrow{\text{fast}} cis\text{-Mn(CO)}_4[\text{P(C}_6\text{H}_5)_3]\text{X} \tag{7}$$

In sharp contrast to the rates of the CO substitution reactions of Mn(CO)$_5$X[9,10] and *cis*-Mn(CO)$_4$LX[11] [L = P(C$_6$H$_5$)$_3$, Sb(C$_6$H$_5$)$_3$, etc.] which decrease dramatically with changes in X in the order Cl > Br > I, the rates of the decomposition reactions of *trans*-Mn(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$X were little affected by changes in X. The decrease in the CO substitution rates with the increasing atomic weight of X has been explained in terms of the electronegativities of the X atoms—the lower the electronegativity of the X atom, the greater the electron density on the manganese atom available for back-bonding to the carbonyl groups, and consequently the stronger the Mn–C bonds. If the Mn–P bond strengths in the *trans*-Mn(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$X compounds are significantly dependent on π bonding, it would be reasonable to expect the observed decomposition rates to show some dependence on X. However, as this was not found to be the case, it appears that the Mn–P bond strengths in the tricarbonyl halides stem mainly from σ- rather than π-bonding effects. Other workers have reached the same conclusion concerning the Mo–P,[12] W–P,[13,14] and Ni–P[15] bond strengths in molybdenum, tungsten, and nickel carbonyl complexes.

The thermal decomposition of *trans*-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br was also studied. However, contrary to what would be predicted from the lower basicity and resultant poorer σ-bonding ability of P(OC$_6$H$_5$)$_3$ by comparison with P(C$_6$H$_5$)$_3$,[13] the reaction proceeded extremely slowly ($t_{1/2} >> 24$ hr). P(OC$_6$H$_5$)$_3$ has also been found to be anomalous in its behavior in the substitution reactions of *trans*-Mo(CO)$_4$L$_2$ [L = P(OC$_6$H$_5$)$_3$ and P(C$_6$H$_5$)$_3$].[12]

In an effort to extend the study, the synthesis of *trans*-Mn(CO)$_3$[Sb(C$_6$H$_5$)$_3$]$_2$Br was attempted. However, only the *cis* complex could be isolated, contrary to what had been previously predicted.[4] Dobson and Houk have recently found[16] that substituted molybdenum carbonyls tend to form *cis* complexes with Sb(C$_6$H$_5$)$_3$ and *trans* complexes with P(C$_6$H$_5$)$_3$ and As(C$_6$H$_5$)$_3$ and attributed the difference to the larger size of the Sb atom. Heating a solution of *cis*-Mn(CO)$_3$[Sb(C$_6$H$_5$)$_3$]$_2$Br did afford *cis*-Mn(CO)$_4$[Sb(C$_6$H$_5$)$_3$]Br but the decomposition appears to be much more complex than the decomposition of the *trans*-Mn(CO)$_3$[P(C$_6$H$_5$)$_3$]$_2$X compounds, as a simple rate plot was not obtained.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
AND THE RADIATION LABORATORY,[1]
UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA 46556

Mössbauer and Infrared Spectra of Tin(IV) Complexes of 2-Pyridinethiol 1-Oxide

BY DEMETRIOS PETRIDIS, F. PATRICIA MULLINS,
AND COLUMBA CURRAN

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The anion of 2-pyridinethiol 1-oxide is an excellent complexing agent for a variety of metal ions. O→M dative bond formation in these complexes is indicated by a decrease in frequency of the absorption attributed to the N–O stretching vibration in the 1200-cm^{-1} region and by absorptions associated with the oxygen–metal stretching vibrations. Mössbauer spectra of tin(IV) complexes containing this ligand give an indication of their configuration and electron distribution.

Experimental Section

Preparation of Compounds.—Tin(IV) fluoride, bromide, and iodide and di-*n*-butyltin dichloride and diphenyltin dichloride were obtained from Alfa Inorganics, Inc. Anhydrous tin(IV) chloride was a J. T. Baker Co. product. The sodium salt of 2-pyridinethiol 1-oxide was obtained from Matheson Coleman and Bell.

