

bonyl stretching frequencies and force constant data,^{2,4-7} although other types of data have been presented, such as equilibrium constants,⁸ metal-ligand and metal-carbon stretching frequencies,⁹ and phosphorus-tungsten coupling constants.^{10,11} To date, however, there has been no comparison of two or more molecular structures of similar compounds (e.g., $\text{LCr}(\text{CO})_5$ and $\text{L}'\text{Cr}(\text{CO})_5$, where L and L' are different phosphorus ligands) in which the π -bonding ability of the ligands are different.

We report here the preliminary results of such a study in which triphenylphosphine and triphenyl phosphite were chosen as the ligands because they have been shown to have somewhat different bonding properties in $\text{LM}(\text{CO})_5$ as determined from infrared spectra and tungsten-phosphorus coupling constant data.¹¹

Crystals of pentacarbonyltriphenylphosphinechromium and pentacarbonyl(triphenyl phosphite)chromium are triclinic, P_1 , with two formula units in the cell. The phosphine complex, $(\text{C}_6\text{H}_5)_3\text{PCr}(\text{CO})_5$, has cell dimensions $a = 9.7086 \pm 0.0031$, $b = 11.9419 \pm 0.0020$, $c = 9.5519 \pm 0.0027$ Å, $\alpha = 91.733 \pm 0.018^\circ$, $\beta = 95.583 \pm 0.038^\circ$, $\gamma = 74.167 \pm 0.015^\circ$; and the phosphite complex, $(\text{C}_6\text{H}_5\text{O})_3\text{PCr}(\text{CO})_5$, has cell dimensions $a = 11.2118 \pm 0.0035$, $b = 11.4971 \pm 0.0044$, $c = 10.6950 \pm 0.0029$ Å, $\alpha = 114.333 \pm 0.039^\circ$, $\beta = 105.583 \pm 0.028^\circ$, $\gamma = 66.500 \pm 0.018^\circ$. Data for both structures were measured to a 2θ of 55° with a General Electric XRD-6 automated diffractometer using niobium-filtered molybdenum radiation (λ 0.71069) and the θ - 2θ scan technique. The structure of the phosphine compound was solved by Patterson and Fourier methods¹² and refined to an R value of 0.043 by least-squares on 4885 reflections. The structure of the phosphite compound was solved by statistical and Fourier methods¹² and refined to an R value of 0.052 on 5263 reflections. The hydrogen atom positions for both structures were assumed from known benzene geometry and refined with isotropic temperature factors.

The salient structural features of these compounds are given in Table I. The phosphorus and five car-

Table I

Bond	Bond length, Å	
	Phosphite	Phosphine
Cr-P	2.309 (1)	2.422 (1)
Cr-C (<i>trans</i>)	1.861 (4)	1.844 (4)
C-O (<i>trans</i>)	1.136 (6)	1.154 (5)
Cr-C (<i>cis</i> , av)	1.896 (4)	1.880 (4)
C-O (<i>cis</i> , av)	1.131 (6)	1.147 (6)

bonyls form an approximate octahedron about chromium, with one carbonyl *trans* to phosphorus and the other four carbonyls *cis* to phosphorus. The π -bonding theory predicts that the *trans* Cr-C distance should

(5) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

(6) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

(7) D. J. Darensbourg and T. L. Brown, *ibid.*, **7**, 959 (1968).

(8) R. J. Angelici and C. M. Ingemanson, *ibid.*, **8**, 83 (1969).

(9) G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967).

(10) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, **89**, 5573 (1967).

(11) S. O. Grim, P. R. McAllister, and R. M. Singer, *Chem. Commun.*, **38** (1969).

(12) Technical Report 67-58, Dec 1967, X-ray 67, Program System for X-ray Crystallography, Computer Science Center, University of Maryland.

be significantly shorter than the *cis* Cr-C distances, and concomitantly that the *cis* C-O distances should be shorter than the *trans* C-O distance. This is indeed observed in each compound. Furthermore, the infrared spectra of these compounds and ^{193}W - ^{31}P coupling (411 Hz for the phosphite and 280 Hz for the phosphine complex)¹¹ in the analogous tungsten compounds suggests, according to the π theory, that triphenyl phosphite is a better π acceptor than triphenylphosphine.^{13,14}

Consequently, it is expected that for the phosphite complex the Cr-P distance should be shorter, the *trans* Cr-C bond should be longer, the *trans* C-O bond should be shorter, the *cis* Cr-C bond should be longer, and the *cis* C-O distance should be shorter than the respective distances in the triphenylphosphine complex. Remarkably, all these expectations are experimentally confirmed. The π -bonding theory^{5,6} also predicts that changes in the π -acceptor ability of the ligand should effect the *trans* CO about twice as much as the *cis* CO's due to the symmetry and number of metal d orbitals involved in the bonding. However, the differences in both the *cis* and *trans* Cr-C and C-O bond lengths between the phosphite and phosphine complexes are roughly equivalent.

