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Reactions of Metal Carbonyl Complexes. VII.[1] Kinetics and Mechanism of the Organosulfide Substitution Reactions of Some (η^5-Cyclopentadienyl)dicarbonyl(organosulfide)manganese(I) Complexes with Tertiary Phosphines and Phosphites[2]

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The organosulfide complexes η^5-$C_5H_5Mn(CO)_2(SR_2)$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph, CH_2Ph) and η^5-$C_5H_5Mn(CO)_2(THT)$ (THT = tetrahydrothiophene, C_4H_8S) undergo substitution of the organosulfide ligands with tertiary phosphines and phosphites (L) to form the η^5-$C_5H_5Mn(CO)_2L$ derivatives. The reaction rates in methylcyclohexane solution are first order in substrate, are independent of both the nature and the concentration of L, and increase with changes in the organosulfide ligand as $SMe_2 < THT < SEt_2 < S(n\text{-}Bu)_2 < S(n\text{-}Pr)_2 < S(CH_2Ph)_2 << SPh_2$. An S_N1 dissociative mechanism involving the rupture of the manganese–sulfur bonds as the rate-determining step is proposed. This mechanism is supported by the observed activation parameters and the small effect of solvent polarity on the rate of reaction of η^5-$C_5H_5Mn(CO)_2(THT)$ with $P(O\text{-}n\text{-}Bu)_3$.

Introduction

Over the last 15 years, numerous transition metal carbonyl complexes containing organosulfide ligands have been synthesized, e.g., $Cr(CO)_3(C_4H_4S)$,[4] $Mo(CO)_5(SEt_2)$,[5] $W(CO)_4(MeSCH_2CH_2SMe)$,[6] and *fac*-$Mo(CO)_3(SMe_2)_3$.[7] Suprisingly, most of the research on them has been concerned with their spectroscopic properties[8] and little is known about the relative labilities of organosulfide ligands in such complexes. In fact, no kinetic studies appear to have been reported for organometallic carbonyls containing even simple monodentate organosulfide ligands such as SMe_2 and SPh_2. However, some kinetic data have been reported for substitution of the bidentate organosulfide ligands 2,5-dithiahexane ($MeSCH_2CH_2SMe$) and 2,2,7,7-tetramethyl-3,6-dithiaoctane [$MeC(Me)_2SCH_2CH_2SC(Me)_2Me$] (L-L), in *cis*-$M(CO)_4(L\text{-}L)$ (M = Cr, Mo, W) by tertiary phosphites.[9,10]

In 1964, Strohmeier and Guttenberger[11] studied the photochemical reactions of η^5-$C_5H_5Mn(CO)_3$ with SEt_2 and SPh_2 and found that the monosubstituted derivatives η^5-$C_5H_5Mn(CO)_2(SEt_2)$ and η^5-$C_5H_5Mn(CO)_2(SPh_2)$ are produced. Moreover, the organosulfide ligands are apparently readily displaced by PPh_3 to form η^5-$C_5H_5Mn(CO)_2(PPh_3)$. As a first step in studying the potential of transition metal–carbonyl–organosulfide complexes for homogeneous catalysis, we have synthesized η^5-$C_5H_5Mn(CO)_2(SR_2)$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph, CH_2Ph) and η^5-$C_5H_5Mn(CO)_2(THT)$ (THT = tetrahydrothiophene, C_4H_8S) and studied the kinetics and mechanism of the organosulfide substitution reactions of these complexes with tertiary phosphines and phosphites (L) (eq 1).

$$\eta^5\text{-}C_5H_5Mn(CO)_2(\text{organosulfide}) + L \rightarrow \eta^5\text{-}C_5H_5Mn(CO)_2L + \text{organosulfide} \quad (1)$$

In this paper, we report the results of our synthetic and kinetic investigation.

Experimental Section

Preparation and Purification of Materials. The organosulfide complexes η^5-$C_5H_5Mn(CO)_2(SR_2)$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph, CH_2Ph) and η^5-$C_5H_5Mn(CO)_2(THT)$ were prepared photochemically from η^5-$C_5H_5Mn(CO)_3$ (a gift from Ethyl Corp.) and the appropriate ligand according to the procedure reported by Strohmeier and Guttenberger[11] for the synthesis of the SEt_2 derivative.[12] Further details of two typical syntheses are given below.

