presence of one doublet resonance for both Cp groups established the trans stereochemistry at both Mo sites. According to the same well-established NMR criterion,[20,24] the cis,cis stereoisomer of **10** would exhibit a singlet, and the cis,trans isomer would provide separate NMR absorptions (singlet downfield of doublet by ca. 0.2 ppm) for the Cp ligands. A similar argument has been used to assign the stereochemistry on *trans,trans*-$[Cp(CO)_2LMo]_2Hg$, L = $P(OMe)_3$, PPh_3.[20b] Supporting evidence for the trans,trans-stereochemical assignment for **10** results from comparing the magnitude of the μ-H to ligating phosphorus spin–spin coupling interaction with related J_{PH} values involving the terminal hydride ligand on *cis*- and *trans*-$Cp(CO)_2PPh_3MoH$ (65 and 21 Hz, respectively).[20c] As expected,[40] J_{PH} for **10** is slightly less than one-half the value for the *trans*-$Cp(CO)_2PPh_3MoH$. The magnitude of this J_{PH} on **10** also precludes its stereochemical nonrigidity (fast averaging of the cis- and trans-Mo centers on the NMR time scale), since the presence of any reasonable concentration of cis-Mo centers on **10** would effect an averaged J_{PH} substantially greater than 10 Hz.[20c] (Also, a broadened singlet resonance for the Cp ligand would probably result.) Taken together, these NMR data for **10** are in accord with the presence of only the trans,trans stereoisomer.

Attempts at carbonylating **5** and **10** at 85 and 800 psig of CO did not lead to CO addition and generation of μ-formyl complexes. Rather, the μ-hydride salt **5** decomposed under CO pressure to mainly Mp_2 plus small amounts of the nitromethane adduct of Mp^+ but not $MpCO^+$. This decomposition in nitromethane or trifluoroethanol effectively was independent of CO, as similar solutions under 1 atm of nitrogen gave identical results. The phosphine-substituted μ-hydride **10** was recovered unchanged after similar carbonylation attempts, although any residual $(C_5H_5)(CO)_2PPh_3Mo^+$ converted to its saturated carbonyl salt $(C_5H_5)(CO)_3PPh_3Mo^+$.

Conclusions

MpH interacts with the organometallic Lewis acid $Mp^+PF_6^-$ and generates a stable μ-hydride complex $Mp{-}H{-}Mp^+PF_6^-$ (**5**). Attempts at converting this μ-hydride salt to bimetallic μ-formyl complexes by using CO, $P(OMe)_3$, or I^- were unsuccessful as other reaction pathways were instead followed. That **5** does not provide a kinetic pathway for hydride–CO insertion contrasts with the pronounced ease for generating analogous μ-acetyl complexes from the interaction of $MpCH_3$ and Mp^+.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged.

Registry No. **5**, 68868-70-2; **10**, 89303-04-8; MpH, 12176-06-6; Mp_2, 12091-64-4; MpI, 12287-61-5; $(C_5H_5)(CO)_2PPh_3MoH$, 33519-69-6; $(C_5H_5)(CO)_2[P(OMe)_3]MoH$, 61950-48-9; $(C_5H_5)Mo(CO)_3P(OMe)_3{}^+PF_6^-$, 68868-07-5; $(C_5H_5)Mo(CO)_2[P(OMe)_3]_2{}^+PF_6^-$, 89303-02-6; $(C_5H_5)(CO)_2PPh_3Mo^+PF_6^-$, 89303-05-9.

---

[40] (a) The NMR of *cis,cis*-$[(Ph_2MeP)(CO)_4Mo]_2H^-$ exhibits a triplet (δ −11.75) for its μ-hydride with a cis J_{PH} = 16.6 Hz; an analogous trans J_{PH} would be expected to be significantly lower, see ref 35. (b) Compare analogous J_{PH} values of 28 and 74 Hz for $[Cp(CO)_2Fe]_2(\mu\text{-H})(\mu\text{-dppe})^+$ and $[Cp(CO)_2FeH]_2(\mu\text{-dppe})$, respectively, where dppe = $Ph_2PCH_2CH_2PPh_2$: LaCroce, S. J.; Menard, K. P.; Cutler, A. R. *J. Organomet. Chem.* **1980**, *190*, C79.

Kinetics and Mechanism of Substitution Reactions of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$

Liang-Nian Ji, Mark E. Rerek, and Fred Basolo*

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received November 7, 1983

The reactions of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with phosphines and phosphites proceed readily in decalin at elevated temperatures to form monosubstituted products. For $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ a second substitution takes place with *P*-*n*-Bu_3 and P-c-Hx_3[1] which proceeds via an η^1-fluorenyl species, $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$. All these reactions take place by a second-order process, first order in metal complex and first order in nucleophile. Reaction rates depend on both size and basicity of the entering ligand. Substitution reactivity of these compounds contrasts the observed[2] thermal substitution inertness of $Mn(\eta^5\text{-}C_5H_5)(CO)_3$. This difference in reactivity is discussed in terms of the *indenyl ligand effect* of the indenyl and fluorenyl ligands vs. the cyclopentadienyl ligand.

