Organometallics 1985, *4*, 187–190

CO_2 when complex 3 is treated with acid. In this case, the vacant site is generated by protonation of the platinum(II)–cyclohexenyl bond and elimination of cyclohexene (Scheme I). Evidently the platinum(II)–acyl bond in 5 is not so readily cleaved by acid, so that β-elimination of CO_2 from the CO_2H group cannot occur and the alternative reaction, viz., removal of OH^- from the CO_2H group, takes over.

As a general conclusion, metallocarboxylic acids seem to be structurally analogous to organic carboxylic acids, but their chemistry is dominated by their abnormal dissociation to $[L_nMCO]^+OH^-$. Their acid–base behavior and the tendency of the CO_2H group to lose CO_2 depend sensitively on the nature of the metal and of the associated ligands in a way that will only be revealed by further studies on related systems.

Substitutional Reactivity of Dodecacarbonyltrimetal Complexes of Iron and Osmium[†]

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The kinetics of the substitution reactions of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been investigated for L = PPh_3, PBu_3, $P(OPh)_3$, and $P(OMe)_3$ in hydrocarbon solution. The substitution of the iron cluster leads to both substitution and fragmentation products with a very small dependence on the entering ligand, typical of a CO dissociative interchange mechanism. Substitution of $Fe_3(CO)_{11}PPh_3$ leads only to fragmentation at a rate which is faster than substitution on $Fe_3(CO)_{12}$. Substitution on $Os_3(CO)_{12}$ occurs in an entering ligand independent reaction to $Os_3(CO)_9L_3$. The reactivities of these clusters are compared to the ruthenium analogue and to the mononuclear complexes $M(CO)_5$.

Mechanistic studies of transition-metal clusters are necessary to test the hypothesis that adjacent metal centers may lead to modes of reaction not found in mononuclear complexes.[1-6] Important questions about the mechanism, such as whether metal–metal bond cleavage occurs, can be answered by careful kinetics studies. The most thoroughly studied cluster system is the substitution reactions of $Ir_4(CO)_{12}$ and its substituted derivatives.[7-11] The reactivity was strongly influenced by the ligands on the cluster. For $Ir_4(CO)_{11}L$ and $Ir_4(CO)_{10}L_2$ the donor ability of the ligand L was important to the reactivity while for $Ir_4(CO)_9L_3$ and $Ir_4(CO)_8L_4$ the size of L became predominant.[8-11] Both of these effects are found in mononuclear complexes. Only in the substitution reactions of $Ir_4(CO)_{12}$ which proceeded primarily through a mechanism dependent on the entering ligand did a difference from mononuclear reactions appear.[7]

Darensbourg and Incorvia have investigated the reactions of $P(OMe)_3$ substituted derivatives of $Co_4(CO)_{12}$.[12-13] Reaction of the mono-substituted complex $Co_4(CO)_{11}P(OMe)_3$ with $P(OMe)_3$ proceeded by a second-order reaction, while reaction of the bis complex $Co_4(CO)_{10}(P(OMe)_3)_2$ with $P(OMe)_3$ to give $Co_4(CO)_9(P(OMe)_3)_3$ was first order in $Co_4(CO)_{10}(P(OMe)_3)_2$ and independent of $P(OMe)_3$.[12,13]

Candlin and Shortland studied CO substitution of $Ru_3(CO)_{12}$ by PPh_3, PPh_2Et, $PPhEt_2$, PBu_3, and PPh_3 (eq 1).[14] These reactions were reported to give only the

$$Ru_3(CO)_{12} + 3L \rightarrow Ru_3(CO)_9L_3 + 3CO \qquad (1)$$

tris-substituted complex with no evidence of the mono- or bis-substituted species.[14] The rate law observed was of the form

$$\text{rate} = \{k_1 + k_2[L]\}[Ru_3(CO)_{12}]$$

very similar to that observed for mononuclear species such as $Mo(CO)_6$.[14,15] Significantly, $Ru(CO)_4PPh_3$ did not yield $Ru_3(CO)_9(PPh_3)_3$ under conditions where CO was known to dissociate from $Ru(CO)_4PPh_3$.[14] CO dissociation from the intact triruthenium complex was suggested as the mechanism for reaction.[14] Subsequent work has confirmed these observations and shown that during reaction with PPh_3 the dissociation of CO is accelerated from $Ru_3(CO)_{11}PPh_3$ and $Ru_3(CO)_{10}(PPh_3)_2$ with respect to $Ru_3(CO)_{12}$.[16-20]

Reaction of the iron and osmium analogues with phosphines have also been reported.[21,22] For the osmium

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[†] Dedicated to the memory of Earl Muetterties, a dedicated scientist, mentor, and friend.