(a) η^5-$C_5H_5Mn(CO)_2(SMe_2)$. (η^5-Cyclopentadienyl)tricarbonylmanganese(I) (2.0 g, 9.8 mmol) and excess SMe_2 (10 ml) were dissolved in deaerated *n*-hexane (200 ml) in a Pyrex photochemical reactor and this mixture was irradiated with a 100-W Hanovia uv lamp for 5 hr. The resulting yellow solution was filtered into a 250-ml Schlenk tube and the filtrate was concentrated under reduced pressure (0° (0.02 Torr)) to about 50 ml. After cooling of this solution to −78°, a yellow, crystalline product was obtained. The supernatant liquid was removed with a syringe and the yellow crystals were dried under vacuum (0° (0.04 Torr)) and then recrystallized from *n*-hexane solution at −78°.

(b) η^5-$C_5H_5Mn(CO)_2[S(CH_2Ph)_2]$. A deaerated *n*-hexane solution (200 ml) of η^5-$C_5H_5Mn(CO)_3$ (2.15 g, 11 mmol) and $S(CH_2Ph)_2$ (3.01 g, 14 mmol) was irradiated as described above for 5 hr. After solvent removal (25° (0.02 Torr)), any unreacted starting materials were removed by sublimation (55° (0.01 Torr)). The dark yellow residue was recrystallized from deaerated *n*-hexane solution at room temperature to give air-stable, yellow-brown needles.

Table I. (η^5-Cyclopentadienyl)dicarbonyl(organosulfide)manganese(I) Complexes[a]

Complex	Yield, %	Mp,[b] °C	% C Calcd	% C Found	% H Calcd	% H Found	% S Calcd	% S Found	Mol wt[c]	ν(CO),[d] cm^{-1}
η^5-$C_5H_5Mn(CO)_2(SMe_2)$	68	31	45.4	45.3	4.7	4.7	13.5	13.2	238	1951 m, 1944 s, 1887 m, 1880 s
η^5-$C_5H_5Mn(CO)_2(SEt_2)$	73	28	49.6	49.5	5.7	5.9	12.0	12.0	266	1951 ms, 1942 s, 1887 ms, 1878 s
η^5-$C_5H_5Mn(CO)_2[S(n\text{-}Pr)_2]$	72	2	53.1	52.9	6.5	6.8	10.9	11.0	294	1949 m, 1941 s, 1885 m, 1878 s
η^5-$C_5H_5Mn(CO)_2[S(n\text{-}Bu)_2]$	76	15	55.9	56.0	7.2	7.4	10.0	9.6	322	1949 ms, 1941 s, 1885 ms, 1877 s
η^5-$C_5H_5Mn(CO)_2(THT)$	63	57	50.0	50.3	5.0	5.2	12.1	11.9	264	1953 m, 1942 s, 1889 m, 1878 s
η^5-$C_5H_5Mn(CO)_2[S(CH_2Ph)_2]$	61	115–118	64.4	64.6	4.9	4.9	8.4	8.2	390	1948 mw, 1939 s, 1886 m
η^5-$C_5H_5Mn(CO)_2(SPh_2)$[e]									362	1946 s, br, 1890 s, 1886 s

[a] The elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory Inc., Woodside, N.Y. [b] Taken on a Gallenkamp melting point apparatus (uncorrected). [c] From mass spectral data. [d] In *n*-hexane solution. The appearence of more than two ν(CO) bands for these dicarbonyl complexes is attributed to conformational isomerism about the Mn-S bonds [cf. I. S. Butler and T. Sawai, *Inorg. Chem.*, **12**, 1994 (1973)]. [e] Too impure for a satisfactory analysis; see ref 12.

The percent yields, melting points, elemental analyses, molecular weights, and ir-active ν(CO) modes of the complexes prepared in the present study are given in Table I. With the exception of the $S(CH_2Ph)_2$ complex (which is slightly soluble only in *n*-hexane and methylcyclohexane), all the complexes are readily soluble in acetone, benzene, chloroform, and aliphatic hydrocarbons. Again, with the exception of the $S(CH_2Ph)_2$ complex, they are all extremely air and light sensitive at room temperature, but they can be handled quite conveniently under a nitrogen atmosphere at lower temperatures. In fact, all the preparative procedures were carried out routinely in a large, walk-in cold room maintained at about 0° in order to minimize the risk of decomposition.