Introduction

Although indenyl analogues of many cyclopentadienyl transition-metal compounds are known, kinetic studies comparing substitution at the metal center for cyclopentadienyl vs. indenyl are rare. In 1969 Hart-Davis and Mawby[3] found that the methyl migration in $Mo(\eta^5\text{-}C_9H_7)(CO)_3CH_3$ was ligand assisted. The S_N2 nature of this reaction was attributed to the ability of indenyl ligands to undergo an η^5 to η^3 migration allowing associative attack on the metal center. They believed that the benzene of the indenyl ring provided stabilization of the η^3-allyl intermediate; the cyclopentadienyl analogue reacted 10 times slower. White, Mawby, and Hart-Davis[4] also compared CO substitution by phosphines for the compounds $Mo(\eta^5\text{-}C_5H_5)(CO)_3X$ and $Mo(\eta^5\text{-}C_9H_7)(CO)_3X$ (X = Cl, Br, I). They found that CO substitution for the cyclopentadienyl compound proceeds by a purely dissociative (S_N1) pathway

---

[1] Abbreviations: P-*n*-Bu_3 = tri-*n*-butylphosphine; P-c-Hx_3 = tricyclohexylphosphine; $P(OEt)_3$ = triethyl phosphite; PPh_3 = triphenylphosphine; $P(O\text{-}i\text{-}Pr)_3$ = triisopropyl phosphite; P-*i*-Bu_3 = triisobutylphosphine; PMe_2Ph = dimethylhenylphosphine.

[2] Angelici, R. J.; Loewen, W. *Inorg. Chem.* **1967**, *6*, 682–686.

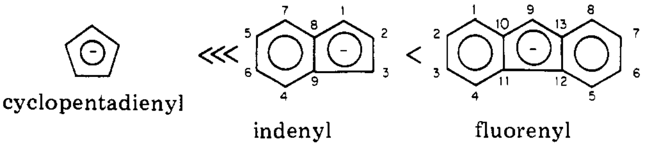
[3] Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403–2407.

[4] White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261–266. White, C.; Mawby, R. J.; Hart-Davis, A. J. *Ibid.* **1970**, *4*, 441–446.

0276-7333/84/2303-0740$01.50/0

whereas the indenyl compound substituted by both an S_N1 and ligand association (S_N2) pathway. There is a rate enhancement of about 6000 for the S_N1 path for the indenyl compound, compared to the cyclopentadienyl compound, in addition to the previously observed creation of an S_N2 path by the indenyl ligand. In another study, Mawby and Jones[5] compared the rate of CO replacement by $P(OEt)_3$ for $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ and $Fe(\eta^5\text{-}C_9H_7)(CO)_2I$. In both cases the replacement of CO by $P(OEt)_3$ proceeds by an S_N1 pathway, with the indenyl compound reacting 575 times faster than the cyclopentadienyl compound. To show that the rate enhancement was due to the electronic nature of the indenyl ligand, they hydrogenated the arene ring and the rate of CO replacement for this compound was only half the rate observed for the cyclopentadienyl compound. Although no kinetic studies comparing fluorenyl to indenyl or cyclopentadienyl have appeared, Diversi, Giusti, Ingrosso, and Lucherini[6] have reported that CO replacement of $P(OR)_3$ is more rapid in $Co(\eta^5\text{-}C_{13}H_9)(P(OR)_3)_2$ than in $Co(\eta^5\text{-}C_9H_7)(P(OR)_3)_2$.

Our investigations[7] of S_N2 CO replacement reactions of the indenyl compound $Rh(\eta^5\text{-}C_9H_7)(CO)_2$ show it to react 10^8 times faster than does the corresponding cyclopentadienyl compound. This *indenyl effect* of such a large rate enhancement prompted us to attempt substitution reactions of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$, although Angelici and Loewen[2] had observed that the corresponding cyclopentadienyl compound is inert to CO substitution even at 140 °C in decalin. We report here that the indenyl ligand does labilize the manganese system for substitution reactions, and our studies show this effect increases with changes in the ligand in the order



Such an indenyl effect on rates of substitution reactions of transition-metal organometallic species can be important in their syntheses and in their uses as homogenous catalysts where substitution lability at the metal center is essential.

Experimental Section

Compounds and Solvents. All experimental operations were carried out under an atmosphere of N_2. Hexane was stored over H_2SO_4 and then distilled from Na/benzophenone. Toluene, *p*-xylene, and decalin were distilled from Na. Decalin used for kinetics was bubbled with N_2 for 1 h after distillation. Dichloromethane was distilled from P_4O_{10}.

The phosphines and phosphites used in this study were obtained from Strem or Aldrich Chemicals. All were distilled from Na except PPh_3 and P-c-Hx_3 which were recrystallized from ethanol. *tert*-Butylpyridine (Reily) was distilled from BaO, and indene (Aldrich) was distilled under N_2. All other chemicals were used as received. The compounds $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ were prepared by methods described[8,9] in the literature and characterized by their IR and NMR spectra.

$Mn(\eta^5\text{-}C_9H_7)(CO)_2$P-c-$Hx_3$. The method of preparation of this compound is similar to that of King and Efraty[8] for the preparation of $Mn(\eta^5\text{-}C_9H_7)(CO)_2PPh_3$. A solution of 0.1 g of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and 0.1 g of P-c-Hx_3 in 25 mL of toluene was exposed to the light of a 550-W low-pressure Hg lamp (Hanovia) for 3 h, at which time the IR spectrum indicated that reaction was complete. The toluene was removed in vacuo, and 5 mL of hexane was added. The solution was allowed to stand overnight in a freezer affording 0.14 g of $Mn(\eta^5\text{-}C_9H_7)(CO)_2$P-c-$Hx_3$ as orange crystals (70% yield): IR (CH_2Cl_2) 1927, 1870 cm^{-1}. Anal. Calcd: C, 68.75; H, 7.98. Found: C, 68.81; H, 8.04.