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Table I. Infrared Spectra in the Carbonyl Stretching Region of Possible Products

compd	solv	absorptns, cm^{-1}
$Fe_3(CO)_{12}$	hexane	2045 (vs), 2015 (m), 1850 (vw-br)
$Fe_3(CO)_{11}P(OPh)_3$[a]	CS_2	2082, 2035, 2011, 1998, 1972, 1844, 1813
$Fe_3(CO)_{10}(P(OPh)_3)_2$[a]	CS_2	2068, 2023, 2003, 2000, 1957, 1830, 1797
$Fe_3(CO)_9(P(OPh)_3)_3$[a]	CS_2	2049, 1986, 1829, 1788
$Fe(CO)_4P(OPh)_3$[b]	decane	2065 (m), 1996 (m), 1959 (vs)
$Fe(CO)_3(P(OPh)_3)_2$[b]	decane	1925
$Fe_3(CO)_{11}PPh_3$[a]	hexane	2080 (m), 2025 (s), 2010 (vs), 1850 (vw-br)
$Fe(CO)_4PPh_3$[b]	hexane	2050 (m), 1970 (s), 1930 (vs)
$Fe(CO)_3(PPh_3)_2$[b]	hexane	1885
$Fe_3(CO)_{11}P(OMe)_3$[a]	CS_2	2082 (m), 2030 (s), 2014 (sh), 2008 (s), 1993 (sh), 1842 (w), 1809 (w)
$Fe_3(CO)_{10}(P(OMe)_3)_2$[a]	CS_2	2062 (m), 2013 (s), 1995 (s), 1978 (m), 1965 (sh), 1828 (w), 1791 (w)
$Fe_3(CO)_9(P(OMe)_3)_3$[a]	CS_2	2040 (m), 1983 (sh), 1980 (s), 1974 (s); 1814 (w), 1770 (w)
$Fe(CO)_4P(OMe)_3$	pentane	2063 (m), 1992 (m), 1963 (s), 1950 (s)
$Fe(CO)_3(P(OMe)_3)_2$	hexane	1998 (w), 1919 (vs), 1910 (vs)
$Os_3(CO)_{12}$	hexane	2070 (s), 2036 (s), 2015 (m), 2003 (m)
$Os_3(CO)_{11}PPh_3$[c]	CCl_4	2108, 2055, 2035, 2019, 2000, 1989, 1978, 1956
$Os_3(CO)_{10}(PPh_3)_2$[c]	$CHCl_3$	2085, 2012, 1998, 1969, 1951
$Os_3(CO)_9(PPh_3)_3$[c]	CS_2	2053, 1998, 1990, 1976, 1944
$Os(CO)_4PPh_3$[c]	C_6H_{12}	2061, 1983, 1946
$Os(CO)_3(PPh_3)_2$[c]	C_6H_{12}	1840

[a] Reference 28. [b] Reference 26. [c] Tripati, S. C.; Srivastava, S. C.; Mani, R. P.; Shrival, A. K. *Inorg. Chim. Acta* **1975**, *15*, 249.

complex $Os_3(CO)_{12}$, both the mono- and bis-substituted species were seen as intermediates, suggesting that the presence of PPh_3 coordinated to an osmium center had little effect on the CO dissociation rate.[21] Reactions of $Fe_3(CO)_{12}$ with nucleophiles led to mononuclear products ($Fe(CO)_4L$ and $Fe(CO)_3L_2$) with the fragmentation increasing with the nucleophilicity of the entering ligand.[22]

Fox, Gladfelter, and Geoffroy have reported kinetics studies on tetranuclear mixed-metal clusters of iron, osmium, and ruthenium.[23,24] The complex $H_2FeRu_3(CO)_{13}$ reacted by a CO dissociative path leading to the ruthenium-substituted isomer although the site of CO dissociation could not be determined. Keister and co-workers have investigated the reactivity of $HRu_3(\mu\text{-COMe})(CO)_{10}$ which reacts by CO dissociation with phosphines in substitution reactions or with H_2 in an oxidative addition.[25] The iron analogue is much more reactive though the mechanism has not been determined.