Bis(2-pyridinethiolato 1-oxide)di-*n*-butyltin(IV) was prepared by mixing absolute ethanol solutions of the sodium salts of 2-pyridinethiol 1-oxide and di-*n*-butyltin dichloride in a 2:1 ratio. The product was crystallized from benzene and melted at 94–96°. The corresponding diphenyl compound was prepared from methanol solutions; the product melted above 210°. Isothiocyanato(2-pyridinethiolato 1-oxide)diphenyltin(IV) was prepared by refluxing a chloroform solution, 50 ml, containing 2 mmol each of diphenyltin diisothiocyanate[2] and 2-pyridinethiol 1-oxide. The solution was filtered and the filtrate was added with stirring to 200 ml of hexane. The white precipitate that formed was dried under vacuum at 56°. The dihalobis(2-pyridinethiolato 1-oxide)tin(IV) complexes were prepared by mixing methanol solutions of the tin(IV) halide and the sodium salt of 2-pyridinethiol 1-oxide, 0.025 and 0.05 *M*, respectively.

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[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-692.

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Table I

Infrared and Mössbauer Data

Compound[a]	% calcd C	% calcd H	% found C	% found H	ν_{N-O}, cm^{-1}	ν_{Sn-O}, cm^{-1}	Isomer shift (mm/sec)	Quadrupole splitting (80°K) (mm/sec)	% absn
$(C_4H_9)_2Sn(2\text{-}SpyO)_2$	44.56	5.39	44.60	5.46	1205, 1195	340	1.45	3.20	15
$(C_6H_5)_2Sn(2\text{-}SpyO)_2$	50.30	3.45	50.39	3.48	1195	356	0.91	1.45	10
$SnF_2(2\text{-}SpyO)_2$	29.37	1.97	29.68	2.32	1190	410, 387	0.32	0.74	5.3
$SnCl_2(2\text{-}SpyO)_2$	27.17	1.82	27.40	2.09	1186	402, 382	0.59	0.86	6.4
$SnBr_2(2\text{-}SpyO)_2$	22.62	1.52	22.53	1.64	1186	397, 373	0.69	0.82	5.5
$SnI_2(2\text{-}SpyO)_2$	19.22	1.29	20.14	1.74	1186	387, 371	0.90	0.6[b]	7.0
$Sn(2\text{-}SpyO)_4$	38.54	2.58	38.26	2.68	1200	355	0.80	...	27
$(C_6H_5)_2Sn(NCS)(2\text{-}SpyO)$	47.29	3.08	46.82	3.10	1205	390	1.12	2.60[b]	2.8

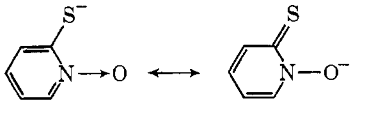
[a] 2-SpyO = C_5H_4NOS. [b] Obtained with palladium–tin source.

2-Pyridinethiol 1-oxide was substituted for the sodium salt in the reaction with SnF_4. The complexes precipitated after stirring for about 30 min. The products were washed with methanol and dried under vacuum at 56° for 12 hr. The difluoro compound melted at 282–283°, the dichloro at 297–298.5°, the dibromo at 293–294°, and the diiodo at 281–282°. Tetrakis(2-pyridinethiolato 1-oxide)tin(IV) was prepared by mixing absolute methanol solutions of tin(IV) chloride and the sodium salt of 2-pyridinethiol 1-oxide, 0.04 and 0.18 *M*, respectively. The yellow precipitate that formed was treated as above, mp 242–243°.

Infrared and Mössbauer Spectra.—The former were obtained with Perkin-Elmer spectrometers, Models 421 and 521, in potassium bromide disks. Mössbauer parameters at 80°K were obtained as described previously.[2,3] The spectra of all compounds were obtained with a palladium–tin source (12% tin by weight) at 80°K and for all but the isothiocyanate with a barium stannate source at room temperature. The isomer shifts for stannic oxide were −1.52 mm/sec relative to Pd–Sn and −0.025 mm/sec relative to $BaSnO_3$. The isomer shifts relative to $BaSnO_3$ are listed in Table I; they are considered to be accurate to ±0.05 mm/sec with a relative precision of ±0.03 mm/sec. The quadrupole splitting for the diiodide with this source was not resolved. The spectrum of $SnCl_2(2\text{-}SpyO)_2$ is illustrated in Figure 1. Dielectric constants of benzene solutions of $(C_4H_9)_2Sn(2\text{-}SpyO)_2$ were obtained as before.[3] The average value of $\Delta\epsilon/wf_2$ for five solutions is 5.6 and the dipole moment calculated at 25° by the Higasi method is 5.0 ± 0.1 D.

