

Substitution of $\text{Mn}(\text{CO})_5$ Is Associative¹

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Abstract: The substitution of $\text{Mn}(\text{CO})_5$ radicals by triphenylphosphine (PPh_3) or triphenylarsine (AsPh_3) in hexane has been studied by observing the manner in which the competition between CCl_4 and PPh_3 or between CH_2Br_2 and AsPh_3 is affected by changes in concentrations of the reactants. In both cases the substitution process shows kinetics behavior indicative of an associative substitution process. The second-order rate constants are $1.7 (\pm 0.2) \times 10^7$ and $6.5 (\pm 0.8) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for PPh_3 and AsPh_3 , respectively, in hexane at 24 °C. Less extensive measurements provide analogous bimolecular rate constants for substitution by $\text{P}(n\text{-Bu})_3$, $\text{P}(i\text{-Pr})_3$, and $\text{P}(O\text{-}i\text{-Pr})_3$ of $1.0 (\pm 0.1) \times 10^9$, $6.7 (\pm 0.7) \times 10^7$, and $3.1 (\pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, respectively. There is no evidence in the results for a concurrent dissociative loss of CO from $\text{Mn}(\text{CO})_5$. On the basis of the data for AsPh_3 , which exhibits the smallest associative rate constant, the first-order dissociative rate constant must be less than about 90 s^{-1} .

During the past dozen years there has been an increasing interest in the properties of organometallic metal-centered radicals. The radicals most widely studied to date involve CO as the sole ligand, or in company with other groups such as $\eta^5\text{-C}_5\text{H}_5$. Many of the most studied species are nonpersistent; they are generated photochemically, by irradiation of metal-metal-bonded dinuclear species,² or arise as intermediates in the course of radical chain reactions.^{3,4}

The reactions of the metal carbonyl radicals, once formed, include the following: (a) recombination to form spin-paired dinuclear compounds (a substantial body of rate constant data derived from flash photolysis and pulsed electrolysis results now exists to show that those radicals that are not sterically hindered recombine at near diffusion-controlled rates⁵⁻⁸), (b) substitution of CO by nucleophilic ligands such as phosphines and amines, (c) atom-transfer reactions, e.g., abstraction of Cl from CCl_4 ,⁹ or H from HSnBu_3 ,¹⁰ (a substantial body of quantitative rate data for halogen atom transfer reactions has recently been reported for $\text{Mn}(\text{CO})_5$ and $\text{Mn}(\text{CO})_L$ radicals¹¹), and (d) outer-sphere electron transfer. Although examples of such reactions have been known for some time,¹² there have been few quantitative studies of the rates of such processes.¹³

Our concern in the present paper is with the substitution reactions of the $\text{Mn}(\text{CO})_5$ radical. The substitution lability of metal carbonyl radicals was established early. It was noted that the quantum yields for photochemical substitution of dinuclear species, e.g., $\text{Mn}_2(\text{CO})_{10}$, are between 0.1 and 1:^{9,14} second, facile substitution of the radicals is a key aspect of their involvement in radical chain substitution processes.³ Various photochemical reactions of metal carbonyls, e.g., of $\text{Re}_2(\text{CO})_{10}$ with H_2 ¹⁵ and H_2O ¹⁶ or of various dinuclear metal carbonyls with hydrides,⁴ are

most readily accounted for in terms of a high lability of the metal carbonyl radical formed via metal-metal bond homolysis.

The lability of the metal carbonyl radicals is of central importance for understanding their chemical behaviors, and the evidence for it is overwhelming. The question that naturally derives from this lability is the mechanism by which substitution occurs. Related to this are the questions of how particular substituents on the metal center affect lability, and the variation in lability among metals. In earlier work from this laboratory, concerned with measurements of the quantum yields for photo-substitution of $\text{Mn}_2(\text{CO})_{10}$ and the dependence of the quantum yield on ligand identity and concentration, Kidd and Brown considered the alternative dissociative and associative pathways for substitution of $\text{Mn}(\text{CO})_5$.¹⁴ They concluded that the evidence, while not definitive, suggested a dissociative pathway. However, the slower substitution of one ligand L for another in $\text{Mn}(\text{CO})_4\text{L}$, or replacement of CO by L in such species, appeared to occur via an associative pathway. Replacement of L by CO in $\text{Mn}(\text{CO})_3\text{L}_2$ species has also been shown to occur via an associative process,¹⁷ as has substitution of CO in $\text{V}(\text{CO})_6$.¹⁸