$Mn(\eta^5\text{-}C_{13}H_9)(CO)_2$P-*n*-$Bu_3$. A solution of 0.5 g of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ and 0.6 mL of P-*n*-Bu_3 (1.5-fold excess) in 30 mL of hexane was exposed to the light of a 550-W low-pressure Hg lamp for 8 h. The volume was reduced to 10 mL and the solution filtered to remove the bright orange precipitate. The precipitate was rinsed with two small portions of methanol to remove excess P-*n*-Bu_3. The washings were added to the supernatant, the volume was reduced, and the collection process was repeated: collected 0.525 g of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2$P-*n*-$Bu_3$ (66%); IR (hexane) 1937, 1873 cm^{-1}. Calcd: C, 67.80; H, 7.60. Found: C, 67.59; H, 7.44.

$Mn(\eta^5\text{-}C_{13}H_9)(CO)$(P-*n*-$Bu_3)_2$. A solution of 0.2 g of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2$P-*n*-$Bu_3$ and 3.0 mL of P-*n*-Bu_3 (30-fold excess) in 15 mL of *p*-xylene was refluxed for 72 h under N_2. After removal of *p*-xylene and most of the P-*n*-Bu_3 in vacuo, the residue was dissolved in hexane and the remaining P-*n*-Bu_3 removed with 2 M HCl. After the solution was dried over $CaCl_2$, removal of solvent afforded 0.216 g of $Mn(\eta^5\text{-}C_{13}H_9)(CO)$(P-*n*-$Bu_3)_2$ (50.3%) as a yellow oil: IR (hexane) 1898 cm^{-1} (ϵ 5700); ^{31}P NMR 42.9 ppm downfield from H_3PO_4 (acetone-d_6).

Instrumentation. A Perkin-Elmer 283 spectrophotometer was used to record IR spectra with 0.2-mm KBr solution cells. For kinetic measurements, the absorbance mode was used. A JEOL FX-270 spectrometer was used to record NMR spectra. Compounds were stored in a Vacuum Atmospheres glovebox, and solutions were prepared by ampule transfer. Samples were thermostated with a silicone oil bath heated on a Corning PC 351 stirring hot plate. The uncertainty in the temperature of the reactions is placed at ±0.05 °C. Elemental analyses were performed by Galbraith Labs Inc., Knoxville, TN.

Kinetic Measurements. Prepared samples of 3.0 or 5.0 mL were placed in a silicone oil bath. The IR cells were flushed with N_2 and sealed with rubber septa before use. Aliquots were removed periodically to monitor at least 3–4 half-lives of reaction. The rates of reaction were followed by monitoring the decrease of the highest energy carbonyl absorption of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$. For substitution of a second CO ligand the increase in carbonyl absorption of the bissubstituted material $Mn(\eta^5\text{-}C_{13}H_9)(CO)L_2$ was monitored. Plots of ln A vs. time or ln $A_\infty - A$ vs. time were linear for more than 3 half-lives, and k_{obsd} was determined from the slope of this line by the least-squares method. The correlation coefficient of the least-squares line ($R^2 > 0.995$) was very good. Approximately 6×10^{-3} M solutions of metal complex were used, and all kinetic experiments were carried out under pseudo-first-order conditions with at least a 10-fold excess of nucleophile.

Only a representative number of kinetic products were prepared, isolated, and characterized as described above. All reactions give very similar carbonyl stretching frequencies, so it was assumed that all analogous reactions proceed similar to the cases where reaction products were isolated and characterized.

Measurements of ^{13}C NMR. The reaction of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with excess P-*n*-Bu_3 was monitored by ^{13}C NMR. A solution of 0.120 g of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ in 3 mL of decalin was prepared in a 10-mm NMR tube under N_2. The top of the NMR tube was sealed with a rubber septum. A 20-fold excess of P-*n*-Bu_3 was added (1 mL) and the tube heated at 135 °C for 45 min. The tube containing a deep green solution was cooled and placed in the probe of a JEOL FX-270 NMR spectrometer. The probe was heated to 120 °C, and the spectrum was taken in the normal manner. The results are given in Table IV.

Results

Substitution reaction rates of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ are summarized in Tables I and II. Substitution of CO takes place with a variety of phosphines and phosphites in decalin at elevated temperatures. All of these reactions are second-order processes. Figure 1 shows the dependence of the reaction of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$

---

[5] Jones, D. J.; Mawby, R. J. *Inorg. Chim. Acta* **1972**, *6*, 157–160.

[6] Diversi, P.; Giusti, A.; Ingrosso, G.; Lucherini, A. *J. Organomet. Chem.* **1981**, *205*, 239–246.

[7] Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208–1209.

[8] King, R. B.; Efraty, A. *J. Organomet. Chem.* **1970**, *23*, 527–533.

[9] Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749–752.

Table I. Rate Constants for the Reaction $Mn(\eta^5\text{-}C_9H_7)(CO)_3 + L \rightarrow Mn(\eta^5\text{-}C_9H_7)(CO)_2L + CO$ in Decalin at 130 °C and CO Stretching Frequencies of the Products

L	k, $M^{-1}\ s^{-1}$	ν_{CO}(product), cm^{-1}
PMe_2Ph	2.03×10^{-4}	1936, 1872
P-*n*-Bu_3	6.46×10^{-5}	1934, 1870
$P(OEt)_3$	4.69×10^{-5}	1950, 1888
P(O-*i*-$Pr)_3$	1.73×10^{-5}	1945, 1885
P(*i*-$Bu)_3$	2.84×10^{-6}	1936, 1870
P-c-Hx_3	2.14×10^{-6}	1929, 1865
PPh_3	1.68×10^{-6}	1944, 1888
4-*tert*-butylpyridine	NR[a]	

[a] No detectable reaction after 3 days.