Discussion

Pertinent infrared frequencies and Mössbauer parameters are listed in Table I. The anion of 2-pyridinethiol 1-oxide is not a good reference for ligand frequencies in metal complexes, as it is a resonance hybrid



The frequencies of the absorptions assigned to the N–O stretching vibrations in Table I are best compared to the value 1248 cm^{-1} reported for 2-benzylthiopyridine 1-oxide.[4] In line with the interpretation of many investigators of complexes of pyridine 1-oxide, the frequencies listed in Table I, significantly lower than 1248 cm^{-1}, are indicative of O→Sn dative bonding. Infrared spectra of several pyridine 1-oxide complexes of tin(IV) have been obtained by Kawasaki and coworkers.[5] They assigned absorptions in the 300–400-cm^{-1} region to the O–Sn stretching vibration. If the oxygen atoms have a *cis* arrangement about the tin atom in a bis complex, two peaks in this region are anticipated, associated with the antisymmetric and symmetric stretching vibrations. The broad peaks in the spectra of $(C_4H_9)_2Sn(2\text{-}SpyO)_2$ and $(C_6H_5)_2Sn(2\text{-}SpyO)_2$ may be envelopes of two unresolved peaks. The higher frequencies of the Sn–O peaks in the dihalides than in the dibutyl and diphenyl complexes suggest stronger oxygen–tin bonds in the dihalides; this order of bond strength is also indicated by the values of the N–O stretching frequencies.

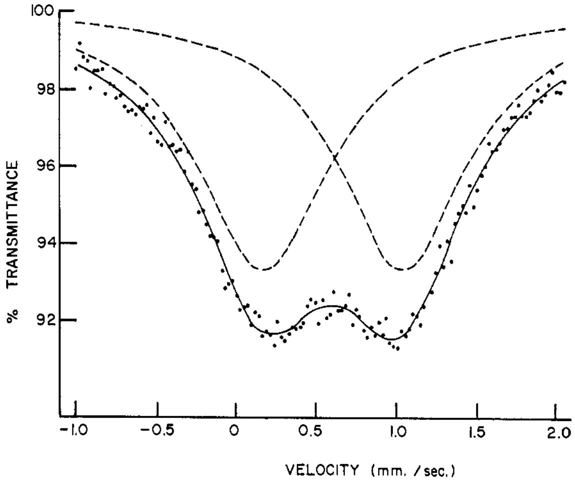
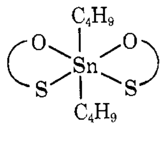


Figure 1.—Mössbauer spectrum of $SnCl_2(2\text{-}SpyO)_2$.

The relative values of the quadrupole splittings obtained for the dibutyl- and diphenyltin complexes, 3.20 and 1.45 mm/sec, respectively, indicate a *trans* arrangement of the butyl and a *cis* arrangement of the phenyl groups.[2] The dipole moment, 5.0 D, of $(C_4H_9)_2Sn(2\text{-}SpyO)_2$ in benzene is indicative of a *cis* arrangement of the oxygen and sulfur atoms



The solubilities of the other complexes in benzene were too low for dipole moment determinations.

The negative isomer shifts of the $SnX_2(2\text{-}SpyO)_2$ complexes vary regularly with the electronegativities of the halogens. The isomer shift for the dichloride,

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[3] M. A. Mullins and C. Curran, *Inorg. Chem.*, **6**, 2017 (1967).

[4] A. R. Katritzky and A. R. Hands, *J. Chem. Soc.*, 2195 (1958).

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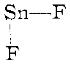
0.59 mm/sec, compares with the value 0.22 mm/sec observed in this laboratory for the corresponding acetylacetonate complex; this indicates a greater electron release by the sulfur than by the oxygen atom to tin. Two infrared absorptions by $SnF_2(2\text{-SpyO})_2$ attributed to the Sn–F stretching vibrations occur at 550 and 535 cm^{-1}, indicating *cis*



$$\begin{array}{l}\text{Sn—F}\\ \,\,\vert\\ \,\text{F}\end{array}$$

bonds. A strong absorption at 293 cm^{-1} by the dichloride is attributed to a Sn–Cl stretching vibration; absorption by the organic ligand below 280 cm^{-1} may obscure any other Sn–Cl absorption.

Absorption by $(C_6H_5)_2Sn(NCS)(2\text{-SpyO})$ at 2040 cm^{-1}, compared to 2100 cm^{-1} for polymeric $(C_6H_5)_2Sn(NCS)_2$ and 2040–2020 cm^{-1} for monomeric octahedral isothiocyanates,[3] suggests that NCS bridging does not occur in the solid and that tin is five-coordinate in this compound. The large quadrupole splitting, 2.60 mm/sec, compares with 2.48 mm/sec for the corresponding oxinate,[3] for which dipole moment data indicate a configuration in which the CSnC bond angle is close to 90°.