The sources and methods of purification of the ligands and methylcyclohexane solvent used in the kinetic studies are as follows: $P(n\text{-}Bu)_3$ and $P(O\text{-}n\text{-}Bu)_3$ from Eastman Kodak Co., fractional distillation at 128–130° (20 Torr) and 134–135° (16 Torr), respectively; PPh_3 from Alfa Inorganics, Inc., recrystallization from *n*-hexane solution; C_7H_{14} from Aldrich Chemical Co., fractional distillation over P_2O_5 under a nitrogen atmosphere at 100°.

Kinetic Studies. (a) Product Identification. The known complex η^5-$C_5H_5Mn(CO)_2(PPh_3)$ was prepared by the published method.[13] A slightly modified procedure of another literature method[14] was used to prepare η^5-$C_5H_5Mn(CO)_2[P(O\text{-}n\text{-}Bu)_3]$. Namely, after the photochemical reaction of η^5-$C_5H_5Mn(CO)_3$ and $P(O\text{-}n\text{-}Bu)_3$ in *n*-hexane, the solvent and excess ligand were removed under reduced pressure (25° (0.1 Torr)) and the product was then chromatographed on an alumina column (3 × 20 cm) under a nitrogen atmosphere using *n*-hexane as eluent. The reaction products of the kinetic runs were identified by the similarity of their ir and uv spectra to those of these two complexes.

(b) Determination of Rates. Since the ir-active CO stretching frequencies of the reactants and products are very similar and no significant intensity changes were observed during the reactions, the rates were determined by a uv photometric method. The $S(CH_2Ph)_2$, THT, PPh_3, and $P(O\text{-}n\text{-}Bu)_3$ monosubstituted complexes obey the Lambert–Beer law in the concentration range studied and this was assumed to be the case for all of the other complexes concerned.

The kinetic studies were carried out under nitrogen following the method described by Angelici and Loewen[15] for the reactions of η^5-$C_5H_5Mn(CO)_2$(olefin) with monodentate ligands (L) to form η^5-$C_5H_5Mn(CO)_2L$. Ten-milliliter volumetric flasks with Teflon stopcocks and fitted with Neoprene serum caps were wrapped in aluminum foil to exclude light. (A small amount of silicon grease proved to be quite effective in ensuring air-tightness of the serum caps over the temperature range studied and no changes in the observed rates were noted.) For determination of the reaction rates [except those of η^5-$C_5H_5Mn(CO)_2(SPh_2)$, vide infra], various concentrations of the ligands in methylcyclohexane solution (10 ml) were placed in the reaction vessels and these were thermostated to ±0.1° in a constant-temperature oil bath for at least 15 min prior to the actual kinetic runs. A desired amount of appropriate complex dissolved in methylcyclohexane was injected with an air-tight syringe into the reaction vessel; the amount of complex used was such that the concentration of the complex in the reaction mixture was approximately 7×10^{-3} *M*. Samples (~0.3 ml) were withdrawn by means of an air-tight syringe at appropriate time intervals and the uv spectra were recorded between 300 and 400 nm in the 0–1.0 absorbance range using standard 1.0-cm silica cuvettes. Except for the $S(CH_2Ph)_2$ and SPh_2 complexes, the maximum absorbance change occurred at ~340 nm and this is where the rates of reaction were determined. The reaction rates of η^5-$C_5H_5Mn(CO)_2[S(CH_2Ph)_2]$ were determined by measuring the absorbance changes at 290 nm. In the case of η^5-$C_5H_5Mn(CO)_2(SPh_2)$, the reactions were carried out in a 1.0-cm standard silica cuvette fitted with a Teflon stopcock. Both this reaction vessel and the reference cell were placed in a thermostated jacket in the uv spectrometer and the absorbance change at 317 nm was monitored continuously. The temperatures within the jacket were determined by means of a calibrated copper–constantan thermocouple and were accurate to ±0.1°.[16]

All of the reactions went to completion and the absorbances measured after at least 10 half-lives were used as the A_∞ values. The first-order rate constants were determined from the absorbance measurements by plotting ln $(A_t - A_\infty)$ vs. time using a standard linear least-squares treatment. These plots were linear to at least 75% completion and the rates were reproducible to within ±7%.