Poë and co-workers have consistently favored an associative pathway for substitution. Fox, Malito, and Poë provided convincing evidence that substitution of $\text{Re}(\text{CO})_5$ by a phosphine ligand occurs via an associative pathway under the conditions that normally obtain in such reactions.¹⁹ Their procedure consisted in evaluating the competition for reaction of the $\text{Re}(\text{CO})_5$ radical with either CCl_4 or phosphine to yield $\text{Re}(\text{CO})_5\text{Cl}$ or $\text{Re}(\text{CO})_4\text{LCl}$, respectively. Extension of this experiment to $\text{Mn}(\text{CO})_5$ seemed important, because the experiment is capable of providing quantitative data regarding the rate constants for substitution. Further, one might expect that the larger Re would more readily accommodate an associative process, while at the same time being less reactive toward a dissociative step (in the spin-paired, 18-electron systems, Re is less reactive toward dissociative CO loss than Mn^{20}). We report in this paper the results of a study of the substitution reactions of $\text{Mn}(\text{CO})_5$ under conditions of competition with halogen atom abstraction, using experimental protocols similar to those employed by Fox, Malito, and Poë. The results show that the substitution is associative for PPh_3 and AsPh_3 , ligands of substantially different nucleophilicity. We report also the rate constants for associative substitution of $\text{Mn}(\text{CO})_5$ by several phosphines in addition to PPh_3 and AsPh_3 .

Experimental Section

Materials. Hexane (C_6H_{14}), obtained from Burdick and Jackson Laboratories, Inc., was washed successively with concentrated H_2SO_4 ,

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H₂O, saturated aqueous NaHCO₃, and H₂O, dried with MgSO₄, refluxed with CaH₂ under N₂ for several hours, and then distilled. The distillate was purged with Ar for 15 min and then subjected to several freeze-pump-thaw cycles before transfer to the glovebox.

Triphenylarsine (AsPh₃), purchased from Alfa Chemical Co., was recrystallized twice from absolute alcohol and dried in vacuo prior to use. A similar procedure was employed to purify triphenylphosphine (PPh₃), purchased from Strem Chemical Co. The other phosphine ligands employed, purchased from Strem, were purified by distillation from CaH₂ under an N₂ atmosphere. Dimanganese decacarbonyl, Mn₂(CO)₁₀, obtained from Pressure Chemical Co., was sublimed (65 °C (1 mm Hg)) and refrigerated under N₂ before use.

Dibromomethane (CH₂Br₂) was obtained from Aldrich Chemical Co. It was washed successively with concentrated H₂SO₄, H₂O, dilute NaOH, and H₂O. After predrying with CaCl₂, it was distilled from P₂O₅ under N₂. Carbon tetrachloride (CCl₄) was purchased from E. K. Industries. It was washed three times with hot ethanolic KOH, washed with H₂O, dried with CaCl₂, and then distilled from P₂O₅ under N₂.

Competition Experiments. Hexane solutions of Mn₂(CO)₁₀, typically 2.5 × 10⁻³ M, were prepared in a glovebox, using actinic glassware. After the desired quantity of L was added, halide donor stock solution was added with a volumetric pipet. The final solution was loaded into a solution IR cell with KBr windows. The IR cell was protected from exposure to light while it was being loaded into a chamber in which the solution was maintained at 0 °C. It was then irradiated for 3 min with radiation from a medium-pressure mercury lamp, filtered to pass only the 366-nm region. This length of irradiation time produced about 15% reaction of the starting Mn₂(CO)₁₀. A low level of conversion was employed to minimize secondary photolysis reactions. It was necessary to maintain the solution at 0 °C during photolysis and during the subsequent period of analysis to prevent a thermal substitution reaction of the ligand L with Mn(CO)₅Cl. The kinetics of this reaction are known;²¹ maintenance of a lowered temperature during the experiment assuredly reduces the thermal substitution process to an inconsequential level.