The quadrupole splitting obtained for $Sn(2\text{-SpyO})_4$ with a palladium–tin source, 0.5 mm/sec, and the large half-width of the spectrum obtained with a barium stannate source, 1.92 mm/sec, indicate quadrupole interaction and suggest that there is not simply a tetrahedral arrangement of sulfur atoms about the tin. Strong absorption at 355 cm^{-1} in the infrared spectrum indicates the presence of oxygen–tin bonds, and the single absorption in the 1200-cm^{-1} region, at 1205 cm^{-1}, is evidence that all four oxygen atoms are bonded to tin. The spectrum resembles those of the other 2-pyridinethiol 1-oxide complexes more closely than the spectra of N-substituted pyridine thiones,[6] suggesting that dangling C=S groups are not present and that tin has a coordination number of 8 in $Sn(2\text{-SpyO})_4$. Eight-coordination is indicated for tin in bis(phthalocyanino)tin(IV), and in $Sn(ox)_4$,[7] but it has not been suggested previously for complexes containing tin–sulfur bonds.

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[7] K. Ramaiah and D. F. Martin, *Chem. Commun.*, 130 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WASHINGTON UNIVERSITY, SAINT LOUIS, MISSOURI 63130

Preparation of Trisilane by the Schlesinger Method[1]

BY PETER P. GASPAR, CARL A. LEVY, AND GERALD M. ADAIR

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Reduction of silicon tetrachloride, $SiCl_4$, and hexachlorodisilane, Si_2Cl_6, with lithium aluminum hydride in ether has been the most widely used laboratory method for the preparation of small quantities of silane, SiH_4, and disilane, Si_2H_6, ever since its introduction by Schlesinger and coworkers in 1947.[2] Yields of disilane as high as 87% have been reported[2] despite warnings that considerable cleavage of silicon–silicon bonds can occur in the reduction of hexachlorodisilane.[3] The need for a small sample of trisilane, combined with a healthy respect for the dangers involved in the fractionation of a large quantity of mixed silanes,[4] prompted the successful attempt at the reduction of octachlorotrisilane, Si_3Cl_8, with lithium aluminum hydride. Thus an extension of the Schlesinger method to the preparation of higher silanes, long thought possible,[5] has been realized.

Octachlorotrisilane was obtained by fractional distillation of a mixture of chlorosilanes prepared by passage of a slow stream of gaseous chlorine through a heated tube containing calcium silicide, $CaSi_2$.[6]

Reduction of octachlorotrisilane to trisilane was carried out by addition of solid lithium aluminum hydride *in vacuo* to a solution of octachlorotrisilane in di-*n*-butyl ether. The reducing agent was added in small portions, and after a few minutes stirring the trisilane together with some solvent was removed from the reaction mixture by expansion into the vacuum manifold. The rapid removal of the product from contact with reducing agent seems responsible for the high yields (60 ± 10%) obtained.

The preparation of higher silanes by this method is entirely feasible and is under active investigation.

Experimental Section

Octachlorotrisilane.—The method of Schumb and Gamble was used.[6] Calcium silicide was used in the form of 10–20-mm irregular pieces. If the pieces are too small or if powdered material is included, much lower yields are obtained because the liquid chlorosilanes retained by absorption on the solids suffer pyrolysis to elementary silicon, unreactive at the temperature employed.

Trisilane.—In a dry, 100-ml, three-necked, round-bottom flask were placed 65 ml of di-*n*-butyl ether (freshly distilled from sodium), 7.55 g (20.5 mmol) of octachlorotrisilane, and a small Teflon-coated magnetic stirring bar. This reaction flask was attached *via* a ground joint and vacuum stopcock to a vacuum manifold capable of attaining low pressures of 10^{-4} Torr. On one neck of the reaction flask was mounted a bent addition tube containing 2.00 g (52.6 mmol) of lithium aluminum hydride.

The liquid phase was frozen with a liquid nitrogen bath, and then the flask was opened to the vacuum manifold and evacuated to less than 1 Torr. With the manifold isolated from the pump, the mixture of octachlorotrisilane in butyl ether was allowed to melt. The freeze–evacuate–thaw cycle was repeated twice in order to thoroughly degas the ether solution. After the last melting, the flask was surrounded by a water–ice bath and rapid magnetic stirring of the liquid phase was begun.

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[1] Financial support from the United States Atomic Energy Commission is gratefully acknowledged. This is AEC Report No. COO-1713-15.

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