useful even in vacuo for siloxanes substrates with appreciable concentrations of $Si(H)R_2OSi(H)R_2$ units.

Our data indicate that the intermediacy of $ClRh(PPh_3)_2$ is paramount of catalytic success. Relatively high concentrations of this intermediate are conveniently generated by photolysis of $ClRh(O_2)(PPh_3)_3$ or via reductive elimination from $HRhCl(PPh_3)_2SiR_3$ at room temperature. The photolytic route works by enhancing Rh–PPh_3 cleavage and by promoting $P(O)Ph_3$ formation via free-radical oxidation of dissociated ligand.

Registry No. TMDS, 3277-26-7; DVTMDS, 2627-95-4; HMCTS, 15721-05-8; 1-pentene, 109-67-1; $ClRh(PPh_3)_3$, 14694-95-2; $ClRh[P(OPh)_3]_4$, 21481-16-3; $ClRh(O_2)(PPh_3)_3$, 15709-77-0; $HRhCl(PPh_3)_2SiMe_2Cl$, 25931-65-1; $Fe(CO)_5$, 13463-40-6; $Rh_2Cl_4(PBu_3)_4$, 76466-42-7; $RhCl_3{\cdot}3H_2O$, 13876-89-6; $Rh_2(CO)_4Cl_2$, 14523-22-9; $P(OPh)_3$, 101-02-0; PBu_3, 998-40-3; $P(OBu)_3$, 102-85-2; $P(OEt)_3$, 122-52-1; O_2, 7782-44-7; 2-phenyl-2-hydroperoxypropane, 80-15-9; $P(O)(OPh)_3$, 115-86-6; $P(O)(OBu)_3$, 126-73-8; $P(O)Bu_3$, 814-29-9.

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Electrophilic Attack at Metal Carbonyls. Kinetics of Reactions of Halogens with Some Trisubstituted Nonacarbonyltriruthenium Clusters

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The kinetics have been studied of the reactions in cyclohexane of $Ru_3(CO)_9(PPh_3)_3$ with iodine, bromine, and iodine chloride and of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ and $Ru_3(CO)_9[P(OPh)_3]_3$ with I_2 and Br_2. Apart from the reaction of ICl all the reactions proceed in two kinetically observable stages to form $Ru(CO)_3LX_2$. Spectroscopic titration studies suggest that the second stage involves reaction of the Ru–Ru-bonded species $Ru_2(CO)_6L_2X_2$. The kinetics are governed by quite complex rate dependence on $[X_2]$ in some cases, and there is clear kinetic, and in one case spectroscopic, evidence for the formation of adducts between the complex and one or more halogen molecules. Even in some cases where simple second-order kinetics are observed, first order in both [complex] and $[X_2]$, it can be shown that this probably arises from reaction of X_2 with a completely formed adduct, complex$\cdot X_2$. It is suggested that the electrophilic nature of the halogens weakens the Ru–Ru bonds by an inductive effect transmitted through the CO ligands to the HOMOs that bind the metal atoms together.

Introduction

Reactions of halogens with metal–metal-bonded carbonyls have long been known as a means of producing mononuclear metal carbonyl halides.[1] Studies of the kinetics of reactions of iodine[2,3] and bromine[4] with a series of substituted dinuclear carbonyls of manganese and rhenium have shown[2,4] that reactions proceed via the rapid preformation of a series of adducts, complex$\cdot nX_2$, which can contain up to four halogen molecules. These adducts then undergo relatively slow intramolecular electron transfer and metal–metal bond fission to form mononuclear products in high yield. The rates of these reactions are very sensitive to the σ basicity of the substituents, and it was concluded that the reactions proceeded by electrophilic attack at the O atoms of the CO ligands. Studies of reactions of Br_2 and Cl_2 with $Os_3(CO)_{12}$ had previously shown[5] that complex$\cdot X_2$ adducts were formed in those cases as well. Since reactions of this sort can provide systematic and quantitative estimates of the stability of such clusters toward fragmentation by electrophilic attack, we have made studies of the kinetics of the reactions in cyclohexane of some halogens with the complexes $[Ru(CO)_3L]_3$ where L = PPh_3, P-*n*-Bu_3, and $P(OPh)_3$.