When the η^5-$C_5H_5Mn(CO)_2$(organosulfide) complexes were allowed to stand in methylcyclohexane solution in the absence of any entering ligand (L), the complexes decomposed slowly to form a brown precipitate and η^5-$C_5H_5Mn(CO)_3$ (as evidenced from the changes in the ir spectra of the mixtures). When a large excess of L was present, as in the kinetic runs, no decomposition products were observed. The rates of decomposition of η^5-$C_5H_5Mn(CO)_2(THT)$, η^5-$C_5H_5Mn(CO)_2[S(CH_2Ph)_2]$, and η^5-$C_5H_5Mn(CO)_2(SPh_2)$ at 95.0° were 5.2×10^{-5}, 10.0×10^{-5}, and 44.0×10^{-5} sec^{-1}, respectively. The first two values are about 35% of the corresponding reaction rates in the presence of excess L, while the latter is only about 10%.

Spectra. All uv spectra were recorded on a Coleman-Hitachi Model 124 spectrophotometer and the wavelength measurements are accurate to ±2 nm. The ir spectra in the ν(CO) region were measured on a Perkin-Elmer Model 521 grating spectrometer using scale expansion; the spectra were calibrated against known bands of CO gas and polystyrene film and are accurate to ±1 cm^{-1}.

Results and Discussion

As mentioned in the Introduction, Strohmeier and Guttenberger[11] had noted that diphenyl sulfide in η^5-$C_5H_5Mn(CO)_2(SPh_2)$ could be replaced by PPh_3 to form η^5-$C_5H_5Mn(CO)_2(PPh_3)$. Our results show that this is one example of the general reaction of such organosulfide complexes with tertiary phosphines and phosphites (L) (eq 1). Detailed kinetic studies were carried out for the reactions of η^5-$C_5H_5Mn(CO)_2(THT)$ with PPh_3, $P(n\text{-}Bu)_3$, and $P(O\text{-}n\text{-}Bu)_3$, and in the case of the latter two ligands good isosbestic points were observed in the uv spectra of the reaction mixtures. No isosbestic points were observed for the reactions with PPh_3

Table II. Rate Constants for the Reaction $\eta^5\text{-}C_5H_5Mn(CO)_2(THT) + L \rightarrow \eta^5\text{-}C_5H_5Mn(CO)_2L + THT$ in Methylcyclohexane Solution[a]

L	Temp, °C	[L], *M*	10^5k_{obsd}, sec^{-1}	10^5k_{av}, sec^{-1}
$P(n\text{-}Bu)_3$	85.0	0.12	3.0	3.1
		0.12	3.0	
		0.12	3.4	
	90.0	0.12	7.4	7.1
		0.12	7.1	
		0.12	7.1	
		0.24	7.1	
		0.25	7.4	
		0.54	6.8	
		0.68	7.0	
	95.0	0.12	14.0	13.5
		0.12	13.6	
		0.12	12.9	
$P(O\text{-}n\text{-}Bu)_3$	85.0	0.22	3.8	3.7
		0.41	3.7	
	90.0	0.09	7.7	7.7
		0.18	7.7	
		0.19	8.1	
		0.19	7.6	
		0.36	7.6	
		0.81	7.4	
	95.0	0.17	16.0	15.0
		0.17	14.5	
		0.37	14.6	
PPh_3	85.0	0.11	3.3	3.6
		0.11	3.6	
		0.11	3.8	
	90.0	0.05	7.0	7.2
		0.10	7.1	
		0.14	7.4	
		0.20	7.7	
		0.25	7.0	
	95.0	0.14	12.4	12.6
		0.26	12.2	
		0.26	13.3	

[a] Substrate concentration ~0.007 *M*.

owing to extensive overlap of the absorption spectrum of the complex with the strong absorption bands of the phenyl groups on the ligand. Kinetic studies on the other organosulfide complexes were restricted to the reactions with $P(O\text{-}n\text{-}Bu)_3$ and in all cases good isosbestic points were obtained. In addition, the rates of appearance of the products were equal to the rates of disappearance of the substrates in every case. All of these observations indicate that only one product, $\eta^5\text{-}C_5H_5Mn(CO)_2L$, was being formed in the reactions.

The reactions of $\eta^5\text{-}C_5H_5Mn(CO)_2(THT)$ with PPh_3, $P(n\text{-}Bu)_3$, and $P(O\text{-}n\text{-}Bu)_3$ in methylcyclohexane at 85.0–95.0° were all first order in substrate (Table II) suggesting the first-order rate law

$$\text{rate} = -d[\eta^5\text{-}C_5H_5Mn(CO)_2(THT)]/dt = k_{obsd}[\eta^5\text{-}C_5H_5Mn(CO)_2(THT)] \qquad (2)$$

Furthermore, since similar first-order behavior was observed for the reactions of all of the other organosulfide complexes studied (vide infra), the SN1 dissociative mechanism of eq 3

$$\eta^5\text{-}C_5H_5Mn(CO)_2(\text{organosulfide}) \xrightarrow[\text{slow}]{-\text{organosulfide}} \eta^5\text{-}C_5H_5Mn(CO)_2 \xrightarrow[\text{fast}]{+L} \eta^5\text{-}C_5H_5Mn(CO)_2L \qquad (3)$$

is proposed for all the reactions.

