Since the estimated experimental uncertainties are ±0.12 and ±0.08 for the σ and π parameters, respectively, this study indicates there is essentially no change in these parameters (or force constants) with amine groups.[15] In fact, there is very little, if any, change in the force constants as one proceeds down the group VI metals.

The lack of sensitivity of carbonyl stretching force constants to the nature of the substituted amine ligands could be taken to indicate that the saturation point for acceptance of electron density of the $M(CO)_5$ moiety is low in the absence of good π-acceptor ligands and therefore all amines investigated may have met this minimum saturation level.[16] Alternatively, the difference in σ-donor abilities of the various amine ligands may not be enough to cause observable changes in the CO stretching force constants. The latter conclusion would imply that CO stretching force constants are not very sensitive to σ effects of these orders of magnitude, assuming pK_a values are good indicators of the amines' donating abilities.

Acknowledgments. Financial support from the Petroleum Research Fund, administered by the American Chemical Society under Grant 1705-G3, is gratefully acknowledged. We also wish to thank the State University of New York at the Buffalo Computing Center for generous donation of computer time.

[15] These results are in disagreement with those of R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

[16] R. J. Angelici and C. M. Ingemanson, *ibid.*, **8**, 83 (1969). These authors however concluded from equilibria studies that the strength of the W–N bond in $W(CO)_5$amine complexes decreases with decreasing basicity of the amine. Our rate studies tend to support this conclusion.

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Metal–Metal Bonded Organometallic Complexes. I. Synthesis of Ligand Derivatives of Tricarbonyl-π-cyclopentadienylmolybdenum Bonded to Dimethyl- and Trimethyltin[1]

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The compounds π-$C_5H_5Mo(CO)_2(L)Sn(CH_3)_3$ (L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)(CH_3)_2$, $P(OCH_2)_3CCH_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$) have been prepared by reaction of the anion $[\pi$-$C_5H_5Mo(CO)_2L]^-$ with $(CH_3)_3SnCl$. π-$C_5H_5Mo(CO)_2P(C_6H_5)_3$-$Sn(CH_3)_3$ was also prepared by the direct reaction of π-$C_5H_5Mo(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$ with or without solvent at 160°. At about 200° all these derivatives liberated $Sn(CH_3)_4$ but only for L = $P(C_6H_5)_3$ or $P(OCH_2)_3CCH_3$ was the other product characterized, namely, $[\pi$-$C_5H_5Mo(CO)_2(L)]_2Sn(CH_3)_2$. These two compounds were also prepared by other routes. Infrared and proton nmr spectra suggest that all the new compounds have a trans configuration.

Introduction

The organometallic compounds with a metal–metal bond between a group VIa transition metal (Cr, Mo, and W) and a group IVb metal (Si, Ge, Sn, and Pb) are well known[2] and preparatively accessible by a number of routes (*e.g.*, eq 1[3] and 2[4]). Previous investigations of the chemistry of these compounds have been limited to metal–metal bond cleavage (*e.g.*, eq 3[5]) and metal–nonmetal bond cleavage reactions (*e.g.*, eq 4,[6] 5,[7] and 6[8]).

$$[\pi\text{-}C_5H_5Cr(CO)_3]Na + (C_6H_5)_3GeCl \longrightarrow \pi\text{-}C_5H_5Cr(CO)_3Ge(C_6H_5)_3 + NaCl \quad (1)$$

$$\pi\text{-}C_5H_5Mo(CO)_3H + (CH_3)_3SiN(CH_3)_2 \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3Si(CH_3)_3 + HN(CH_3)_2 \quad (2)$$

$$\pi\text{-}C_5H_5Mo(CO)_3GeR_3 + HCl \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3H + R_3GeCl \quad (3)$$

$$\pi\text{-}C_5H_5Mo(CO)_3Sn(C_6H_5)_3 + HCl \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3Sn(C_6H_5)_2Cl + C_6H_6 \quad (4)$$

$$\pi\text{-}C_5H_5Mo(CO)_3SnCl_3 + 8\text{-}C_9H_6NOH \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3Sn(8\text{-}C_9H_6NO)Cl + HCl + Cl^- \quad (5)$$

$$\pi\text{-}C_5H_5Mo(CO)_3Sn(CH_3)_3 + P(OC_6H_5)_3 \longrightarrow \pi\text{-}C_5H_5Mo(CO)_2P(OC_6H_5)_3Sn(CH_3)_3 + CO \quad (6)$$