The reactivity order for substitution reactions of metal clusters

$$Fe > Ru > Os$$

is in contrast to that observed for the mononuclear metal carbonyl complexes, although in each case investigated the mechanism has been described as CO dissociation.[26] To determine the origin of this *reactivity* difference between cluster complexes and mononuclear complexes, we have investigated the kinetics of the substitution reactions of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$ as a comparison to the data for $Ru_3(CO)_{12}$.

Experimental Section

Triiron dodecacarbonyl was prepared and purified as previously described.[22,27] Triosmium dodecacarbonyl was purchased from Pressure Chemical Co. and used without further purification. Triphenylphosphine (Aldrich Chemical Co.) was used as received. Tri-*n*-butylphosphine, triphenyl phosphite, and trimethyl phosphite were purified by vacuum distillation. Hexane (used as solvent in the $Fe_3(CO)_{12}$ kinetic studies) and decane (used as solvent in the $Os_3(CO)_{12}$ kinetic studies) were purified by mixing with sulfuric acid, washing with water, passing down an alumina column, and storing over sodium.

The synthesis of $Fe_3(CO)_{11}PPh_3$ was accomplished by the following procedure.[28] To a chloroform solution of PPh_3 (0.26 g) and $Fe_3(CO)_{12}$ (0.50 g) at -78 °C under N_2 was added a chloroform solution of Me_3NO dropwise. The solution was stirred for 20 min and then allowed to warm to room temperature. The solvent was removed under vacuum, giving a dark green solid which was extracted with hexane repeatedly. This hexane solution was concentrated and chromatographed under argon on activated silica gel. The column was eluted with cyclohexane repeatedly to remove $Fe_3(CO)_{12}$ and $Fe(CO)_4PPh_3$ until a clear solution was obtained. This clear solution was checked by IR for the presence of $Fe(CO)_4PPh_3$. Often the column had to be washed with more cyclohexane to remove this impurity. The green band of $Fe_3(CO)_{11}PPh_3$ was eluted with CCl_4 while the $Fe(CO)_3(PPh_3)_2$ remained at the top of the column. To obtain the pure product another chromatographic run may be necessary (yield 19%). The purified compound is light and air sensitive. Its infrared spectrum is reported in Table I.

The kinetic reactions were accomplished under a nitrogen atmosphere in foil-wrapped vessels in darkened hoods and followed by infrared spectroscopy with use of a Beckman 4240 spectrophotometer and matched 1.0-mm NaCl cells. All kinetic reactions were performed under pseudo-first-order conditions, with a ligand excess of greater than 10 times that of $M_3(CO)_{12}$. In a typical kinetic experiment, 15 mL of a 5.0×10^{-4} M solution of $M_3(CO)_{12}$ was stirred under N_2 at the desired temperature. A solution (hexane for M = Fe and decane for M = Os) of the ligand was added to $M_3(CO)_{12}$ by syringe. A Haake FS constant temperature circulator was used to maintain the reaction at the desired temperature, to within ±0.1 °C.

The reactions of $Fe_3(CO)_{12}$ with $P(OPh)_3$, $P(OMe)_3$, PPh_3, and PBu_3 were studied between 25 and 35 °C. In these reactions the kinetic data were obtained by monitoring the decrease in absorbance at 2045 cm^{-1} due to $Fe_3(CO)_{12}$ for a minimum of 3 half-lives.

The reactions of $Os_3(CO)_{12}$ with PPh_3, $P(OMe)_3$, and PBu_3 were

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Table II. Rate Constants for Substitution of $Fe_3(CO)_{12}$ and $Fe_3(CO)_{11}PPh_3$

L	ratio $Fe_3(CO)_{12}$/L	$10^{-5}k$, s^{-1}	temp, °C
$P(OPh)_3$	1:30	5.62 ± 0.80	30
	1:50	5.76 ± 1.3	30
PPh_3	1:10	1.69 ± 0.10	25
	1:10	4.0 ± 0.17	30
	1:10	8.82 ± 1.2	35
	1:100	6.25 ± 1.0	30
$P(OMe)_3$	1:10	5.68 ± 0.68	30
	1:30	7.45 ± 0.77	33.5
PBu_3	1:10	5.02 ± 0.38	30
	ratio $Fe_3(CO)_{11}PPh_3$/L		
PPh_3	1:5	19.8 ± 2.9	30
	1:10	22.2 ± 1.3	30
	1:20	22.7 ± 0.8	30
	ratio $Fe_3(CO)_{11}PPh_3$/L		
$P(OMe)_3$	1:5	14.5 ± 2.9	30
	1:20	17.0 ± 1.4	30

Table III. Activation Parameters for Substitution on $M_3(CO)_{12}$[a]

$M_3(CO)_{12}$	L	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Fe_3(CO)_{12}$	PPh_3	29.1 ± 1.5	17.6 ± 5.0
$Ru_3(CO)_{12}$[b]	PPh_3	32.2 ± 1.7	22.7 ± 3.7
$Os_3(CO)_{12}$	PPh_3	38.6 ± 0.50	24.2 ± 1.5

[a] *Error limits represent 95% confidence limits.* [b] Reference 14.

studied at temperatures between 82 and 102 °C by following the decrease in absorbance at 2070 cm^{-1} for $Os_3(CO)_{12}$ for a minimum of 3 half lives.