The constant-temperature chamber was moved to the cell compartment of a Nicolet Model 7199C FT-IR spectrophotometer, following irradiation of solutions containing L = PPh₃ or AsPh₃, and a spectrum of the CO stretching region was obtained. Spectra were obtained with a Beckman Model 4240 IR spectrophotometer for L = P(*n*-Bu)₃, P(*i*-Pr)₃, or P(*o*-i-Pr)₃. For all ligands studied, a second spectrum was taken immediately after the first, to ensure that no change in the spectrum due to thermal reaction had occurred.

In the reaction of Mn₂(CO)₁₀ with PPh₃, the IR spectra of the halogen atom transfer product species overlap in part with those of the starting Mn₂(CO)₁₀ and with Mn₂(CO)₉PPh₃, formed as a minor product. The spectra of Mn₂(CO)₁₀ and Mn₂(CO)₉PPh₃ were subtracted from the irradiated solution spectrum with spectral analysis routines to yield a spectrum containing only the absorbances due to Mn(CO)₅Cl and Mn(CO)₄PPh₃Cl. Having determined the extinction coefficient of a band at 2045 cm⁻¹ due to Mn(CO)₅Cl and of a corresponding band in the vicinity of 2090 cm⁻¹ due to Mn(CO)₄PPh₃Cl, we could calculate the relative concentrations, of these two species in the solution. A similar procedure was followed in analyzing the spectra from the reaction of Mn₂(CO)₁₀ with AsPh₃ and CH₂Br₂, except that the presence of Mn₂(CO)₉AsPh₃ could be ignored in the analysis because its absorbances did not overlap with those due to Mn(CO)₅Br or Mn(CO)₄AsPh₃Br. A series of solutions containing Mn₂(CO)₁₀, PPh₃, and CCl₄ was studied in which the ratio $a = [\text{CCl}_4]/[\text{PPh}_3]$ was maintained constant, but in which the concentrations of both species were successively diluted. The value a was chosen to give IR bands due to Mn(CO)₅Cl and Mn(CO)₄PPh₃Cl of comparable intensity. The advantages of this procedure over the alternative of maintaining a constant concentration of CCl₄ and varying the concentration of L are discussed below. It was not possible to follow this practice in the case of AsPh₃, because the ligand substitution process is relatively much slower and higher concentrations of AsPh₃ and CH₂Br₂ were required to compete with recombination of Mn(CO)₅ radicals than is the case for PPh₃. Accordingly, the procedure described by Fox, Malito, and Poë¹⁹ was followed.

Results and Discussion

Photochemical Reaction of Mn₂(CO)₁₀ with CCl₄ and PPh₃. Irradiation with 366-nm radiation of a hexane solution of Mn₂(CO)₁₀, CCl₄, and PPh₃ at 0 °C leads to Mn₂(CO)₉PPh₃, Mn(CO)₅Cl, and Mn(CO)₄LCl as the only observable products, as identified by FT-IR. The concentration of Mn₂(CO)₁₀ used was 5.0 × 10⁻⁴ M. The concentration of PPh₃ was varied over the