Experimental Section

The ruthenium complexes were those used in a previous study[6] and were kindly provided by Dr. S. K. Malik. Resublimed I_2 (Baker Chemical Co.) and Br_2 (Baker analyzed grade) were used as received. Iodine chloride was prepared as described in the literature[7] (λ_{max} = 460 nm, ϵ = 150 $dm^3\ mol^{-1}\ cm^{-1}$). Cyclohexane (AnalaR grade, BDH Chemicals Ltd.) was dried over molecular sieves.

Solutions of the complexes $[Ru(CO)_3PPh_3]_3$ and $[Ru(CO)_3P(OPh)_3]_3$ were prepared by dissolving weighed amounts in a little dichloromethane which was subsequently removed under reduced pressure after addition of cyclohexane. $[Ru(CO)_3PBu_3]_3$ was much more soluble, and solutions for reaction in cyclohexane were prepared by dilution of a 0.01 M stock solution in decalin. All manipulations of the solutions were carried out in dim light. Reactions of the complexes with oxygen were shown to be much slower than any of the reactions with halogens so that no attempts were made to exclude air from the reaction solutions.

Unless otherwise indicated all the reactions were followed at 25.0 ± 0.1 °C. Reactions with half-lives up to ca. 20 s were followed in a "Canterbury" stopped-flow spectrophotometer,[4] and slower reactions were followed in 10-mm silica cells in the thermostated cell compartment of a Cary 16K spectrophotometer set to the continuous drive mode. Wavelengths were chosen so as to monitor the eventual disappearance of the absorption bands in the near-UV which can be assigned to transitions involving metal cluster molecular orbitals.[8] In general the overall reaction proceeded in two stages, but the difference in rates between them was always sufficiently large that no difficulty was encountered in estimating values of the absorbance or transmission at the end of a given reaction. Absorbance changes during a reaction were generally $\lesssim 0.1$ units so that plots of log $(T_\infty - T)$ against time obtained from the stopped-flow data were equivalent to plots of log $(A - A_\infty)$ (T = percent transmission, A = absorbance).[4] Rate plots were generally linear for ca. 2 half-lives.

Reactions were followed over wide ranges of $[X_2]$ and, where possible, over quite wide ranges of initial concentration, c_0, of complex. The rate equations were initially derived by graphical analysis of the dependence of the pseudo-first-order rate constants, k_{obsd}, on $[X_2]$ after which the various individual constants in the rate equation were evaluated by computer analysis using least-squares procedures described previously.[2,4] Unless otherwise indicated the uncertainties quoted are estimates of the standard deviations that have been corrected for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling them.

The final products of all the reactions were characterized in solution by IR and UV–vis spectroscopy, and the IR spectra of the products

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Table I. Rate Equations for Reactions of Halogens with $Ru_3(CO)_9L_3$ in Cyclohexane

k_{obsd}[a]	eq	reacn no.	L	X_2	stage
$k_2[X_2]$	1	i	PPh_3	I_2	I
		ii	PPh_3	Br_2	II
		iii	PBu_3	I_2	I
$k_2[X_2] + k_3[X_2]^2$[b]	2	iv	PPh_3	ICl	II
$k_2[X_2]/(1 + \beta_1[X_2])$	3	v	PPh_3	Br_2	I
		vi	$P(OPh)_3$	Br_2	II
$k_3[X_2]^2/(1 + \beta_1[X_2])$	4	vii	PPh_3	ICl	III
$k_1 + k_2[X_2]$	5	viii	PPh_3	I_2	II
		ix	PPh_3	ICl	I
$k_1 + k_2[X_2] + k_3[X_2]^2$	6	x	PBu_3	I_2	II
		xi	$P(OPh)_3$	I_2	I
$(k_1 + k_2[X_2])/(1 + \beta_1[X_2])$	7	xii	PBu_3	Br_2	II
$k_3[X_2]^2/(1 + \beta_2[X_2]^2 + \beta_3[X_2]^3)$	8	xiii	$P(OPh)_3$	I_2	II

[a] The pseudo-first-order rate constant. [b] $k_{obsd} = a + b[Ru_3(CO)_9L_3]$.

of the first stage of reaction were also examined in several cases.