The observed high positive entropies of activation (~20 eu, Tables III and IV) support this dissociative mechanism which is similar to that proposed by Angelici and Loewen[15] for the olefin substitution reactions of $\eta^5\text{-}C_5H_5Mn(CO)_2(\text{olefin})$ with various ligands (L) to form $\eta^5\text{-}C_5H_5Mn(CO)_2L$. The existence of the reactive, coordinatively unsaturated intermediate, $\eta^5\text{-}C_5H_5Mn(CO)_2$, has been demonstrated recently by matrix ir spectroscopy at low temperatures.[17]

Table III. Activation Parameters for the Reaction $\eta^5\text{-}C_5H_5Mn(CO)_2(THT) + L \rightarrow \eta^5\text{-}C_5H_5Mn(CO)_2L + THT$ in Methylcyclohexane Solution[a]

L	10^5k_{av} (90°), sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$P(n\text{-}Bu)_3$	7.1	38 ± 2	27 ± 7
$P(O\text{-}n\text{-}Bu)_3$	7.7	37 ± 1	22 ± 3
PPh_3	7.2	34 ± 1	16 ± 5

[a] The errors quoted represent one standard deviation.

Table IV. Activation Parameters for the Reaction $\eta^5\text{-}C_5H_5Mn(CO)_2(\text{organosulfide}) + P(O\text{-}n\text{-}Bu)_3 \rightarrow \eta^5\text{-}C_5H_5Mn(CO)_2[P(O\text{-}n\text{-}Bu)_3] + \text{organosulfide}$ in Methylcyclohexane Solution[a]

Organosulfide	10^5k_{av} (85.0°), sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
SMe_2	3.0	35 ± 2	18 ± 6
THT	3.7	37 ± 1	22 ± 3
SEt_2	4.5	35 ± 1	19 ± 2
$S(n\text{-}Bu)_2$	6.3	36 ± 1	22 ± 2
$S(n\text{-}Pr)_2$	7.1	35 ± 1	19 ± 3
$S(CH_2Ph)_2$	8.1	32 ± 1	13 ± 3
SPh_2	610	32 ± 1	19 ± 2

[a] The errors quoted represent one standard deviation.

To substantiate further the validity of the SN1 dissociative mechanism proposed in eq 3, the rates of reaction of $\eta^5\text{-}C_5H_5Mn(CO)_2(THT)$ with $P(O\text{-}n\text{-}Bu)_3$ in a more polar solvent were investigated at 85.0°. In methylcyclohexane, the observed first-order rate constant was 3.7×10^{-5} sec^{-1}, while in nitromethane it was 2.3×10^{-5} sec^{-1}. Despite the large difference in the dielectric constants of these two solvents (2 and 36, respectively, at 20°), the difference in polarity of the solvents apparently has only a small effect on the rate of reaction. Such a small solvent effect would be expected for a dissociative mechanism involving the loss of a neutral organosulfide ligand in the rate-determining step.

The main purpose of our investigation was to gain some insight as to the relative labilities of various organosulfide ligands in a series of related metal carbonyl derivatives. To this end, we studied the kinetics of reaction 1 where the organosulfide ligand was SMe_2, SEt_2, $S(n\text{-}Pr)_2$, $S(n\text{-}Bu)_2$, SPh_2, and $S(CH_2Ph)_2$ and L was $P(O\text{-}n\text{-}Bu)_3$, and then we compared the results with those for the reaction of $\eta^5\text{-}C_5H_5Mn(CO)_2(THT)$ with the same ligand. As mentioned earlier, all the reaction rates were independent of both the nature and the concentration of the entering ligand (Table V) and this is why we proposed the SN1 dissociative mechanism given in eq 3. The associated activation parameters are listed in Table V.