Table II. Rate Constants for the Reactions $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3 + L \xrightarrow{k_1} Mn(\eta^5\text{-}C_{13}H_9)(CO)_2L + CO$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3 + 2L \xrightarrow{k_2'} Mn(\eta^5\text{-}C_{13}H_9)(CO)L_2 + 2CO$ in Decalin at 130 °C and CO Stretching Frequencies of the Products

L	k_1, $M^{-1}\ s^{-1}$	ν_{CO}, cm^{-1}	k_2', $M^{-1}\ s^{-1}$	ν_{CO}, cm^{-1}
P-*n*-Bu_3	2.14×10^{-2}	1937, 1873	5.04×10^{-4}	1898
$P(OEt)_3$	1.82×10^{-2}	1955, 1884	NR	
PPh_3	1.13×10^{-4}	1945, 1880	NR	
P-c-Hx_3	5.06×10^{-5}	1928, 1852	4.92×10^{-6}	1888

on the concentration of P-*n*-Bu_3 and of $P(OEt)_3$. As shown in this figure, there is a direct dependence of the rate of reaction on the concentration of added nucleophile. The zero intercepts indicate there is no detectable dissociative reaction. The activation parameters, shown in Table III, further support the S_N2 nature of these reactions, especially the large negative values of $\Delta S^{\ddagger}$.

The expected changes in the carbonyl stretching region of the IR spectra are obtained for reactions yielding monosubstituted products. This is also true for substitution of CO by P-*n*-Bu_3 in $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ affording $Mn(\eta^5\text{-}C_9H_7)(CO)_2P$-*n*-$Bu_3$ as the only product. Throughout the course of reaction, the only observed peaks are assignable to either $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ or $Mn(\eta^5\text{-}C_9H_7)(CO)_2P$-*n*-$Bu_3$. In contrast to this, the reaction of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with P-*n*-Bu_3 is not as straightforward as that observed for the indenyl compound. During the course of reaction, new ν_{CO} peaks grow in and then disappear (Figure 2), which are not attributable to starting material or mono- or bissubstituted products. Appearance of these new peaks is also accompanied by the reaction solution becoming green in color. Eventually the only remaining carbonyl absorption is that of $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$, which gives a light yellow solution. Although more species are present than those indicated by two consecutive substitution reactions, the kinetics of these

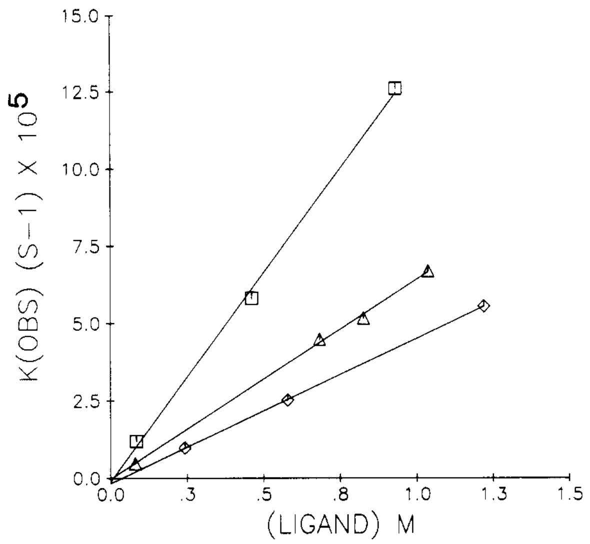


Figure 1. Plot of k_{obsd} (s^{-1}) vs. ligand concentration (M) for the reaction $Mn(\eta^5\text{-}C_9H_7)(CO)_3 + L \rightarrow Mn(\eta^5\text{-}C_9H_7)(CO)_2L + CO$ in decalin: △ P-*n*-Bu_3 (130 °C; ◇ $P(OEt)_3$ (130 °C); □, P-*n*-Bu_3 (140 °C).

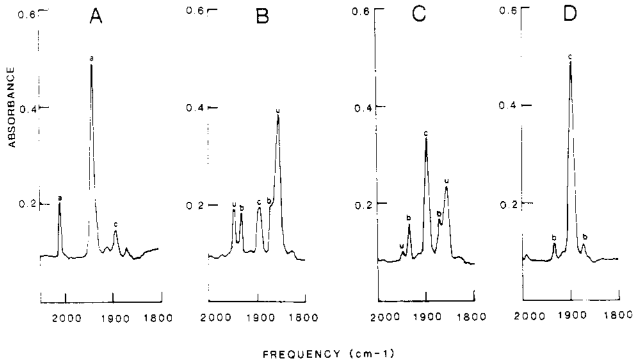


Figure 2. Spectral changes of δ_{CO} for the reaction $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3 + 2P\text{-}n\text{-}Bu_3 \rightarrow Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2 + 2CO$ in decalin at 140 °C: A, 6 min; B, 45 min; 4.5 h; D, 27 h; a, $Mn(\eta^5\text{-}C_9H_7)(CO)_3$; b, $Mn(\eta^5\text{-}C_{13}H_9(CO)_2P$-*n*-$Bu_3$; c, $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$; u, unknown species.