This paper describes the preparation of ligand derivatives of π-$C_5H_5Mo(CO)_3Sn(CH_3)_3$ (Table I) and an interesting high-temperature redistribution reaction (eq 7).

$$2\pi\text{-}C_5H_5Mo(CO)_2(L)Sn(CH_3)_3 \longrightarrow [\pi\text{-}C_5H_5Mo(CO)_2(L)]_2Sn(CH_3)_2 + Sn(CH_3)_4 \quad (7)$$

Results and Discussion

π-$C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$ was prepared by three different routes. The reaction of π-C_5H_5Mo-$(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$ in diglyme, or without solvent, at 160° gave the monosubstituted derivative as a white product. The preparation from the substituted anion $[\pi$-$C_5H_5Mo(CO)_2P(C_6H_5)_3]^-$ and $(CH_3)_3$-$SnCl$, however, gave a pale yellow product. An exhaustive comparison by ir, proton nmr, uv, and mass spectroscopy showed that the two compounds were identical. The white product gave a yellow solution in organic solvents. Earlier attempts to prepare the $P(C_6H_5)_3$ derivative by irradiation were un-

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[1] Presented in part at the 160th American Chemical Society Meeting, Chicago, Ill., Sept 1970; T. A. George, *Chem. Commun.*, 1632 (1970).

[2] E. H. Brooks and R. J. Cross, *Organometal. Chem. Rev., Sect. A*, **6**, 227 (1970).

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

[4] D. J. Cardin, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc. A*, 2594 (1970).

[5] A. Carrick and F. Glocking, *ibid.*, *A*, 913 (1968).

[6] A. N. Nesmeyanov, K. N. Anisimov, N. E. Kalobova, and M. Ya. Zakharova, *Dokl. Akad. Nauk SSSR*, **156**, 612 (1964).

[7] F. Bonati and G. Minghetti, *J. Organometal. Chem.*, **16**, 333 (1969).

[8] R. B. King and K. H. Pannell, *Inorg. Chem.*, **7**, 2356 (1968).

TABLE I
PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	Color	Mp,[a] °C	% C		% H		Yield, %
			Calcd	Found	Calcd	Found	
$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3I$	Orange	255 dec	29.3	29.8	2.9	3.3	72
$C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$	White[b]	203–204	52.3	52.4	4.5	4.5	81
$C_5H_5Mo(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$[c]	Yellow	135–136	48.6	48.7	4.2	4.3	58
$C_5H_5Mo(CO)_2P(C_6H_5)(CH_3)_2Sn(CH_3)_3$	Yellow	115–116	41.6	41.3	4.8	5.0	67
$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3Sn(CH_3)_3$	Yellow	170–172	34.0	34.1	4.3	4.2	77
$C_5H_5Mo(CO)_2As(C_6H_5)_3Sn(CH_3)_3$	Yellow	186–188	49.0	48.8	4.2	3.9	60
$C_5H_5Mo(CO)_2Sb(C_6H_5)_3Sn(CH_3)_3$	Yellow	188–189	45.8	45.9	4.0	4.0	58
$[C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$	Green	210 dec	56.5	56.7	4.6	4.3	60–80
	Yellow-green[d]	210 dec	56.5	56.3	4.6	4.3	30
$[C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2Sn(CH_3)_2$	Yellow[e]	>250[f]	35.5	35.3	3.9	4.1	41–80

[a] Sealed tube, uncorrected. [b] See Experimental Section, procedure A. [c] See ref 8. [d] See Experimental Section, procedure A. Mo analysis: calcd, 17.3; found, 17.4. [e] Procedure A. [f] Did not melt below 250°.

TABLE II
^1H NMR SPECTRAL DATA[a]