Results

Reaction of $Ru_3(CO)_9(PPh_3)_3$ with I_2. This reaction proceeded in two clearly defined stages, the second always being at least 10^3 times slower than the first. The absorbance in the near-UV increased during the first stage, the final absorbance itself changing with $[I_2]$ as shown in Figure 1. The spectrum of the product of the first stage was obtained by measuring A_∞ at a series of wavelengths, and one such spectrum is shown in Figure 2. At values of $[I_2]$ below ca. 5×10^{-4} M the spectra of the product solutions are less intense and show a broad plateau centered at ca. 380 nm; i.e., the spectrum is intermediate between that of the unreacted complex and that of the product shown in Figure 2. The change of the electronic spectrum during the second stage of the reaction was followed only in the presence of a large molar excess of I_2 when there was a general decrease of absorbance at wavelengths above ca. 370 nm.

The IR spectra of the final products of reactions with a large excess of I_2 showed bands at 2116 s, 2060 vs, and 2038 m cm^{-1} in excellent agreement with published values[9] for isolated $Ru(CO)_3(PPh_3)I_2$.

The kinetics of the first stage of the reaction were followed by monitoring the growth of absorbance at 390 nm with the stopped-flow apparatus. Wide ranges of c_0 and $[I_2]$ were used (Table II). Half-lives varied from 50 down to ca. 4 ms, the limit of reliable measurement by the apparatus. The reaction is first order in c_0 and follows rate equation 1 (Table I). There was excellent agreement between the sets of runs with variable c_0 and variable $[I_2]$. Excellent agreement was also obtained with the Eyring equation over almost 20 °C. The second stage of the reaction was studied by using the continuous-drive mode of the Cary 16K spectrophotometer set to measure the decreasing absorbance at 390 nm. Half-lives from 80 to 300 s were obtained. A wide range of values of c_0 (Table II) showed the reaction to be accurately first order in complex, but the dependence of k_{obsd} on $[I_2]$ followed eq 5 (Table I) in this case. The values of k_1 and k_2 obtained from the least-squares analysis predict a value for 10^5k_{obsd} at $[I_2] = 7.5 \times 10^{-5}$ M of 351 ± 10 s^{-1} in excellent agreement with the value found at this value of $[I_2]$ and varying c_0.

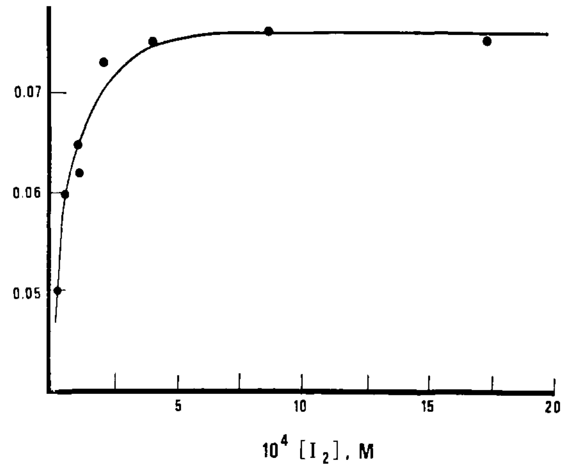

Figure 1. Dependence on $[I_2]$ of absorbance at the end of stage I of reaction of I_2 with $Ru_3(CO)_9(PPh_3)_3$ ($c_0 = 194 \times 10^{-8}$ M, λ = 390 nm).