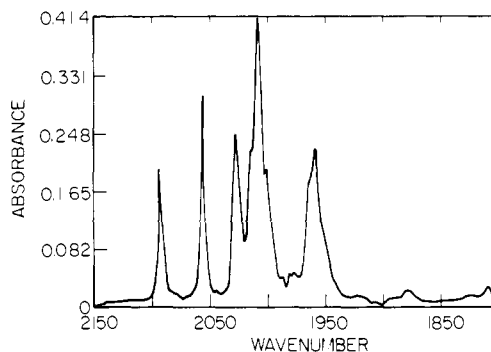
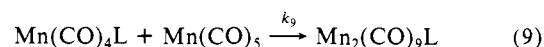
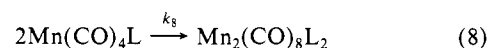
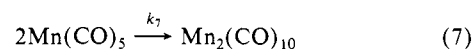
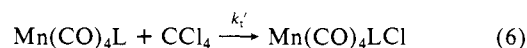
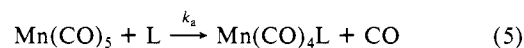
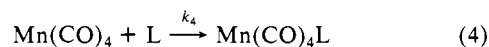
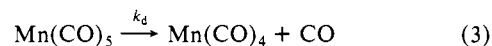
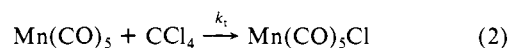
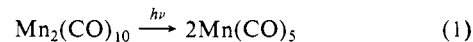


Figure 1. Product IR spectrum in hexane solution following irradiation of Mn₂(CO)₁₀ in the presence of PPh₃ and CCl₄. Absorbances due to Mn₂(CO)₁₀ and Mn₂(CO)₉PPh₃ have been subtracted out.

range 1 × 10⁻³ to 1 × 10⁻¹ M, while maintaining the ratio [CCl₄]/[PPh₃] = 8.3. Upon subtraction of the absorbances due to Mn₂(CO)₁₀ and Mn₂(CO)₉PPh₃, the spectrum shown in Figure 1 results. All bands can be assigned to either of the product halides, based on the spectra of the pure compounds. The 2092-cm⁻¹ band in Figure 1, due to Mn(CO)₄PPh₃Cl, and that at 2055 cm⁻¹, due to Mn(CO)₅Cl, were employed in the analysis.

The reaction system can be analyzed in terms of the following scheme:



Under the conditions of the photochemical experiments the radicals produced in step 1 do not exhibit any luminescence behavior. On the microsecond time scale of their recombination or reaction with a nucleophile or with a halogen atom donor, they are presumably in their ground electronic states and thermally equilibrated with surrounding solvent molecules.

The ratio of product concentrations, [Mn(CO)₄LCl]/[Mn(CO)₅Cl], can be expressed in terms of the rate constants in the scheme above and concentrations of L and CCl₄

$$\frac{[\text{S}]}{[\text{U}]} = \frac{[\text{Mn}(\text{CO})_4\text{LCl}]}{[\text{Mn}(\text{CO})_5\text{Cl}]} = \frac{k_d + k_a[\text{L}]}{k_i[\text{CCl}_4]} \quad (10)$$

When [L] is varied with [CCl₄] constant, the ratio [S]/[U] vs. [L] is a straight line with slope $k_a/(k_i[\text{CCl}_4])$, and intercept $k_d/(k_i[\text{CCl}_4])$. When [CCl₄]/[L] is a constant, a , the ratio [S]/[U] vs. 1/[L] is linear, with slope k_d/ak_i and intercept k_a/ak_i .

$$\frac{[\text{S}]}{[\text{U}]} = \frac{k_d}{ak_i[\text{L}]} + \frac{k_a}{ak_i} \quad (11)$$

A graph of [S]/[U] vs. 1/[L] for the competition with L = PPh₃ is shown in Figure 2. Least-squares analysis of the data results in a correlation of 0.96, with slope 1.1 (±2.0) × 10⁻⁴ and intercept 1.5 ± 0.1. Although the data exhibit considerable scatter as a result of the small absorbances measured, it is evident that the slope is quite small. The slope equals k_d/ak_i . The value of k_i ,