Table III. Rate Constants and Activation Parameters for the Substitution Reactions of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ in Decalin

complex	L	*T*, (°C)	k, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Mn(\eta^5\text{-}C_9H_7)(CO)_3$	P-*n*-Bu_3	121	4.04×10^{-5}	+17.0 ± 0.6	−36.2 ± 1.5
		130	6.46×10^{-5}		
		143	1.34×10^{-4}		
$Mn(\eta^5\text{-}C_9H_7)(CO)_3$	$P(OEt)_3$	121	2.75×10^{-5}	+16.8 ± 0.7	−37.3 ± 1.8
		130	4.69×10^{-5}		
		140	7.77×10^{-5}		
$Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$	P-*n*-Bu_3	100	3.90×10^{-3}	+15.8 ± 0.8	−27.6 ± 2.1
		120	1.07×10^{-2}		
		130	2.14×10^{-2}		
		140	3.30×10^{-2}		
$Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$	$P(OEt)_3$	98	3.07×10^{-3}	+16.3 ± 0.1	−26.5 ± 0.2
		120	1.11×10^{-2}		
		130	1.82×10^{-2}		
$Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$[a]	2-P-*n*-Bu_3	120	2.61×10^{-4}	+19.4 ± 0.5	−26.1 ± 1.2
		130	5.04×10^{-4}		
		140	1.01×10^{-3}		
$Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P$-*n*-$Bu_3$[b]	P-*n*-Bu_3	140	1.5×10^{-5}		

[a] k_2', see Scheme I. [b] k_2, see Scheme I.

reactions appear to be straightforward. Good kinetics for the first substitution reaction are obtained by monitoring the decrease of starting material peaks, and likewise good kinetics are observed for the second substitution by monitoring the increase of the peak of bissubstituted product. The rate of the second substitution was also measured starting with a solution of independently prepared $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$, and the rate constant was different than that obtained starting with $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$. Both reactions produce 60–70% of $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$ based on starting material concentration.

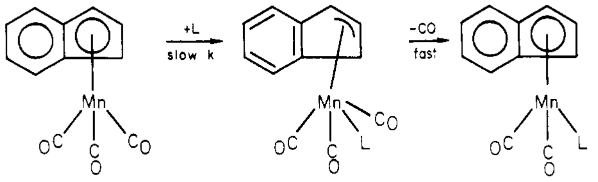
Discussion

In contrast to the reported[2] thermal CO substitution inertness of $Mn(\eta^5\text{-}C_5H_5)(CO)_3$, $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ readily substitutes one CO ligand with a variety of phosphines and phosphites in decalin at elevated temperatures. The reaction is S_N2, being first order in both metal complex and nucleophile (Figure 1). In addition to activation parameters (Table III) that support the S_N2 assignment, substitution is sensitive to both size and basicity of the nucleophile. Smaller more basic ligands react more rapidly than larger less basic ones. However, an attempt to correlate the rate of reaction with either cone angle[10] (size) or ΔHNP[11] (proton basicity) fails. Both factors are important enough that neither predominates the reactivity of a given nucleophile. Comparing ligands of similar cone angle, P-*i*-Bu_3 and PPh_3, the more basic P-*i*-Bu_3 reacts more rapidly. Conversely, comparing ligands of similar basicity, $P(OEt)_3$ and $P(O\text{-}i\text{-}Pr)_3$, the smaller $P(OEt)_3$ reacts faster. Finally, it should be noted that the good base 4-*tert*-butylpyridine does not react with $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ under our experimental conditions. This is probably due to the soft Mn(I) center preferring more polarizable (soft) ligands so the hard N ligand atom is often a poorer nucleophile than its proton basicity would suggest, a phenomenon often observed.[12]

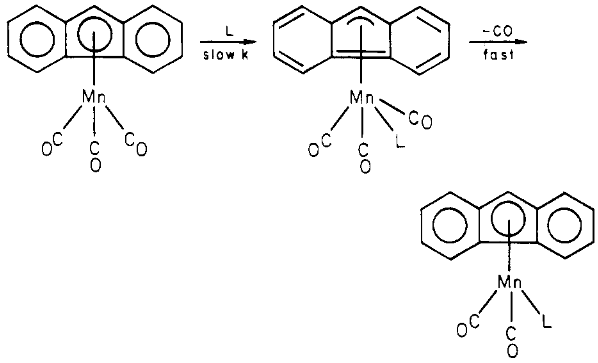
Carbon monoxide substitution chemistry of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ is more complicated than that of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$, as shown in Figure 2. For substitution of one CO ligand, the rate of reaction depends on the nature and concentration of entering nucleophile. This first-order dependence on reagent concentration and the activation parameters (Table III) support an S_N2 mechanism. For a given ligand, substitution is more rapid for the fluorenyl compound compared to the indenyl compound. This is true even though the larger fluorenyl ligand introduces a greater steric retardation on the rate of substitution than does the indenyl ligand. The very small but weakly basic $P(OEt)_3$ reacts 388 times faster with $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ than with $Mn(\eta^5\text{-}C_9H_7)(CO)_3$, but the strongly basic and very large P-c-Hx_3 reacts only 45 times faster. Once again both size and basicity are important in determining the reactivity of a given nucleophile.

Although the fluorenyl ligand exerts a greater steric influence on the rate of substitution than does the indenyl ligand, it does not do so to the extent that does pentamethylcyclopentadienyl on CO substitution[18] from $Co(\eta^5\text{-}C_5(CH_3)_5)(CO)_2$ or $Rh(\eta^5\text{-}C_5(CH_3)_5)(CO)_2$. For these two compounds a ligand with a cone angle greater than 145° does not react at all, regardless of its basicity. Thus, the fluorenyl ligand slows down reactions with larger nucleophiles but does not stop substitution as does the pentamethylcyclopentadienyl ligand.

All of these results support the mechanism first proposed by Hart-Davis and Mawby[3] for the S_N2 reactions of indenylmetal carbonyl compounds. These can be represented by one and two for $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$, respectively.