Compound	τ[b] (rel area)			J[c]		
	$(CH_3)_3Sn$	C_5H_5	Others [assignment]	$^{119}Sn–CH$	$^{117}Sn–CH$	$P–C_5H_5$
$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3I$	...	4.62 (5)	9.11 (3) $[CH_3]$ 5.57 (6) $[CH_2]$[d]	...	...	2.0
$C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$	9.63 (9)	5.21 (5)	2.55 (15.2) $[C_6H_5]$	[e]	[e]	1.0
$C_5H_5Mo(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$[f]	9.76 (9)	5.42 (5)	2.68 (15) $[C_6H_5]$	48	45.8	0.8
$C_5H_5Mo(CO)_2P(C_6H_5)(CH_3)_2Sn(CH_3)_3$	9.67 (9)	5.20 (4.8)	8.16 (6) $[CH_3]$[g] 2.50 (5) $[C_6H_5]$	47	44.8	1.0
$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3Sn(CH_3)_3$	9.66 (9)	4.95 (5)	9.21 (3) $[CH_3]$ 5.76 (6.1) $[CH_2]$[h]	48	45.9	0.8
$C_5H_5Mo(CO)_2As(C_6H_5)_3Sn(CH_3)_3$	9.59 (9)	5.13 (5)	2.58 (15.2) $[C_6H_5]$	46.4	44.3	...
$C_5H_5Mo(CO)_2Sb(C_6H_5)_3Sn(CH_3)_3$	9.52 (9)	5.02 (5)	2.56 (15) $[C_6H_5]$	46.5	44.5	...
$[C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$[i]	9.17 (9)	4.95 (5)	2.62 (15) $[C_6H_5]$	...	...	0.8
$[C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2Sn(CH_3)_2$[j]	...	...	...	...	...	...

[a] In $CDCl_3$ solution unless stated otherwise. [b] Relative to $Si(CH_3)_4$. [c] Hz. [d] $J(P–OCH_2)$ = 5.0 Hz. [e] Not observed. [f] See ref 8. [g] $J(P–CH_3)$ = 8.8 Hz. [h] $J(P–OCH_2)$ = 2.5 Hz. [i] Solution in 2:1 $CCl_2{=}CCl_2–CH_2Cl_2$ mixture. [j] Not soluble enough to measure.

successful. The high-temperature substitution reactions with or without solvent proved unsatisfactory for the preparation of the other ligand derivatives. The reaction of the substituted anions $[\pi\text{-}C_5H_5Mo(CO)_2(L)]^-$ with $(CH_3)_3SnCl$ gave good yields of the expected products. Manning had previously used this method to prepare similar ligand derivatives of triphenyltin, $\pi\text{-}C_5H_5Mo(CO)_2(L)Sn(C_6H_5)_3$.[9]

King and Pannell have reported the preparation of two isomers of $\pi\text{-}C_5H_5Mo(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$:[8] an insoluble isomer, by allowing $[\pi\text{-}C_5H_5Mo(CO)_2P(OC_6H_5)_3]^-$ to react with $(CH_3)_3SnCl$, and a soluble isomer, from the irradiation of $\pi\text{-}C_5H_5Mo(CO)_3Sn(CH_3)_3$ and $P(OC_6H_5)_3$. We have obtained only the soluble isomer although prepared by the former method. The melting point and ir and pmr spectra compare very well suggesting that they are indeed the same compound. The triphenyl phosphite derivative was less stable than the unsubstituted $\pi\text{-}C_5H_5Mo(CO)_3Sn(CH_3)_3$ whereas all the other substituted derivatives were more stable. Even *in vacuo*, in the dark, the triphenyl phosphite derivative began turning blue after a few days suggesting decomposition. The same blue coloration was observed to form more rapidly in the air.

The existence of two isomeric forms of the compounds $\pi\text{-}C_5H_5Mo(CO)_2LX$ (X = H, alkyl, aryl, acyl, Cl, Br, I, $Sn(C_6H_5)_3$), based upon a square-pyramidal geometry, has been recognized for some time.[10] Recently the cis–trans isomerization has been studied as a function of L and X.[11] An assignment of the stereochemistry can be made from the infrared and proton nmr spectra.

The proton nmr resonance of the $\pi\text{-}C_5H_5$ ring in the compounds $\pi\text{-}C_5H_5Mo(CO)_2(L)Sn(CH_3)_3$ where L is a phosphine or phosphite ligand (Table II) indicated only one, the trans, isomer present. In all four of these cases the $\pi\text{-}C_5H_5$ resonance appeared as a doublet (J = 0.8–1.0 Hz) in the range τ 4.95–5.42. The triphenylarsine and triphenylstibine compounds exhibited a singlet at τ 5.13 and τ 5.02, respectively, for the $\pi\text{-}C_5H_5$ resonance.