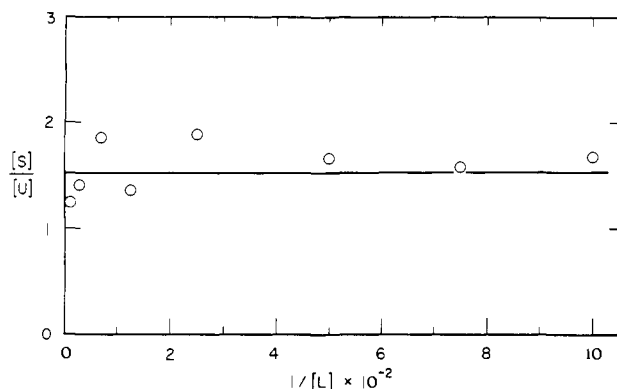


Figure 2. Ratio of concentrations $[\text{Mn}(\text{CO})_4\text{PPh}_3\text{Cl}]/[\text{Mn}(\text{CO})_5\text{Cl}] = [\text{S}]/[\text{U}]$ as a function of $[\text{PPh}_3]^{-1}$.

recently measured in our laboratories with a laser flash apparatus,¹¹ was found to be $1.4 (\pm 0.1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Given that $a = 8.3$, this places an upper limit of about $2 \times 10^3 \text{ s}^{-1}$ on k_d .

The intercept corresponds to k_a/ak_t . Thus we estimate that $k_a = 1.7 (\pm 0.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. It should be noted that these values of rate constant are referenced to the value for k_t , which was obtained at 24 °C, even though the competition experiment was conducted at 0 °C. Both k_a and k_t are large rate constants for processes that are not expected to have large enthalpies of activation. Thus, the ratio k_a/k_t should not vary significantly over the 24 °C temperature interval, as compared with the other uncertainties in the experiment.

To test the validity of the reaction scheme in light of the estimated rate constants, computer modeling experiments were carried out with a modification of the HAVCHM program.²² The values of the rate constants for reactions 2, 7, and 8 were taken from the literature and were taken from the current experiments for reactions 5 and 3, using the upper bound for the latter. The rate constant for reaction 9 was estimated to be the geometric average of the values of reactions 7 and 8. The rate constant for reaction 4 was set at $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, on the assumption that the 15-electron species would be strongly nucleophilic. (The value for this rate constant is not important, so long as the process is assumed to be fast.) The rate constant for reaction 6 could be estimated from the values for closely related reactions.¹¹ The rate of production of $\text{Mn}(\text{CO})_5$ radicals could be estimated to be on the order of 10^{-6} M s^{-1} from actinometry results involving the type of lamp employed in the study. The value chosen for this quantity is not important so long as physically reasonable values are employed.

The concentrations of $\text{Mn}(\text{CO})_5\text{Cl}$, $\text{Mn}(\text{CO})_4\text{PPh}_3\text{Cl}$, $\text{Mn}_2(\text{CO})_9\text{PPh}_3$, and $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ were calculated as a function of time. The amounts of all dinuclear products were found to be negligible. The ratio $[\text{Mn}(\text{CO})_4\text{PPh}_3\text{Cl}]/[\text{Mn}(\text{CO})_5\text{Cl}]$ was calculated to be 1.51, in excellent agreement with the experimentally determined intercept (Figure 2). Virtually identical results are obtained when reactions 3 and 4 were omitted entirely. These calculations confirm not only that the analysis of the experimental data is numerically reasonable, but also that the radicals present during reaction are not forming significant amounts of products other than $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{Mn}(\text{CO})_4\text{PPh}_3\text{Cl}$. (The small amount of $\text{Mn}_2(\text{CO})_9\text{PPh}_3$ formed during reaction is undoubtedly due to reaction of PPh_3 with $\text{Mn}_2(\text{CO})_9$, formed via CO loss.²³) These calculations reveal what is evident from the experimental results shown in Figure 2: over a wide range of PPh_3 concentration, extending to as low as 10^{-3} M , the substitution of $\text{Mn}(\text{CO})_5$ by PPh_3 is entirely associative in character.

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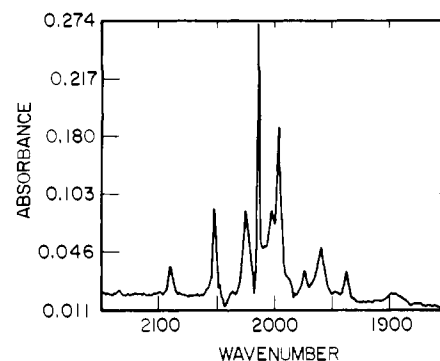


Figure 3. Product IR spectrum in hexane following irradiation of $\text{Mn}_2(\text{CO})_{10}$ in the presence of AsPh_3 and CH_2Br_2 . Absorbances due to $\text{Mn}_2(\text{CO})_{10}$ have been subtracted out.