(1)



(2)

An alternative mechanism, also consistent with the kinetic data, is one where the η^5 and η^3 ring species of the starting compounds are in rapid preequilibrium followed by rate-determining attack on the η^3 intermediate by the entering nucleophile. The large increase ($\sim 10^8$ times) in rate of substitution of indenyl compounds compared to corresponding cyclopentadienyl compounds has been attributed[3,13,14] to benzene stabilization of the η^3-allyl intermediate. Rate enhancement of the fluorenyl ligand is perhaps due to delocalization of the π electrons over all three rings. The intermediate in (2) is a localized representation; since one does not expect aromatic stabilization from this representation, a much more delocalized system is envisioned. Cyclopentadienyl compounds have no resonance stabilization of the ene fragment of the allyl–ene intermediate, and this may be responsible for their slower rates of reaction. In further support of this hypothesis as to why indenyl- and fluorenylmetal complexes react more rapidly than corresponding cyclopentadienyl compounds is the fact that compounds containing both η^3-indenyl and η^3-fluorenyl ligands have been isolated; $W(\eta^5\text{-}C_9H_7)(\eta^3\text{-}C_9H_7)(CO)_2$[15] and $Zr(\eta^5\text{-}C_{13}H_9)(\eta^3\text{-}C_{13}H_9)(Cl)_2$[16] are examples.

Substitution reactions of fluorenyl compounds are further different from the indenyl compounds in that upon treatment with very basic phosphines such as P-*n*-Bu_3 or P-c-Hx_3, a second substitution reaction takes place. This is also in contrast to other cyclopentadienylmetal carbonyl compounds that often undergo substitution[17,18] of a second

---

(10) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(11) Henderson, W. A.; Streuli, C A. *J. Am. Chem. Soc.* **1960**, *82*, 5791–5974.

(12) (a) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 3929–3936. (b) Pearson, R. G. "Hard and Soft Acids and Bases", Dowden, Hutchinson, and Ross, Inc., StroudsBourg, PA, 1973.

(13) Eshtiagh-Hosseini, H.; Nixon, J. F. *J. Less Common Met.* **1978**, *61*, 107–121.

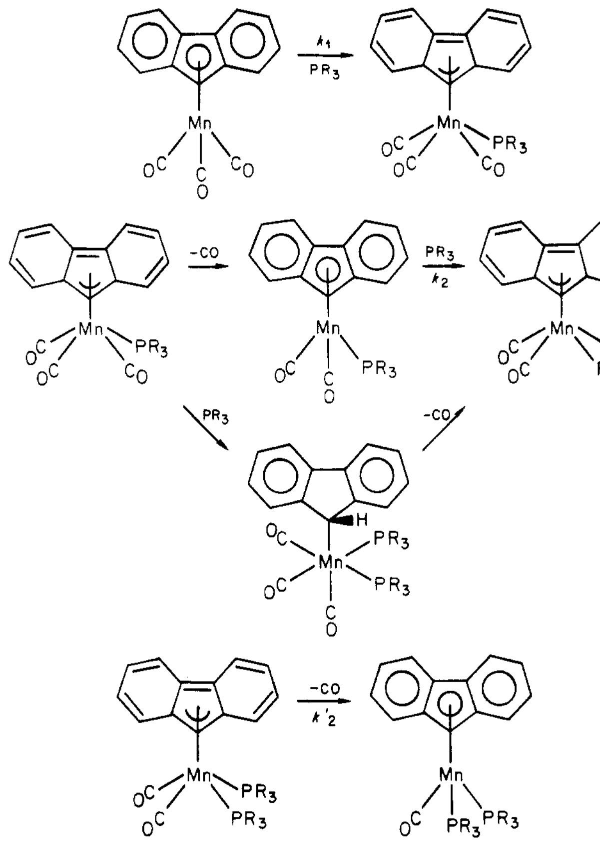
(14) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648–649; *J. Chem. Soc., Dalton Trans.* **1980**, 962–967.

(15) Nesmeyanov, A. N. et al. *J. Organomet. Chem.* **1978**, *159*, 189–200.

(16) Kowala, C.; Wunderlich, J. A. *Acta Crystallogr., Sect. B* **1976**, *B32*, 820–823.

(17) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663.

Scheme I. Proposed Mechanism for the Reaction of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with Excess P-*n*-Bu_3



CO when treated with good π-bonding ligands, such as phosphites or isocyanides, which compete with CO for π density in an S_N2 transition state. For corresponding fluorenyl compounds it appears that it is the fluorenyl ligand which competes with CO for π density so that the second substitution depends on the σ-donating ability (basicity) of the entering nucleophile, not η acceptance.

The spectral changes observed during the course of the second substitution reaction of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ are complicated (Figure 2). More peaks are present in the carbonyl region than can be accounted for by the presence of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$, $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$, and $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$. Similar spectra are obtained for the reaction with P-c-Hx_3. Appearance of the large 1850-cm^{-1} peak is accompanied by a color change from yello-orange to green. At the end of reaction, only the 1898-cm^{-1} peak of $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$ remains and the green color has disappeared. When an aliquot is removed from the green solution and allowed to stand at room temperature, both the green color and the 1850-cm^{-1} absorption gradually decrease and then disappear. The only peaks that remain are attributable to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$ or $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$.