The infrared spectra (Table III) of all the trimethyltin complexes show two ν(CO) bands with the low-frequency band being of higher intensity than the high-frequency band. This observation is in agreement with a trans configuration for all the trimethyltin derivatives.[9] The proposed stereochemistry of these derivatives is summarized and compared with analogous triphenyltin and iodo complexes (Table IV).[12]

The variation in ν(CO) bands, $\tau(\pi\text{-}C_5H_5)$, and τ $[Sn(CH_3)_3]$ resonance positions with change of the ligand for the trimethyltin derivatives showed no obvious correlation with steric or electronic effects associated with the ligand. However, these variations were larger than observed when molybdenum was replaced by tungsten and trimethyltin was replaced by triphenyltin.[3] The proton–tin coupling constants for the trimethyltin derivatives (except for the triphenylphosphine complex) showed a decrease in the order $P(OC_6H_5)_3 \approx P(OCH_2)_3CCH_3 > P(C_6H_5)(CH_3)_2 > Sb(C_6H_5)_3 \approx As(C_6H_5)_3$ which parallels the increase in basicity of the ligands. Surprisingly, the change

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[9] A. R. Manning, *J. Chem. Soc. A*, 651 (1968).

[10] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

[11] J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

[12] R. J. Mawby and G. Wright, *J. Organometal. Chem.*, **21**, 169 (1970).

TABLE III

IR AND UV–VISIBLE SPECTRAL DATA

Compound	Carbonyl str freq,[a] cm^{-1}			Max,[b] nm (*E*)	
$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3I$	1991 (0.44)	1915 (1.0)[c]		467 (455)	295 (6200)
$C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$	1901 (0.55)	1833 (1.0)		346 (2770)	260 (26,500) sh
$C_5H_5Mo(CO)_2P(OC_6H_5)_3Sn(CH_3)_3$[d]	1918 (0.52)	1853 (1.0)		327 (2530)	255 (15,700) sh
$C_5H_5Mo(CO)_2P(C_6H_5)(CH_3)_2Sn(CH_3)_3$	1894 (0.54)	1825 (1.0)		350 (2300)	261 (10,000) sh
$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3Sn(CH_3)_3$	1929 (0.56)	1862 (1.0)		325 (2840)	254 (13,200) sh
$C_5H_5Mo(CO)_2As(C_6H_5)_3Sn(CH_3)_3$	1902 (0.53)	1835 (1.0)		257 (1770)	269 (8480) sh
$C_5H_5Mo(CO)_2Sb(C_6H_5)_3Sn(CH_3)_3$	1902 (0.46)	1837 (1.0)		355 (2520)	270 (7900) sh
$[C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$	1896 (0.44)	1844 (0.25)	1820 (1.0)[c]	. . .	. . .
$[C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2Sn(CH_3)_2$	1918 s	1898 s	1834 s[e]	. . .	. . .

[a] CCl_4 solution unless stated otherwise. [b] CH_3CN solution. [c] CH_2Cl_2 solution. [d] See ref 8. [e] Nujol mull.

TABLE IV

STEREOCHEMISTRY OF THE DERIVATIVES $C_5H_5Mo(CO)_2LX$

L	I[a]	$Sn(C_6H_5)_3$[a]	$Sn(CH_3)$[b]
$P(C_6H_5)_3$	Mixture	Trans	Trans
$P(OC_6H_5)_3$	Cis	Trans	Trans
$P(C_6H_5)(CH_3)_2$	Cis[b,c]	. . .	Trans
$P(OCH_2)_3CCH_3$	Trans[b]	. . .	Trans
$AsPh_3$	Cis	. . .	Trans
$SbPh_3$	Cis	Trans	Trans

[a] From ref 9. [b] This work. [c] Reported as a cis–trans mixture; see ref 12.

in proton–tin coupling constants correlated with the change in position of the lower energy band in the uv–visible spectra (Table II).

It was observed that when π-$C_5H_5Mo(CO)_2P(C_6H_5)_3$-$Sn(CH_3)_3$ or a mixture of π-$C_5H_5Mo(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$ was heated at about 200°, a green product was formed in good yield. Mass spectral analysis of the volatile product(s) showed only tetramethyltin to be present. The green product was shown to be $[\pi$-$C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$. The other ligand derivatives were also heated to about 200° and, although color changes were observed, only in the case where L was $P(OCH_2)_3CCH_3$ was a dimethyltin derivative isolated and characterized. However, in all cases tetramethyltin was characterized as one of the products. Even unsubstituted π-$C_5H_5Mo(CO)_3$-$Sn(CH_3)_3$ liberated tetramethyltin at 200°, but the dimethyltin complex was not isolated. Redistribution reactions are well known for the main-group organometallic compounds[13] but less well documented for the transition metal organometallic compounds involving the cleavage of a metal–metal bond (*e.g.*, eq 8[14]).