Plots of ln (A_t) vs. time yielded the pseudo-first-order rate constants. Arrhenius plots provided the activation parameters, ΔH^* and ΔS^*, for both trinuclear clusters, $M_3(CO)_{12}$. The assignments of reaction products were based on comparison of the infrared spectra to those of independently prepared samples (for M = Fe) or to spectra reported in the literature (M = Os).

Results

Reaction of $Fe_3(CO)_{12}$ with $P(OPh)_3$. Reaction of the triiron cluster with $P(OPh)_3$ leads successively to the mono-substituted ($Fe_3(CO)_{11}P(OPh)_3$), bis-substituted ($Fe_3(CO)_{10}(P(OPh)_3)_2$), and tris-substituted ($Fe_3(CO)_9(P(OPh)_3)_3$) clusters. These products were identified and monitored by the absorbances at 2082, 2060, and 2045 cm^{-1}, respectively (most of the $Fe_3(CO)_{12}$ was consumed by the time $Fe_3(CO)_9(P(OPh)_3)_3$ began to appear). The products of fragmentation of the cluster were also observed (eq 2).[26] The rate constants for the first step, which proceeded cleanly to $Fe_3(CO)_{11}P(OPh)_3$, are reported in Table II.

$$Fe_3(CO)_{12} \xrightarrow[-CO]{+P(OPh)_3} Fe_3(CO)_{11}P(OPh)_3 \xrightarrow[-CO]{+P(OPh)_3} Fe_3(CO)_{10}(P(OPh)_3)_2 \xrightarrow[-CO]{+P(OPh)_3} Fe_3(CO)_9(P(OPh)_3)_3 + Fe(CO)_3(P(OPh)_3)_3 + Fe(CO)_4P(OPh)_3 \quad (2)$$

Table IV. Rate Constants for Substitution of $Os_3(CO)_{12}$ + L

L	cluster/L ratio	$10^{-5}k$, s^{-1}	temp, °C
PPh_3	1:10	0.33 ± 0.01	82
		1.12 ± 0.14	92
		4.44 ± 0.24	102
	1:50	1.12 ± 0.10	92
$P(OMe)_3$	1:30	1.02 ± 0.12	92
	1:50	1.14 ± 0.05	92
PBu_3	1:10	3.36 ± 0.07	100
	1:30	3.02 ± 0.12	100

Reaction of $Fe_3(CO)_{12}$ with PPh_3. During the course of the reaction, $Fe_3(CO)_{11}PPh_3$, $Fe(CO)_4PPh_3$, and $Fe(CO)_3(PPh_3)_2$ were observed. The mono-substituted cluster is formed first, and then mononuclear complexes are formed with no evidence for $Fe_3(CO)_{10}(PPh_3)_2$ or $Fe_3(CO)_9(PPh_3)_3$ (eq 3). The rate constants and activation parameters are given in Tables II and III. Reaction of independently prepared $Fe_3(CO)_{11}PPh_3$ with $P(OMe)_3$ and PPh_3 was also investigated. In both cases fragmentation rather than further substitution occurred with a rate constant that had only a very small dependence on the nature or concentration of the entering ligand. The fragmentation of $Fe_3(CO)_{11}PPh_3$ occurs ~5 times more rapidly than substitution of $Fe_3(CO)_{12}$. The rate constants are shown in Table II.

$$Fe_3(CO)_{12} + PPh_3 \xrightarrow{-CO} Fe_3(CO)_{11}PPh_3 \xrightarrow[-CO]{PPh_3} Fe(CO)_4PPh_3 + Fe(CO)_3(PPh_3)_2 \quad (3)$$

Reaction of $Fe_3(CO)_{12}$ with PBu_3. The reaction of $Fe_3(CO)_{12}$ with PBu_3 proceeds very similarly to the PPh_3 reaction, leading to $Fe_3(CO)_{11}PBu_3$ and mononuclear products. The rate constant is given in Table II.