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(13) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

(14) W. Strohmeier and F. J. Müller, *Chem. Ber.*, **100**, 2812 (1967).

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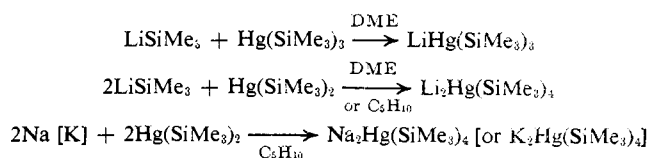
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Trimethylsilylmercury Complexes¹

Sir:

The recent communication² on the possible intermediacy of methylmercury complexes in the exchange between methyl lithium and dimethylmercury in ether and THF (tetrahydrofuran) prompts us to report our observations on trimethylsilylmercury complexes.

We have prepared a series of highly colored compounds (Table I) containing tris(trimethylsilyl)mercury or tetrakis(trimethylsilyl)mercury complexes by the reactions



The decrease in the ^{199}Hg - ^1H coupling constant from the bis- to the tetrakis(trimethylsilyl)mercury compounds is similar to that observed for increasing alkyl substitution in other organometallic compounds.³ If a

(1) Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract INORG 152.

(2) L. M. Seitz and S. D. Hall, *J. Organometal. Chem.*, **15**, P7 (1968).

(3) M. L. Maddox, S. L. Stafford, and H. P. Kaesz in "Advances in Organometallic Chemistry," Vol. 3, F. G. A. Stone and R. West, Ed, Academic Press, New York, N. Y., 1965, Chapter I.

Table I. ^1H Chemical Shifts, Coupling Constants, and Colors for Trimethylsilyl Metal Compounds

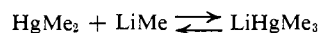
Compound	Color	δ , ^a ppm	J , Hz	
			$^{199}\text{Hg}-^1\text{H}$	$^{29}\text{Si}-^1\text{H}$
$\text{Hg}(\text{SiMe}_3)_2$	Yellow	1.30 ^d	40.8 ^d	6.7 ^d
$\text{LiHg}(\text{SiMe}_3)_3(\text{DME})_3^b$	Red	1.36 ^{c,e}	25.8 ^{c,e}	5.2 ^{c,e}
$\text{Li}_2\text{Hg}(\text{SiMe}_3)_4(\text{DME})_4^b$	Yellow	1.56 ^{c,e}	18.1 ^{c,e}	4.8 ^{c,e}
$\text{Li}_2\text{Hg}(\text{SiMe}_3)_4$	White			
$\text{Na}_2\text{Hg}(\text{SiMe}_3)_4$	Light violet			
$\text{K}_3\text{Hg}(\text{SiMe}_3)_4$	Blue-gray			
LiSiMe_3	Yellow	1.73 ^c /1.33 ^d		2.8 ^c /3.5 ^d

^a All relative to cyclopentane and at higher field. ^b DME = dimethoxyethane. ^c In dimethoxyethane. ^d In cyclopentane. ^e At low temperature (~ -40 to -55°).

Fermi contact is the dominant term in this coupling, the decrease is consistent with the hybridization being sp in $\text{Hg}(\text{SiMe}_3)_2$, sp^2 in $\text{LiHg}(\text{SiMe}_3)_3$, and sp^3 in $\text{Li}_2\text{Hg}(\text{SiMe}_3)_4$. It should be noted, however, that $\text{LiHg}(\text{SiMe}_3)_3(\text{DME})_3$ contains more DME (dimethoxyethane) than would be required to satisfy all the acceptor sites on the lithium and may involve coordination of the ether to the mercury.