$$2[(CH_3)_3Pb]_2Fe(CO)_4 \longrightarrow [(CH_3)_2PbFe(CO)_4]_2 + 2Pb(CH_3)_4 \quad (8)$$

The observed redistribution reaction was the first example noted for a Sn–Mo bonded compound (eq 7). When $[\pi$-$C_5H_5Mo(CO)_3]_2Sn(CH_3)_2$ was heated at 160° under vacuum π-$C_5H_5Mo(CO)_3Sn(CH_3)_3$ sublimed out of the reaction suggesting that further redistribution may have occurred.

The triphenylphosphine complex prepared from $[\pi$-$C_5H_5Mo(CO)_3]_2Sn(CH_3)_2$ was yellow-green. The same compound prepared at 200° was green. However, the yellow-green coloration became darker when it was heated and both compounds exhibited the same melting point. The two compounds had the same infrared and proton nmr spectra and it was assumed that both compounds were identical. Since the dimethyltin derivatives can exist in a number of isomeric forms, it is possible that the compound prepared at the lower temperature is a different isomer or contains a mixture of isomers. The infrared and proton nmr spectra do not necessarily support this proposal.

In the preparation of $[\pi$-$C_5H_5Mo(CO)_2P(OCH_2)$-$CCH_3]_2Sn(CH_3)_2$ from the anion a yellow and a green product were obtained. The separation of the two compounds was extremely difficult because of their low solubility in almost all organic solvents, which also precluded proton nmr spectra being run. In fact the green compound probably was not obtained pure. The yellow compound had the same melting point and infrared spectrum as the high-temperature product. The green compound did not change color when heated to 250° which suggested that the green compound was not a simple structural isomer of the yellow compound.

It seems possible that the mechanism of the redistribution reaction involves a bimolecular process proceeding through a four-centered activated complex. The absence of products such as hexamethylditin argues against a random bond-breaking, bond-making process. The relative lability of one of the methyl groups is supported by the mass spectral data which are discussed below.

The mass spectrum of all the trimethyltin derivatives exhibited certain similarities. Of the tin–molybdenum fragments, the $[\pi$-$C_5H_5Mo(CO)_2LSn(CH_3)_2]^+$ was by far the most abundant. The ratio $(M^+ - 15)/M^+$ (where M^+ is the parent ion) was much greater than for unsubstituted π-$C_5H_5Mo(CO)_3Sn(CH_3)_3$[15] and was at a maximum for the phosphite ligand derivatives (100). The most abundant fragments, however, were associated with $[\pi$-$C_5H_5MoL]^+$ and loss of the ligand substituents, except when L was $P(OCH_2)_3CCH_3$, to give ultimately $[\pi$-$C_5H_5MoX]^+$, where X is $P(C_6H_5)$, $P(OC_6H_5)$, $As(C_6H_5)$, and $Sb(C_6H_5)$. $[MoL]^+$ was also one of the most abundant fragments except when L was $P(OCH_2)_3CCH_3$.

The new compound π-$C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3I$ exhibited a doublet ($J = 2.0$ Hz) for the π-C_5H_5 resonance at τ 4.62 in the proton nmr spectrum and two ν(CO) bands in the infrared spectrum at 1991 (0.44) and 1915 (1.0). These data support a trans configuration.

Experimental Section

All reactions and work-up were carried out under a nitrogen atmosphere. Hexane and benzene were dried by distillation from calcium hydride, tetrahydrofuran and diglyme were dried by distillation from lithium aluminum hydride, and dichloro-

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(13) K. Moedritzer, *Advan. Organometal. Chem.*, **6**, 171 (1968).

(14) F. Hein and W. Jehn, *Justus Liebigs Ann. Chem.*, **684**, 4 (1965).