Reaction of $Fe_3(CO)_{12}$ with $P(OMe)_3$. This reaction is quite similar to the reaction with $P(OPh)_3$ in that $Fe_3(CO)_{12-n}L_n$ is formed (n = 1–3) along with mononuclear products. Rate constants are given in Table II.

Substitution Reactions of $Os_3(CO)_{12}$. Substitution of $P(OMe)_3$, PBu_3, or PPh_3 on $Os_3(CO)_{12}$ leads successively to $Os_3(CO)_{11}L$, $Os_3(CO)_{10}L_2$, and $Os_3(CO)_9L_3$. Overlap of infrared absorptions prohibited quantitative determination of the rates of substitution of $Os_3(CO)_{11}L$ and $Os_3(CO)_{10}L_2$. The observation of these complexes ($Os_3(CO)_{11}L$ and $Os_3(CO)_{10}L_2$) indicates that the rates are similar for the further substitution. No fragmentation is observed. Activation parameters and rate constants are given in Tables III and IV.

Discussion

The reactions under investigation are ligand substitution reactions of $M_3(CO)_{12}$ (M = Fe, Os) (eq 4 and 5). The reactions of the iron cluster were followed by infrared spectroscopy between 25 and 35 °C. The reactions of the osmium cluster could be conveniently studied by infrared spectroscopy between 82 and 102 °C.

$$Fe_3(CO)_{12} + L \rightarrow Fe_3(CO)_{11}L + Fe_3(CO)_{10}L_2 + Fe_3(CO)_9L_3 + Fe(CO)_3L_2 + Fe(CO)_4L \quad (4)$$

$$Os_3(CO)_{12} + L \rightarrow Os_3(CO)_{11}L + Os_3(CO)_{10}L_2 + Os_3(CO)_9L_3 \quad (5)$$

$$L = P(OPh)_3,\ PPh_3,\ P(OMe)_3,\ PBu_3$$

The product at completion of the reaction of the osmium cluster was the tris-substituted complex $Os_3(CO)_9L_3$ for each L. The clusters with one or two CO's substituted by L could be identified by infrared spectra during the course of the reaction. The products of substitution on the iron cluster involved fragmentation in addition to substitution with the exact distribution dependent on the nature of the entering ligand. For L = $P(OPh)_3$ and $P(OMe)_3$ the mono-, bis-, and tris-substituted clusters were observed along with fragmentation products $Fe(CO)_3L_2$ and $Fe(CO)_4L$. A plot of the growth of each trinuclear species is shown in Figure 1 for L = $P(OPh)_3$, showing the successive formation of the more highly substituted complexes. For other entering

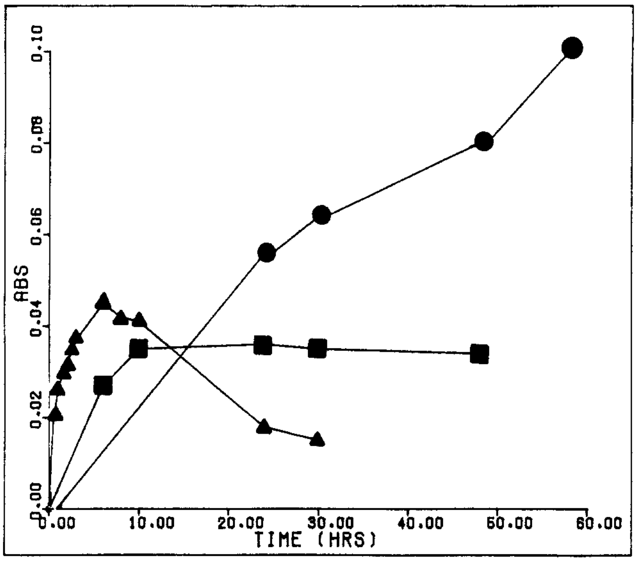

Figure 1. Absorptions for $Fe_3(CO)_{11}P(OPh)_3$ (▲), $Fe_3(CO)_{10}(P(OPh)_3)_2$ (■), and $Fe_3(CO)_9(P(OPh)_3)_3$ (●) during the reaction of $P(OPh)_3$ with $Fe_3(CO)_{12}$ at 30 °C in hexane. The pattern is typical for consecutive substitution reactions.

ligands the overlap of infrared absorptions was too severe for quantitative measurements. For L = PPh_3 and PBu_3 the mono-substituted cluster $Fe_3(CO)_{11}L$ was observed with the fragmentation products $Fe(CO)_4L$ and $Fe(CO)_3L_2$. There was no evidence for $Fe_3(CO)_{10}L_2$ or $Fe_3(CO)_9L_3$ for L = PPh_3 or PBu_3.