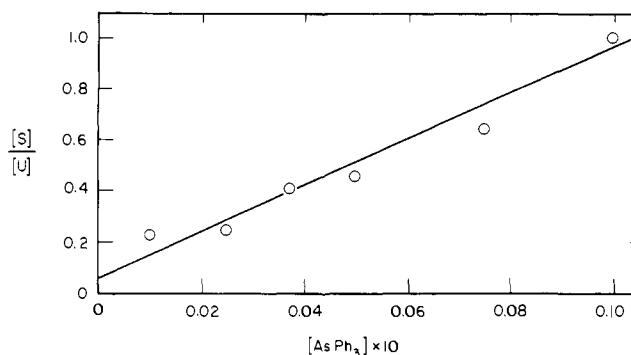


Figure 4. Ratio of concentrations $[\text{Mn}(\text{CO})_4\text{AsPh}_3\text{Br}]/[\text{Mn}(\text{CO})_5\text{Br}] = [\text{S}]/[\text{U}]$ as a function of $[\text{AsPh}_3]$.

Photochemical Reaction of $\text{Mn}_2(\text{CO})_{10}$ with CH_2Br_2 and AsPh_3 .

The upper limit that can be placed on k_d by the experiments involving PPh_3 and CCl_4 is still quite large. This is so because the associative rate constant is so large. In an effort to set a lower value for upper bound to k_d we have examined the competition reaction for AsPh_3 as ligand. There is considerable evidence in the literature to the effect that AsPh_3 is a poorer nucleophile toward low-valent metal centers than PPh_3 .^{24,25} In the present work it was soon evident that indeed AsPh_3 was less reactive toward $\text{Mn}(\text{CO})_5$ than the phosphine ligands. To carry out the competition experiment it was necessary to identify a halogen atom donor for which the halogen atom transfer rate constant is correspondingly lower than for CCl_4 . Dibromomethane proved to be satisfactory. Direct measurement of the Br atom transfer rate leads to the value of $7.2 (\pm 1.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.¹¹

To preclude formation of significant amounts of $\text{Mn}_2(\text{CO})_8(\text{AsPh}_3)_2$, it was necessary to maintain a fairly high concentration of CH_2Br_2 , on the order of 0.1 M. This in turn militated against use of the same procedure employed for PPh_3 , because that would have required that some solutions contain undesirably high CH_2Br_2 concentrations. Accordingly, we employed the procedure used by Fox, Malito, and Poč, varying the AsPh_3 concentration over the range 1.0×10^{-3} to $1.0 \times 10^{-2} \text{ M}$. Computer modeling of the reaction, using known rate constants and estimates in the manner described earlier for PPh_3 , led to the conclusion that $\text{Mn}_2(\text{CO})_8(\text{AsPh}_3)_2$ would not be formed in significant concentrations under these conditions and that $\text{Mn}(\text{CO})_5\text{Br}$ and $\text{Mn}(\text{CO})_4\text{AsPh}_3\text{Br}$ would be formed in comparable amounts.

Photolysis of a hexane solution containing $\text{Mn}_2(\text{CO})_{10}$, AsPh_3 , and CH_2Br_2 leads to formation of $\text{Mn}(\text{CO})_5\text{Br}$, $\text{Mn}(\text{CO})_4\text{AsPh}_3\text{Br}$, and $\text{Mn}_2(\text{CO})_9\text{AsPh}_3$. Figure 3 shows the spectrum of a solution following irradiation for 3 min, after subtracting out the bands due to $\text{Mn}_2(\text{CO})_{10}$. The absorbances at 1960 cm^{-1} , due to $\text{Mn}(\text{CO})_4\text{AsPh}_3\text{Br}$, and at 2055 cm^{-1} , due