(15) R. B. King, *Org. Mass Spectrom.*, **2**, 657 (1969).

methane was dried by distillation from phosphorus pentoxide. All solvents were deaerated with nitrogen gas before use. All ligands were obtained from commercial sources and used without further purification, except 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, which was prepared by Mr. Duane Thompson of this laboratory by a published procedure.[16] The known compounds were prepared by literature procedures: $C_5H_5Mo(CO)_3I$,[17] $C_5H_5Mo(CO)_3Sn(CH_3)_3$,[3] $[C_5H_5Mo(CO)_3]_2Sn(CH_3)_2$,[3] $[C_5H_5Mo(CO)_3]_2$,[17] $C_5H_5Mo(CO)_2LI$ [L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(C_6H_5)(CH_3)_2$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$].[9]

Microanalyses (Table I) were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Proton nmr spectra (Table II) were obtained by means of a Varian A-60D spectrometer. Infrared spectra (Table III) were determined using a Perkin-Elmer Model 621 grating spectrometer. Ultraviolet–visible spectra (Table III) were measured with a Cary Model 14 spectrophotometer. Mass spectra were obtained with a Perkin-Elmer Hitachi RMV-6D double-focusing spectrometer at 70-eV ionizing energy. *m/e* values, where appropriate, were calculated for ^{120}Sn, ^{98}Mo, and ^{121}Sb.

Preparation of $C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3I$.—A solution of 0.8 g (5.4 mmol) of $P(OCH_2)_3CCH_3$ and 2.0 g (5.4 mmol) of $C_5H_5Mo(CO)_3I$ in 65 ml of benzene was irradiated (120 W) for 44 hr under nitrogen in a Pyrex flask with magnetic stirring and with internal cooling to maintain the solution at room temperature. The suspension was filtered and the precipitate washed with dichloromethane (two 50-ml portions). The combined filtrates were stripped to dryness *in vacuo* and chromatographed on an alumina column prepared with deaerated hexane. A red-purple fraction eluted with a 1:1 hexane–benzene mixture. Attempts to characterize this fraction were unsuccessful. Elution with a 1:1 benzene–dichloromethane mixture gave an orange solution. Crystallization from a 3:1 hexane–dichloromethane solvent mixture gave 1.91 g (3.88 mmol, 72%) of pure $(C_5H_5)Mo(CO)_2P(OCH_2)_3CCH_3I$.

Preparation of $C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$. (A) From $C_5H_5Mo(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$ in Diglyme.—A solution of 0.8 g (1.95 mmol) of $C_5H_5Mo(CO)_3Sn(CH_3)_3$ and 0.51 g (1.95 mmol) of $P(C_6H_5)_3$ in 30 ml of diglyme was refluxed for 6 hr under nitrogen. Solvent was partly removed *in vacuo* and the resulting precipitate was filtered off and washed with pentane (50 ml). Crystallization from approximately 10 ml of a 3:1 ethanol–dichloromethane solvent mixture gave 1.03 g (1.58 mmol, 81%) of pure $C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$ (parent ion: calcd for $C_{28}H_{29}MoO_2PSn$; 646; found, 646).

(B) From $C_5H_5Mo(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$, No Solvent.—$C_5H_5Mo(CO)_3Sn(CH_3)_3$ (0.8 g (1.95 mmol)) and 0.51 g (1.95 mmol) of $P(C_6H_5)_3$ were heated together at 160° for 12 hr. Upon cooling, the product was purified as in (A) above (50%).

(C) From $C_5H_5Mo(CO)_2P(C_6H_5)_3I$ and $(CH_3)_3SnCl$.—A solution of 1.42 g (2.35 mmol) of $C_5H_5Mo(CO)_2P(C_6H_5)_3I$ in 30 ml of tetrahydrofuran was added to 20 g of a 1% sodium amalgam in a 150-ml 3-neck flask with a mercury run-off tap on the bottom, equipped with an addition funnel, a nitrogen inlet, and a mechanical stirrer. After stirring for 10 min, excess sodium amalgam was run off and 0.5 g (2.5 mmol) of trimethyltin chloride in 20 ml of tetrahydrofuran was added and stirring maintained for a further 20 min. After filtration and removal of solvent *in vacuo* the pale yellow product was crystallized from approximately 20 ml of a 3:1 ethanol–dichloromethane solvent mixture (78%).

Preparation of $C_5H_5Mo(CO)_2LSn(CH_3)_3$.—The other ligand derivatives were prepared by procedure (C) above and crystallized from ethanol–dichloromethane solvent mixtures except for L = $P(C_6H_5)(CH_3)_2$ which was crystallized from hot hexane by cooling to 0°. Each compound gave the appropriate parent ion in its mass spectrum.