The rate of replacement of two CO ligands by excess P-*n*-Bu_3 in $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$,designated by k_2', is approximately 70 times faster at 140 °C than the rate of CO replacement by P-*n*-Bu_3 in $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$, designated as k_2 (see Scheme I). Since both reactions afforded $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$, but at different rates, a different path must be available to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ which is not accessible to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$. Such a pathway is shown in Scheme I. The first step in substitution of CO in $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with P-*n*-Bu_3 probably involves generation of the intermediate $Mn(\eta^3\text{-}C_{13}H_9)(CO)_3P\text{-}n\text{-}Bu_3$. For poor nucleophiles such as PPh_3 and $P(OEt)_3$ this intermediate only loses CO to form monosubstituted η^5-fluorenyl species. A second path is possible for good nucleophiles such as P-*n*-Bu_3 or P-c-Hx_3 which can attack $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3P\text{-}n\text{-}Bu_3$ to form $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$. Loss of CO by $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$ or attack of P-*n*-Bu_3 on $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$ produces $Mn(\eta^3\text{-}C_{13}H_9)(CO)_2(P\text{-}n\text{-}Bu_3)_2$ which may lose CO to give $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P\text{-}n\text{-}Bu_3)_2$ as the final product. We do not rule out the possibility that several species may be in equilibria, nor do we have information on the geometries of some of the species.

Table IV. ^{13}C NMR Spectrum of the η^1 Intermediate in the Fluorenyl Region for the Reaction $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3 + 2P\text{-}n\text{-}Bu_3 \longrightarrow Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$ in Decalin at 120 °C

peak, ppm	assignment
146.4, 143.4	quaternary carbons (10-13)
128.6, 128.0, 125.5,120.9,	arene C-H carbons (1-8)
51.9	complexed five-membered ring carbon (9)

There are several attractive features of this mechanism. First all species contain favored 18-electron manganese centers. Second it satisfactorily explains the difference in rate of the second CO substitution on whether the starting material is $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ or $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$. The important species in Scheme I is $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$ which we believe is responsible for the unknown ν_{CO} absorptions in Figure 2. Principle support for the presence of $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$ comes from examination of the reaction of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with excess P-*n*-Bu_3 by ^{13}C NMR spectroscopy. At 120 °C under pseudo-first-order conditions, the ^{13}C fluorenyl resonance shown in Table IV were obtained. Seven resonances are observed as expected for an η^1-fluorenyl species. Four arene resonances are observed at 128.6, 128.0, 125.5, and 120.9 ppm which are appropriate for arene carbons bonded to hydrogen. These are very similar to those observed by Treichel and Johnson[9] for $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ which are at 127.7, 124.9 (2), and 124.5 ppm. The major difference between $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ and $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$ is where the quaternary carbon resonances occur. When coordinated, they are observed at higher field than the arene resonances; they are observed[9] at 106.1 and 95.2 ppm for $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$. Noncoordinated quaternary carbons are observed at lower field than the arene resonances; we observe these at 146.4 and 143.4 ppm. Finally C(9) is observed at 51.9 ppm which is appropriate for C(9) coordinated to a metal, being downfield from free C(9) which is observed[9] at 37.9 ppm. Although a few minor peaks are also seen which are attributable to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P\text{-}n\text{-}Bu_3$, the resonances listed in Table IV predominate the fluorenyl region of the ^{13}C NMR spectrum. It may be concluded from ^{13}C NMR spectroscopy that $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$ is the major species at the intermediate time of the reaction of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with excess P-*n*-Bu_3.

Furthermore, there is ample precedence for phosphine attack on organometallic species resulting in η^5 to η^1 ligand migration. Casey and co-workers[19] have observed that excess PMe_3 reacts with $Re(\eta^5\text{-}C_5H_5)(CO)_3$ in hexane at 55 °C to form (*fac*-$Re(\eta^1\text{-}C_5H_5)(CO)_3(PMe_3)_2$. This is the reason we have shown a facial arrangement for the η^1-

---

(18) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372–376.

(19) Casey, C. P.; O'Conner, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535–538.

fluorenyl species. Other compounds in which a cyclopentadienyl ligand undergoes an η^5 to η^1 shift upon treatment with PMe_3 include $W(\eta^5\text{-}C_5H_5)(CO)_2NO$,[20] $Mo(\eta^5\text{-}C_5H_5)(CO)_2NO$,[20] and $Re(\eta^5\text{-}C_5H_5)(CO)(Me)(NO)$.[21] Green and co-workers[14] have found that treatment of $Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2$ with excess *tert*-butyl isocyanide affords $Rh(\eta^1\text{-}C_9H_7)(CN\text{-}t\text{-}Bu)_4$, where the indenyl ligand has undergone the η^5 to η^1 migration. The reaction of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with excess P-*n*-Bu_3 to give $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$ appears to be the first example of an η^5 to η^1 migration involving the fluorenyl ligand.

In conclusion, it has been shown that the idenyl ligand can stabilize both lower coordination[4,5] (S_N1) and higher coordination (S_N2) intermediates,[3] but it appears to have about a 10^5 time greater effect on S_N2 reactions than it does on S_N1 reactions. This means that regardless of mechanism, substitution reactions of indenyl (and of fluorenyl) metal complexes are faster than are the same reactions of corresponding cyclopentadienyl compounds. The fluorenyl ligand is capable of $\eta^5 \rightarrow \eta^1$ rearrangements upon treatment with strongly basic alkylphosphines. Further studies are underway to examiine other ligands that may enhance the rate of S_N2 substitution at metal centers.

Acknowledgment. We thank the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation for support of this research. L.-N.J. was on leave from Zhongshan (Sun Yatsen) University and thanks the Ministry of Education of the People's Republic of China for support. We thank one of the reviewers who suggested the presence of an η^1 intermediate, which prompted us to go back to the laboratory and get ^{13}C NMR evidence in support of an η^1 species.