The rates of reaction of $\eta^5\text{-}C_5H_5Mn(CO)_2(\text{organosulfide})$ with $P(O\text{-}n\text{-}Bu)_3$ in methylcyclohexane at 85.0° increase with changes in organosulfide as $SMe_2 < THT < SEt_2 < S(n\text{-}Bu)_2 < S(n\text{-}Pr)_2 < S(CH_2Ph)_2 \ll SPh_2$. That the rate of reaction for the SPh_2 complex is significantly greater than those for the other organosulfide complexes may reflect the electronic inductive effect of the substituents on the sulfur atoms. However, the most important factor in determining the relative reaction rates seems to be the steric interaction of these substituents with the $\eta^5\text{-}C_5H_5Mn(CO)_2$ moiety—the bulkier the substituent, the faster the reaction rate. Owing to its cyclic structure, the THT ligand in $\eta^5\text{-}C_5H_5Mn(CO)_2(THT)$ might be expected to experience less steric interaction with the $\eta^5\text{-}C_5H_5Mn(CO)_2$ moiety than is the case for the other organosulfide ligands (except SMe_2), and so its rate of substitution should be relatively slow, as is observed.

The rate of decomposition of $\eta^5\text{-}C_5H_5Mn(CO)_2(SPh_2)$ at 95.0° is about 10% of its rate of reaction with $P(O\text{-}n\text{-}Bu)_3$

Table V. Rate Constants for the Reaction η^5-$C_5H_5Mn(CO)_2$(organosulfide) + P(O-*n*-$Bu)_3$ → η^5-$C_5H_5Mn(CO)_2$[P(O-*n*-$Bu)_3$] + organosulfide in Methylcyclohexane Solution[a]

Organosulfide	Temp, °C	[L], *M*	10^5k_{obsd}, sec^{-1}	10^5k_{av}, sec^{-1}
SMe_2	85.0	0.10	2.8	2.8
		0.10	2.7	
		0.12	2.8	
	90.0	0.05	5.2	5.1
		0.12	4.9	
		0.12	5.0	
		0.12	5.1	
		0.20	5.4	
		0.73	5.0	
	95.0	0.11	11.1	10.6
		0.11	10.3	
		0.11	10.4	
		0.11	9.7	
		0.12	11.3	
SEt_2	85.0	0.11	4.6	4.5
		0.11	4.6	
		0.11	4.4	
	90.0	0.05	8.7	8.8
		0.11	9.3	
		0.12	8.3	
		0.12	8.8	
		0.22	9.2	
		0.38	8.5	
		0.80	8.9	
	95.0	0.11	16.3	17.2
		0.11	17.4	
		0.12	17.8	
S(*n*-$Pr)_2$	85.0	0.10	7.3	7.1
		0.11	7.1	
		0.11	7.1	
	90.0	0.05	13.8	14.1
		0.11	14.1	
		0.11	13.6	
		0.11	14.5	
		0.20	14.1	
		0.37	14.7	
		0.74	14.2	
	95.0	0.10	28	27
		0.10	26	
		0.10	28	
		0.11	27	
S(*n*-$Bu)_2$	85.0	0.11	6.3	6.3
		0.11	6.4	
		0.11	6.3	
	90.0	0.05	12.5	12.4
		0.12	12.6	
		0.12	12.2	
		0.12	12.4	
		0.22	12.7	
		0.43	12.1	
		0.94	12.2	
	95.0	0.13	24	25
		0.14	25	
		0.14	25	
$S(CH_2Ph)_2$	85.0	0.041	8.2	8.1
		0.043	8.1	
		0.043	8.2	
	90.0	0.042	15.8	14.9
		0.096	14.6	
		0.096	14.2	
		0.34	15.1	
	95.0	0.037	28	28
		0.042	28	
THT[b]	85.0			3.7
	90.0			7.7
	95.0			15.0
SPh_2	75.0	0.12	170	170
		0.12	170	
		0.12	170	
	80.0	0.01	290	320
		0.02	330	
		0.04	300	
		0.12	360	
		0.16	340	
		0.32	330	
		0.64	310	
	85.0	0.12	620	610
		0.12	600	

[a] The substrate concentrations were ~0.007 *M*, except in the case of the $S(CH_2Ph)_2$ complex (~0.003 *M*). [b] For the complete data, see Table II.

under the same conditions. The decomposition rates of the other organosulfide complexes are about 35% of their substitution rates. The anomalous behavior of the SPh_2 complex may be due to its extreme instability in that during its original preparation it may have already partially decomposed. The resulting methylcyclohexane solution of the complex could very well have contained some free SPh_2 which would interact with the η^5-$C_5H_5Mn(CO)_2$ intermediate and thus decrease the observed overall rate of decomposition. The actual rate of decomposition at 95.0° should therefore be much greater than the 4.4×10^{-4} sec^{-1} observed. However, in the presence of a large excess of the more nucleophilic P(O-*n*-$Bu)_3$ there seems to be no competition with free SPh_2.