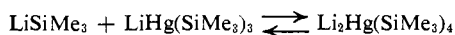
The proton nmr of $\text{LiHg}(\text{SiMe}_3)_3$ in DME solution gives a single broadened peak at 40° . The broadening is due to exchange of trimethylsilyl groups between different mercury sites and partial collapse of the ^{199}Hg satellites. At -40° the central peak and the satellites are sharp. From the consistency of the chemical shift for 40 to -40° , it appears that there is no significant dissociation of the anion in this range. If the $\text{LiHg}(\text{SiMe}_3)_3$ contains even very small amounts of $\text{Hg}(\text{SiMe}_3)_2$, a single sharp peak with no ^{199}Hg satellites results even at -60° . The $^{29}\text{Si}-^1\text{H}$ coupling is still observed indicating that exchange of methyl groups between silicon atoms is slow. The complete collapse of the ^{199}Hg satellites is due to the very rapid transfer of a trimethylsilyl group (and associated lithium) between $\text{Hg}(\text{SiMe}_3)_2$ and $\text{LiHg}(\text{SiMe}_3)_3$. A dissociation mechanism would appear to be unlikely because of the relatively slow self-exchange of $\text{LiHg}(\text{SiMe}_3)_3$. The exchange of trimethylsilyl groups on $\text{Hg}(\text{SiMe}_3)_2$ is slow as shown by the sharpness of the central peak and satellites at room temperature.

Seitz and Hall's proposal that a very small amount of LiHgMe_3 would cause broadening of the ^{199}Hg satellites of dimethylmercury by rapid exchange of methyl groups (and associated lithium) seems quite reasonable in light of the very fast exchange between $\text{Hg}(\text{SiMe}_3)_2$ and $\text{LiHg}(\text{SiMe}_3)_3$. The concentration of LiHgMe_3 would not have to be large although the rate of exchange would have to be considerably faster than the reaction



or the LiMe resonance would also be broadened.

DME solutions containing $\text{Li}_2\text{Hg}(\text{SiMe}_3)_4$ undergo rapid self-exchange, exchange with $\text{LiHg}(\text{SiMe}_3)_3$, or exchange with LiSiMe_3 . This is due to the rapid equilibrium reaction in ethereal solutions.

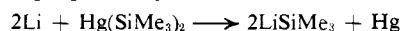


This equilibrium lies far to the left at room temperature, imparting a red color to the solutions. At low temperature the equilibrium lies to the right, the solutions are green, and all three species can be observed in the proton nmr spectrum. The form of the equilibrium constants is not known, since the association of the

various species have not been determined, but ΔH is negative for the reaction as written. $\text{Na}_2\text{Hg}(\text{SiMe}_3)_4$ undergoes a similar equilibrium, but it appears to be much less dissociated under similar conditions.

The analyses of the solid complexes were performed as follows. A weighed sample of a complex was placed in an nmr tube. A measured amount of benzene and sufficient water to hydrolyze the sample was added by distillation from the vacuum line and the tube sealed off. The amount of HSiMe_3 , $\text{Hg}(\text{SiMe}_3)_2$, and DME produced by hydrolysis was determined by careful integration against the benzene standard. The tube was broken open and hydroxide produced was titrated against standard HCl. The determination satisfactorily accounted for the total weight of the sample.

All the compounds are air and water sensitive except $\text{Hg}(\text{SiMe}_3)_2$ which is stable to water. The alkali metal compounds should be considered pyrophoric. All manipulations were performed under high vacuum or a nitrogen atmosphere dried by sodium-potassium alloy. LiSiMe_3 was prepared by the reaction



in benzene or ether.^{4,5} If made in benzene LiSiMe_3 can be sublimed under high vacuum and 60° . LiSiMe_3 is much less reactive to DME than *t*-butyllithium. $\text{Hg}(\text{SiMe}_3)_2$ was made by the method of Eaborn⁶ and sublimed before use. Nmr spectra were obtained on a Varian Associates A-60A spectrometer. Chemical shifts were obtained on dilute solutions and calibrated vs. cyclopentane as internal standard.

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(4) E. Hongge and N. Holtschmidt, *J. Organometal. Chem.*, **12**, P5 (1968).

(5) N. S. Vyazankin, G. A. Razuvalv, E. N. Gladyshev, and S. P. Korneva, *ibid.*, **7**, 353 (1967).

(6) C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Chem. Soc.*, C, 2188 (1967).

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The Metal Ion Dependence of the Tin(II)-Vanadium(V) Reaction in Perchloric Acid

Sir:

In perchloric acid solutions both the stoichiometry and the rate of the $\text{Sn(II)}-\text{V(V)}$ reaction differ markedly from those observed in hydrochloric acid solutions.¹

(1) D. J. Drye, W. C. E. Higginson, and P. Knowles, *J. Chem. Soc.*, 1137 (1962).