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Table I. Associative Rate Constants for Substitution into Mn(CO)₅

ligand	ν , cm ⁻¹	θ	k_a , M ⁻¹ s ⁻¹
P(<i>n</i> -Bu) ₃	2060	132	1.0 (±0.1) × 10 ⁹
P(<i>i</i> -Pr) ₃	2059	160	6.7 (±0.7) × 10 ⁷
P(<i>O-i</i> -Pr) ₃	2076	130	3.1 (±0.3) × 10 ⁷
PPh ₃	2066	145	1.7 (±0.2) × 10 ⁷
AsPh ₃		~140	6.5 (±0.8) × 10 ⁴

to Mn(CO)₅Br, were employed in evaluating the relative amounts present of these two species.

The data obtained from irradiations of several solutions containing varying concentrations of AsPh₃ were analyzed as described previously. Figure 4 shows a graph of [S]/[U] vs. [AsPh₃]. The expected relationship, eq 10, is linear, with slope $k_a/(k_t[\text{CH}_2\text{Br}_2])$ and y intercept $k_d/(k_t[\text{CH}_2\text{Br}_2])$. The correlation coefficient for the line shown in Figure 4 is 0.97; the slope leads to a value of $k_a = 6.5 (\pm 0.8) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, and the intercept to $k_d \leq 9 \times 10^1 \text{ s}^{-1}$.

The much smaller value of k_a for AsPh₃ as ligand is consistent with its expected lower nucleophilicity and the operation of an associative reaction pathway. By examining the values of k_a [AsPh₃] vs. k_d , it can be seen that the k_d can be making a contribution only at the lowest values of AsPh₃. Use of AsPh₃ thus makes it possible to set a lower estimated upper bound for k_d .

If the substitution of Mn(CO)₅ by PPh₃ or AsPh₃ is associative, it seems safe to assume that the associative pathway will prevail also for other phosphorus ligands such as the trialkylphosphines or trialkyl phosphites. With this assumption, the ratio of products is given by $[\text{S}]/[\text{U}] = k_a[\text{L}]/(k_t[\text{CCl}_4])$. For any given ligand L the relative concentrations of L and CCl₄ are adjusted to provide an appropriate ratio of absorbances, from which [S]/[U] follows from a knowledge of the extinction coefficients. Since k_t is known, k_a can be determined. The experimental procedure for treatment of spectra is as described earlier. By this approach, the values of k_a were determined for three additional ligands, listed in Table I with the k_a values determined for PPh₃ and AsPh₃. Note that the value for k_a shows a dependence on both the bulk of the ligand, as reflected in the cone angle θ ,²⁶ and on nucleophilicity, or donor ability, as reflected in the frequency of the A₁ CO stretching mode in Ni(CO)₃L compounds.²⁶ This variation is, in itself, another demonstration of the associative character of the substitution process. The associative character of the process is reflected also in the higher rate constant for P(*n*-Bu)₃ as compared with the less nucleophilic P(*O-i*-Pr)₃ of comparable steric requirement. It is noteworthy that for P(*n*-Bu)₃, the rate constant approaches the diffusion-controlled limit. The Mn(CO)₅ radical is indeed remarkably labile toward substitution.

Origin of Metal Carbonyl Radical Lability. The high lability of Mn(CO)₅ is consistent with previously published data for other metal carbonyl radicals.¹⁷⁻¹⁹ However, there remains the question of why the rate constants for this reaction should be so high. The metal centers are nominally 17-electron in the ground state of the reactant and 19-electron in the transition state for the substitution process. In those species involving a ligand such as $\eta^5\text{-C}_5\text{H}_5$, the hapticity of the ligand could differ in the transition state as compared with the ground state. Basolo and co-workers have shown that substitution into 18-electron metal carbonyl species can follow an associative rather than the more commonly observed dissociative path when an NO ligand is bound to the metal.²⁴ The NO ligand presumably shifts from a 3-electron to a 1-electron donor character in the course of forming the transition state. Similarly, the $\eta^5\text{-C}_5\text{H}_5$ ligand is capable of tautomeric behavior of a similar sort, thus favoring an associative pathway.²⁷ Similar behavior could account, at least in part, for the associative pathway in substitution of species such as CH₃C₅H₄Mn(CO)₂L⁺²⁸ or for the apparent tendency of species such as $\eta^5\text{-C}_5\text{H}_5\text{V}(\text{CO})_3$, $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3$, or $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ to form 19-electron intermediates.^{29,30} However, such arguments are not applicable to simple binary carbonyl radicals such as Re(CO)₅ or Mn(CO)₅, which nonetheless exhibit a low free energy barrier to associative substitution.