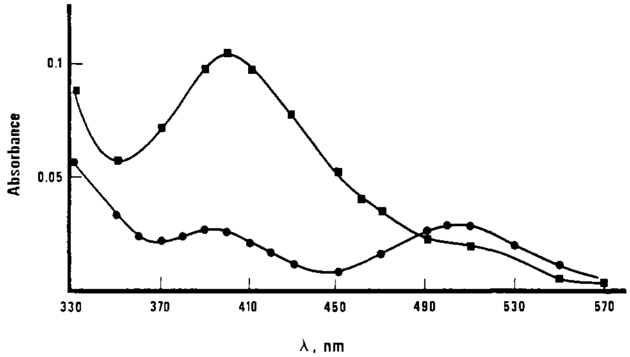

Figure 2. Spectrum of $Ru_3(CO)_9(PPh_3)_3$ (●) and dependence on λ of absorbance at the end (■) of stage I of reaction of I_2 with $Ru_3(CO)_9(PPh_3)_3$ ($c_0 = 194 \times 10^{-8}$ M, $[I_2] = 11 \times 10^{-4}$ M).

Reaction of $Ru_3(CO)_9(PPh_3)_3$ with Br_2. This reaction also proceeded in two stages, but the absorbance at 390 nm de-

Table II. Kinetic Data for Reactions of $Ru_3(CO)_9(PPh_3)_3$ with I_2, Br_2, and ICl at 25 °C[a] in Cyclohexane

X_2	10^6c_0, M	$10^4[X_2]$, M	stage	rate eq[b]	rate const[c]	$\sigma(k_{obsd})$, %
I_2	1-13 (6)[d]	2	I		$\bar{k}_{obsd}$[e] = 14.4 ± 0.5	6.2
	5	3.4-23 (13)	I	1	$10^{-2}k_2 = 750 \pm 4$	2.1
	5	1-3 (24)	I	1	$\Delta H_2^\ddagger = 5.42 \pm 0.28$,[f] $\Delta S_2^\ddagger = -54.7 \pm 0.9$[f]	5.3
	4-50 (12)	0.75	II		$10^5k_{obsd} = 356 \pm 7$	6.2
	13	2-300 (30)	II	2	$10^5k_1 = 211 \pm 6$, $10^3k_2 = 186 \pm 9$, $10^{-4}\beta_1$ = ca. 3[g]	8.8
Br_2	3-10 (12)	9.6	I		$10\bar{k}_{obsd} = 122 \pm 4$	9.4
	8	0.40-4 (23)	I	3	$10^{-3}k_2 = 113 \pm 6$, $10^{-1}\beta_1 = 517 \pm 27$	8.5
	6-20 (5)	800	II		$10^3k_{obsd} = 223 \pm 8$	8.2
	15	86-407 (7)	II	1	$10^2k_2 = 246 \pm 7$[h]	7.1
	15	89-740 (12)	II	1	$10^2k_2 = 273 \pm 6$[i]	7.0
ICl	5-25 (8)	1.0	I		$10\bar{k}_{obsd} = 115 \pm 3$	7.5
	8	0.2-2.4 (18)	I	2	$10^2k_1 = 179 \pm 32$, $10^{-2}k_2 = 940 \pm 42$	10.3

[a] Unless specified otherwise. [b] Numbers correspond to equations in Table I. [c] $\bar{k}_{obsd}$ in units of s^{-1}, k_n in M^{1-n} s^{-1}, β_n in M^{-n}, $\Delta H_2^\ddagger$ in kJ mol^{-1}, $\Delta S_2^\ddagger$ in J K^{-1} mol^{-1}. [d] Numbers in parentheses are numbers of runs followed over the specified concentration ranges. [e] Average value of k_{obsd}. [f] Temperature range 22.7-39.9 °C. [g] From dependence of absorbance on $[I_2]$ at the end of stage I. [h] At 24.0 °C. [i] At 24.9 °C.