Thermal Redistribution. General Procedure.—About 1 mmol of the trimethyltin derivative was heated in an enclosed flask under vacuum at temperatures between 150 and 200° for times varying from 30 to 60 min. Upon cooling to room temperature, volatile products were allowed to diffuse into a small evacuated bulb and the contents transferred to the mass spectrometer. Mass spectral analysis indicated that tetramethyltin was the only volatile product.

Preparation of $[C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$. (A) From $[C_5H_5Mo(CO)_3]_2Sn(CH_3)_2$ and $P(C_6H_5)_3$.—A solution of 0.64 g (1 mmol) of $[C_5H_5Mo(CO)_3]_2Sn(CH_3)_2$ and 0.56 g (2 mmol) of $P(C_6H_5)_3$ in 25 ml of diglyme was refluxed under nitrogen for 8 hr. Solvent was removed *in vacuo* and the greenish solid was stirred with 60 ml of dichloromethane for 5 min and then filtered; the precipitate was washed with 10 ml of dichloromethane. Ethanol (10 ml) was added to the solution and dichloromethane removed on a rotary evaporator at room temperature using a water aspirator. The resulting solid was filtered off, washed with ethanol (two 25-ml portions), and dried *in vacuo*, yielding 0.545 g (0.49 mmol) of product. Recrystallization from 20 ml of a 3:1 ethanol–dichloromethane solvent mixture gave 0.35 g (0.3 mmol, 30%) of yellow-green product believed to be $[C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$. Upon heating to 200° the compound became dark green and melted at 210° (dec).

(B) Heating $C_5H_5Mo(CO)_2P(C_6H_5)_3Sn(CH_3)_3$.—The above compound (0.55 g (0.85 mmol)) was heated at 205° for 2 hr under nitrogen. Upon cooling, the green product was dissolved in a hot 1:1 dichloromethane–tetrachloroethylene solvent mixture. Crystallization at 0° gave 0.38 g (0.34 mmol, 80%) of green $[C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$.

(C) From $C_5H_5Mo(CO)_3Sn(CH_3)_3$ and $P(C_6H_5)_3$, No Solvent.—$C_5H_5Mo(CO)_3Sn(CH_3)_3$ (0.8 g (1.95 mmol)) and 0.51 g (1.95 mmol) of $P(C_6H_5)_3$ were heated under nitrogen at 200° for 10 hr. Upon cooling the green product was worked up as in (B) above, to give 0.65 g (0.59 mmol, 60%) of $[C_5H_5Mo(CO)_2P(C_6H_5)_3]_2Sn(CH_3)_2$.

Preparation of $[C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2Sn(CH_3)_2$. (A) Heating $C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3Sn(CH_3)_3$.—The above compound (0.41 g (0.79 mmol)) was heated at 205° for 2 hr under vacuum. Upon cooling the solid was washed with boiling dichloromethane and then boiling hexane and dried *in vacuo* to give 0.29 g (0.33 mmol, 85%) of bright yellow product.

(B) From $C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3I$ and $(CH_3)_2SnCl_2$.—A solution of 0.64 g (1.3 mmol) of $C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3I$ in 25 ml of tetrahydrofuran was added to 30 g of 1% sodium amalgam in a flask as described above and stirred for 1 hr. After removing the excess sodium amalgam, 0.12 g (0.57 mmol) of dimethyltin dichloride in 20 ml of tetrahydrofuran was added and stirred for 20 min. The solution changed through shades of green and yellow color. The suspension was filtered and the residue extracted with hot tetrahydrofuran (20 ml) and hot acetone (20 ml) leaving a green product which was washed with water, ethanol, and pentane and dried *in vacuo*. Attempted crystallization from excess dichloromethane at 0° gave 0.1 g of green powder [*Anal.* Found: C, 33.3; H, 3.61; mp 250° (remained green); ir (2000–1700 cm^{-1}): Nujol mull, 1931 (vs), 1911 (s), 1846 (vs); CH_2Cl_2 solution, 1942 (0.58), 1923 (0.65), 1875 (1.0), 1852 (0.95)]. The original filtrate was combined with the tetrahydrofuran and acetone extracts and the solvent removed *in vacuo*. The orange-yellow solid was extracted with hot dichloromethane (from which a small amount of the green product was isolated) and dried *in vacuo* to give 0.23 g (0.27 mmol, 41%) of yellow $[C_5H_5Mo(CO)_2P(OCH_2)_3CCH_3]_2Sn(CH_3)_2$, mp > 250°.

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[16] J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).

[17] R. B. King, "Organometallic Syntheses," Academic Press, London, 1965.