Analysis of the EPR spectra of Mn(CO)₅ or Mn(CO)₃L₂ radicals^{31,32} suggests that about 60% of the unpaired electron density is centered on the metal. The barrier to formation of the transition state or intermediate would be lowered by a further delocalization of the metal-centered electron onto the carbonyl ligands. There is evidence of such a delocalization process in the EPR spectra of γ -irradiated metal carbonyls in single-crystal matrices. The most telling example is Fe(CO)₅⁻, which appears to possess a square-pyramidal geometry about Fe, with the apical CO bent.³³ Analysis of the spectra leads to an estimate of 24% spin density on carbon, with about 38% remaining on the metal. In this species the "ligand" can be thought of as an unshared pair of electrons on Fe, as contrasted with an electron pair from the attacking ligand in the associative substitution process. Similarly, in Mn(CO)₄NO⁻, there is evidence that the NO is bent, suggesting a delocalization of the unpaired spin onto the NO ligand.³⁴ In Mn(CO)₅Cl⁻ the unpaired spin is delocalized onto Cl.³⁵

Further support for a σ -acyl-like carbonyl ligand comes from the electrochemical studies by Narayanan and Kochi.³⁶ Eighteen-electron metal carbonyl compounds were reduced to the corresponding 19-electron species in the presence of HSnBu₃. The observed products were all formyl species: Cr(CO)₅CHO⁻, Fe(CO)₄CHO⁻, and Mn(CO)₃(PPh₃)₂CHO. A direct hydrogen atom transfer to carbon would be consistent with a considerable spin density at that site. One important aspect of this work is that the 19-electron species must persist for a sufficiently long time following reduction to engage in the bimolecular atom transfer. Hence, there is the possibility, not yet fully demonstrated, of a 19-electron intermediate in solution.

The importance of 19-electron species in the substitution reactions of metal carbonyl radicals thus seems firmly established. It remains to be learned whether in the general case these are transition states or intermediates. Further, the role of 19-electron species in electron-transfer reactions from metal carbonyl radicals needs further study and clarification. There also remains a question of whether there are *any* instances in which CO dissociative loss is the rate-determining process in the reactions of the metal carbonyl radicals. Photochemical reactions of Re₂(CO)₁₀ with H₂ or H₂O¹⁶ and reactions of other metal carbonyls with HSnBu₃ and other hydrides, which are thought to proceed via the 17-electron radicals,⁴ would seem to involve an oxidative addition step. The process has been formulated in the past in terms of CO loss from the 17-electron species, followed by oxidative addition to the 15-electron metal center. New experimental tests are needed to further distinguish among the viable possibilities.

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Registry No. Mn₂(CO)₁₀, 10170-69-1; Mn(CO)₅, 14971-26-7; Mn₂(CO)₅PPh₃, 14592-26-8; Mn(CO)₅Cl, 14100-30-2; Mn(CO)₄PPh₃Cl, 14841-08-8; Mn(CO)₃Br, 14516-54-2; Mn(CO)₄AsPh₃Br, 14841-06-6; Mn₂(CO)₉AsPh₃, 75039-06-4; PPh₃, 603-35-0; AsPh₃, 603-32-7; P(*n*-Bu)₃, 998-40-3; P(*i*-Pr)₃, 6476-36-4; P(*O-i*-Pr)₃, 116-17-6; CH₂Br₂, 74-95-3; CCl₄, 56-23-5.

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