Finally, it is worth noting that the organosulfide substitution reactions are, in general, somewhat slower than the analogous olefin substitution reactions. For example, ignoring the rate of the SPh_2 complex, the average rate for the substitution of an organosulfide ligand in η^5-$C_5H_5Mn(CO)_2$(organosulfide) by P(O-*n*-$Bu)_3$ at 90.0° in methylcyclohexane solution is 1.1×10^{-4} sec^{-1}, whereas the rates of olefin substitution in η^5-$C_5H_5Mn(CO)_2$(olefin) (olefin = ethylene, norbornadiene, and norbornylene) by PPh_3 under the same conditions are 1.7×10^{-4}, 5.1×10^{-4}, and 5.8×10^{-4} sec^{-1}, respectively.[15] Nevertheless, the organosulfides are still good leaving ligands and use of this has been made in their reactions with CS_2–PPh_3 to form the monothiocarbonyl complex η^5-$C_5H_5Mn(CO)_2(CS)$.[18] Indeed, the displacement of SEt_2 in the related η^5-$C_5H_5Mn(CO)(CS)(SEt_2)$ complex with CS_2–PPh_3 is a good way to synthesize the dithiocarbonyl complex η^5-$C_5H_5Mn(CO)(CS)_2$ (eq 4).[19]

$$\eta^5\text{-}C_5H_5Mn(CO)(CS)(SEt_2) + CS_2 + PPh_3 \rightarrow \eta^5\text{-}C_5H_5Mn(CO)(CS)_2 + PPh_3S + SEt_2 \qquad (4)$$

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Registry No. η^5-$C_5H_5Mn(CO)_2(SMe_2)$, 40674-63-3; η^5-$C_5H_5Mn(CO)_2(SEt_2)$, 40674-64-4; η^5-$C_5H_5Mn(CO)_2$[S(*n*-$Pr)_2$], 40674-65-5; η^5-$C_5H_5Mn(CO)_2$[S(*n*-$Bu)_2$], 40674-66-6; η^5-$C_5H_5Mn(CO)_2$(THT), 40674-67-7; η^5-$C_5H_5Mn(CO)_2[S(CH_2Ph)_2]$, 56391-54-9; η^5-$C_5H_5Mn(CO)_2(SPh_2)$, 56391-53-8; P(*n*-$Bu)_3$, 998-40-3; P(O-*n*-$Bu)_3$, 102-85-2; PPh_3, 603-35-0; η^5-$C_5H_5Mn(CO)_3$, 12079-65-1.

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Pentachlorocyclopentadienyl Derivatives of Manganese and Rhodium

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Reaction of diazotetrachlorocyclopentadiene, I, with di-μ-chloro-bis(1,5-cyclooctadienerhodium), $[RhCl(1,5\text{-}C_8H_{12})]_2$, gives high yields of ($\eta^5$-pentachlorocyclopentadienyl)(1,5-cyclooctadiene)rhodium, $Rh(\eta^5\text{-}C_5Cl_5)(COD)$, II. A similar reaction between I and pentacarbonylchloromanganese, $MnCl(CO)_5$, gave two products: pentacarbonyl(η^1-pentachlorocyclopentadienyl)manganese, $Mn(\eta^1\text{-}C_5Cl_5)(CO)_5$, III, and tricarbonyl($\eta^5$-pentachlorocyclopentadienyl)manganese, $Mn(\eta^5\text{-}C_5Cl_5)(CO)_3$, IV. III is the first transition metal complex containing a η^1-$C_5Cl_5^-$ ring and for which there is no analog in $C_5H_5^-$–Mn chemistry. These compounds and other polychloro-substituted cyclopentadienyl complexes have been characterized by infrared, Raman, ^{13}C nuclear magnetic resonance, and ^{35}Cl nuclear quadrupole resonance spectroscopy. Qualitative results from investigations into the mechanism of the insertion reactions of diazocyclopentadienes into manganese–halogen bonds are discussed.