The rate law for substitution of $M_3(CO)_{12}$ (M = Fe, Os)

$$d[M_3(CO)_{12}]/dt = k[M_3(CO)_{12}]$$

is independent of the nature of the entering ligand as shown in Tables II and IV. The data may indicate a small dependence on the concentration of L for Fe. Such a concentration dependence is best ascribed to a small component of dissociative interchange.[29-31] The activation parameters for $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$ are similar to those obtained for $Ru_3(CO)_{12}$ as shown in Table III. The positive entropies of activation (~20 eu) are indicative of a dissociative reaction. All of these data are consistent with CO dissociation from the trimetal dodecacarbonyl for the initial substitution to $M_3(CO)_{11}L$. The mechanisms diverge at this point depending on M and L.

In what appears to be a first-order process $Fe_3(CO)_{11}PPh_3$ fragments in the presence of either PPh_3 or $P(OMe)_3$. This fragmentation of $Fe_3(CO)_{11}PPh_3$ occurs more rapidly than substitution of $Fe_3(CO)_{12}$. Although we did not determine activation parameters, the small ligand dependence (both nature and concentration) indicates a dissociative process. Indeed it is difficult to visualize a second-order process that would be more rapid for $Fe_3(CO)_{11}PPh_3$ than for $Fe_3(CO)_{12}$.

The rapidity of the substitution of CO by an entering nucleophile from $Fe_3(CO)_{12}$ in comparison to $Fe(CO)_5$ is surprising. In a binary carbonyl cluster this reactivity could arise from labile Fe–CO bonds or labile Fe–Fe bonds. Thermochemical measurements have been used to calculate metal–metal and metal–ligand bond strengths in $M_3(CO)_{12}$ clusters;[32,33] however, as average values these bond energies do not necessarily provide a measure of the energy of the bond broken in the rate-determining step. Structural data have been reported for the clusters $M_3(CO)_{12}$ and for $Fe(CO)_5$.[34-37] No obvious explanation of the reactivity is apparent from the structural data, and detailed consideration is complicated by the continuing uncertainty over the solution structure(s) of $Fe_3(CO)_{12}$.[34,38-41] The lack of dependence on the entering ligand L indicates that iron–iron bond breaking can participate in the reaction only if the subsequent diradical (or cation/anion) is activated toward CO dissociation. Studies on $V(CO)_6$ and $Mn(CO)_3L_2$ show that these 17-electron complexes undergo substitution by associative pathways.[43,44] Thus we believe that $Fe_3(CO)_{12}$ reacts by a CO dissociation mechanism.[45] A role of clusterification in the facile substitution of $Fe_3(CO)_{12}$ in relation to $Fe(CO)_5$ would seem to be ruled out by the similar reactivities of the ruthenium ($Ru(CO)_5$ and $Ru_3(CO)_{12}$) and osmium ($Os(CO)_5$ and $Os_3(CO)_{12}$) analogues. Steric effects could be involved considering the importance of nonbonded interactions on an interpretation of the structures of $Fe_3(CO)_{12}$ and derivatives.[38-40] Steric effects could also account for the increased reactivity of $Fe_3(CO)_{11}PPh_3$ over $Fe_3(CO)_{12}$ although an explanation of a ligand effect of this type in terms of electronic factors has also been offered.[31]

The order of reactivity of the dodecacarbonyl clusters $M_3(CO)_{12}$ (M = Fe > Ru > Os) toward CO dissociation is the same as the decacarbonyl complexes $HM_3(\mu\text{-}COMe)(CO)_{10}$.[45] The lack of reactivity of $Fe(CO)_5$ appears to be unusual and may well be attributable to a transition-state effect such as crystal field activation energy.[26]

In summary the substitution reactions of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been shown to proceed by CO dissociation. For iron, substitution is accompanied by fragmentation, with the relative amount of substitution and fragmentation dependent on the ligand. The reactions of $Fe_3(CO)_{12}$ evidently proceed through $Fe_3(CO)_{11}L$ which fragments for L = phosphines but substitutes and fragments for L = phosphites.

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Supplementary Material Available: Sample plots of ln *A* vs. time and log (k_{av}) vs. $1/T$ (2 pages). Ordering information is given on any current masthead page.

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