Registry No. $Mn(\eta^5\text{-}C_9H_7)(CO)_3$, 12203-33-7; $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$, 31760-87-9; $Mn(\eta^5\text{-}C_9H_7)(CO)_2P(c\text{-}Hx)_3$, 89415-04-3; $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P(n\text{-}Bu)_3$, 89397-45-5; $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P(n\text{-}Bu)_3)_2$, 89415-05-4; $Mn(\eta^5\text{-}C_9H_7)(CO)_2PME_2Ph$, 89415-06-5; $Mn(\eta^5\text{-}C_9H_7)(CO)_2P(n\text{-}Bu)_3$, 89415-07-6; $Mn(\eta^5\text{-}C_9H_7)(CO)_2P(OEt)_3$, 89415-08-7; $Mn(\eta^5\text{-}C_9H_7)(CO)_2P(O\text{-}i\text{-}Pr)_3$, 89415-09-8; $Mn(\eta^5\text{-}C_9H_7)(CO)_2P(i\text{-}Bu)_3$, 89415-10-1; $Mn(\eta^5\text{-}C_9H_7(CO)_2P(c\text{-}Hx)_3$, 89415-04-3; $Mn(\eta^5\text{-}C_9H_7)(CO)_2PPh_3$, 31871-85-9; $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P(n\text{-}Bu)_3$, 89397-45-5; $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P(OEt)_3$, 89415-11-2; $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2PPh_3$, 31760-88-0; $Mn(\eta^5\text{-}C_{13}H_9(CO)_2P(c\text{-}Hx)_3$, 89415-12-3; $Mn(\eta^5\text{-}C_{13}H_9)(CO)(P(c\text{-}Hx)_3)_2$, 89415-13-4; $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P(n\text{-}Bu)_3)_2$, 89415-14-5; $P(c\text{-}Hx)_3$, 2622-14-2; $P(n\text{-}Bu)_3$, 998-40-3; PMe_2Ph, 672-66-2; $P(OEt)_3$, 122-52-1; $P(O\text{-}i\text{-}Pr)_3$, 116-17-6; $P(i\text{-}Bu)_3$, 4125-25-1; PPh_3, 603-35-0; 4-*tert*-butylpyridine, 3978-81-2.

---

[20] Casey, C. P.; Jones, W. D.; Harsey, S. G. *J. Organomet. Chem.* **1981**, *206*, C38–C42.

[21] Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154–6156.

Hydrolysis Pathway Leading to the Formation of Novel Oxo- and Halo-Bridged Tin(IV) Ladder Compounds. The Molecular Structure of the Dimeric Distannoxanes $[Ph_2(Cl)SnOSnPh_2(OH)]_2 \cdot 2(CH_3)_2CO$ and $[Ph_2(Cl)SnOSnPh_2(Cl)]_2$[1,2]

Jean F. Vollano,[3] Roberta O. Day, and Robert R. Holmes*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received November 17, 1983

Acid–base adduct formation occurs in benzene solutions of Ph_2SnCl_2 with quinuclidine, Dabco, and acridine as ligands. By use of the latter base, the dichlorodistannoxane $[Ph_2ClSnOSnPh_2Cl]_2$ (**6**) also was isolated. In more polar solvents, hydrolysis reactions of Ph_2SnCl_2 occur more readily, leading to dimeric distannoxanes. The hydroxystannoxane $[Ph_2ClSnOSnPh_2OH]_2 \cdot 2(CH_3)_2CO$ (**5**) is isolated from the reaction of Ph_2SnCl_2 and quinuclidine in acetonitrile solution. It is also obtained by the analogous reaction of Dabco in acetone. Further characterized from these reactions were anionic complexes $[Ph_2SnCl_4][base \cdot H]_2$ (base = quinuclidine, Dabco, or acridine). The isolation and structural characterization of successive members in the hydrolysis lead to a mechanism of formation of the dimeric distannoxanes **5** and **6**. X-ray analysis shows they both possess "ladder" structures with tin atoms in trigonal-bipyramidal conformations. This is the first structural study of distannoxanes containing directly bonded aryl groups. **5** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.758 (2) Å, b = 19.327 (3) Å, c = 11.649 (1) Å, β = 92.87 (1)°, and Z = 2. The structure was refined to R = 0.028 and R_w = 0.039. For **6**, the monoclinic space group $P2_1/c$ was obtained with a = 10.284 (2) Å, b = 10.513 (3) Å, c = 22.143 (4) Å, β = 100.75 (2)°, and Z = 2. The structure was refined to R = 0.023 and R_w = 0.034.

Introduction

Partial hydrolysis of diorganotin dihalides leads to interesting classes of tetraorganodistannoxanes, $R_2XSnOSnR_2X$ and $R_2XSnOSnR_2OH$.[4-7] Solution work established dimeric formulations as early as 1939 for the halo derivatives $[Et_2XSnOSnEt_2(OH)]_2$ (X = Br, I).[8] Later work supported the dimeric nature of this class of

---

[1] Pentacoordinated Molecules. 52. Previous paper in the series: Holmes, R. R.; Day, R. O.; Harland, J. J; Holmes, J. M. *Organometallics* **1984**, *3*, 347.

[2] Presented at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983; Abstr. INOR 207.

[3] This work represents in part a portion of the Ph.D. Thesis of Jean F. Vollano, University of Massachusetts, Amherst.

[4] Okawara, R.; Wada, M. *J. Organomet. Chem.* **1963**, *1*, 81.

[5] Alleston, D. L.; Davies, A. G.; Hancock, M. *J. Chem. Soc.* **1964**, 5744.

[6] Alleston, D. L.; Davies, A. G.; Hancock, M.; White, R. F. M. *J. Chem. Soc.* **1963**, 5469.

[7] Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137–167 and references cited therein.

[8] Harada, T. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn)* **1939**, *35*, 290.

0276-7333/84/2303-0745$01.50/0