The vast and rapid development of the chemistry of cyclopentadienylmetal compounds was aided by their convenient preparation using a variety of methods. However, the synthesis of pentasubstituted-cyclopentadienyl complexes, no less potentially interesting, has presented problems. In the past few years some of these problems have been solved and sound preparative routes to pentamethylcyclopentadienyl derivatives, for example, have been found. These efforts have been rewarded by new structures and reactivity imparted to the complexes by pentamethyl substitution. Recently pentachlorocyclopentadienyl complexes have attracted attention; the presence of five electronegative groups would be expected to modify the bonding and chemistry of the complexes in new and exciting ways.

The first of such compounds, decachloroferrocene and decachlororuthenocene were obtained by repetitive metalation exchange–halogenation reactions.[2,3] These showed a very high resistance to oxidation and also some interesting structural features.[4] Unsubstituted cyclopentadienyl complexes are conveniently prepared by the reactions of alkali metal, Grignard, or thallium derivatives of $C_5H_5^-$ with transition metal compounds.[5] Although LiC_5Cl_5[6] and the corresponding Grignard reagent have been known for some time, attempts to use them as reagents for the preparation of transition metal–pentachlorocyclopentadienyl complexes have been unsuccessful.[3,7] More recently salts of the $C_5Cl_5^-$ anion with large cations such as Tl^+, $(C_4H_9)_4P^+$, and $(C_2H_5)_3NH^+$ were isolated.[8,9] These were found to be thermally unstable, decomposing in the solid above −15° and in solution at −30°. For example, TlC_5Cl_5 "ignites spontaneously at −15° in air or in nitrogen atmosphere with emission of orange light but without violence".[8] All attempts to effect reaction of these compounds with transition metal halides to give perchlorocyclopentadienyl complexes failed. However, thallium pentachlorocyclopentadienide proved to be a useful reagent in the synthesis of a series of σ-bonded mercurial derivatives of the type $Hg(\eta^1\text{-}C_5Cl_5)_2$ and $Hg(\eta^1\text{-}C_5Cl_5)X$ (X = Cl, Br, Ph).[9,10]

We have reported that reactions of diazocyclopentadiene with dihalo-bridged rhodium dimers such as $[RhCl(1,5\text{-}C_8H_{12})]_2$ or with manganese pentacarbonyl halides give halo-substituted cyclopentadienyl complexes.[11] Since 2,3,4,5-tetrachlorodiazocyclopentadiene, I, is known, a logical extension of these insertion reactions was to investigate the suitability of this compound as a reagent for the preparation of pentachlorocyclopentadienyl complexes. This has been carried out with some success. We report here the facile high-yield syntheses of some derivatives of $C_5Cl_5^-$ including $Mn(\eta^1\text{-}C_5Cl_5)(CO)_5$, the first transition metal complex in which the $C_5Cl_5^-$ ligand is σ bonded. A preliminary communication has appeared.[12]

Experimental Section

Inert-atmosphere techniques were used in the synthesis of all new compounds described. Nitrogen gas (Liquid Carbonic, "Hi pure") was used without further purification. All solvents although of "spectroquality", were dried over molecular sieves (BDH, Type 5A) and were vacuum degassed or purged with nitrogen before use.

Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer. For typical spectra, calibration was accomplished using the 1602-cm^{-1} peak of polystyrene. For accurate determination of carbonyl stretching frequencies the instrument was run on expanded scale (ca. 1 cm^{-1}/mm of chart paper). Each spectrum was calibrated by recording the spectrum of indene[13] in the region 2300–1900 cm^{-1} before the sample was run. Reported values of $\nu(C{\equiv}O)$ are probably accurate to ±1 cm^{-1}.

Raman spectra were obtained from crystalline samples using a Spex Model 1400 spectrometer. The 5146-Å line of the argon laser was employed, and a cooled, spinning-cell technique was required to avoid thermal decomposition of the compounds. Nuclear quadrupole resonance spectra were recorded on a Decca Radar NQR spectrometer at 77°K.

^1H NMR spectra were run on a Varian Associates HA-100 spectrometer at 100 MHz with tetramethylsilane as an internal reference–lock signal. The ^{13}C NMR spectra were obtained using a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.2 MHz. Chemical shifts were measured in dichloromethane solution relative to the internal CD_2Cl_2 solvent resonance and are reported in ppm downfield (positive) from TMS using the conversion $\delta_{TMS} = \delta_{CD_2Cl_2} + 53.61$ ppm.

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