Table III. Kinetic Data for Reaction of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ with I_2 and Br_2 at 25 °C in Cyclohexane

X_2	10^6c_0, M	$10^4[X_2]$, M	stage	rate eq[a]	rate const[b]	$\sigma(k_{obsd})$, %
I_2	1.6-26 (23)[c]	1.0	I		$10\bar{k}_{obsd} = 168 \pm 14$	4.0
	10	0.6-8 (20)	I	1	$10^{-3}k_2 = 165 \pm 3$	6.2
	8-110 (10)	74	II		$10^5k_{obsd} = 277 \pm 3$	3.7
	10	7-220 (13)	II	6	$10^5\underline{k}_1 = 163 \pm 11$, $10^3k_2 = 150 \pm 35$, $10^2k_3 = 614 \pm 187$	6.5
Br_2	2-14 (5)	150	II		$10^2\bar{k}_{obsd} = 114 \pm 5$	9.7
	14	3-550 (34)	II	7	$10^3k_1 = 78$,[d] $10k_2 = 889$,[d] $10\beta_1 = 171$[d]	5.4

[a] Numbers correspond to equations in Table I. [b] Units as in Table II. [c] Numbers in parentheses are numbers of runs followed. [d] The VA04A program does not provide standard deviations of derived parameters.[10]

Table IV. Kinetic Data for Reactions of $Ru_3(CO)_9[P(OPh)_3]_3$ with I_2 and Br_2 at 25 °C in Cyclohexane

X_2	10^6c_0, M	$10^4[X_2]$, M	stage	rate eq[a]	rate const[b]	$\sigma(k_{obsd})$, %
I_2	1-17 (18)[c]	33	I		$10^2\bar{k}_{obsd} = 339 \pm 4$	5.0
	10	0.8-62 (51)	I	6	$10^4\underline{k}_1 = 804 \pm 35$, $k_2 = 369 \pm 18$, $10^{-3}k_3 = 104 \pm 5$	6.4
	6-82 (14)	82	II		$10^4\bar{k}_{obsd} = 142 \pm 7$	18
	10	34-360 (36)	II	8	$k_3 = 156$, $10^{-1}\beta_2 = 180$, $10^{-2}\beta_3 = 687$	7.2
Br_2	3-18 (7)	57	II		$10^3\bar{k}_{obsd} = 223 \pm 3$	3.9
	17	2.5-440 (19)	II	3	$k_2 = 424 \pm 24$, $10^{-1}\beta_1 = 157 \pm 12$	5.8

[a] Numbers correspond to equations in Table I. [b] Units as in Table II. [c] Numbers in parentheses are numbers of runs followed.

creased during both. The final IR spectrum after reaction with a large excess of Br_2 showed bands at 2125 m, 2070 s, and 2035 m cm^{-1} (cf. 2128 m, 2073 s, and 2036 m for $Ru(CO)_3(PPh_3)Br_2$ in cyclohexane).[9]

The kinetics of the first stage of the reaction were followed over the ranges of concentrations shown in Table II by monitoring the decreasing absorbance at 390 nm in the stopped-flow apparatus. Half-lives varied from 47 to 230 ms, and the reaction was accurately first order in [complex] up to ca. 10^{-5} M. Above this the values of k_{obsd} began to increase steadily, suggesting the existence of a path greater than first order in [complex]. The dependence on $[Br_2]$ is shown by eq 3 (Table I) for $[Br_2]$ up to 4×10^{-4} M. The second stage of the reaction was also followed at 390 nm in the stopped-flow apparatus, and values of $t_{1/2}$ from 4 to 40 s were obtained. The reaction is simply first order in c_0 and $[Br_2]$ over the ranges of concentrations shown in Table II. The agreement between the sets of data at 24.0 and 24.9 °C is excellent, allowing for the slight difference in temperature.

Reaction of $Ru_3(CO)_9(PPh_3)_3$ with ICl. This reaction was unique in proceeding in three stages. The absorbance at 390 nm rose during the first stage and decreased during the second and third, the relative rates being approximately in the ratios 10^3:10:1. The first two stages were followed by using the stopped-flow apparatus, and the third was followed by using the Cary 16K spectrophotometer. The final product of the reaction showed two peaks in the IR at 2081 vs and 2030 s cm^{-1}.

The kinetics of the first stage showed half-times in the range 30–150 ms under the conditions used. The reaction showed good first-order dependence on c_0, and the [ICl] dependence followed eq 5. The second stage was unusual in showing a first- and second-order dependence on c_0. Under conditions where ca. 75% of the reaction was going via the second-order path, the dependence on [ICl] followed eq 2, k_{obsd} being the apparent first-order rate constant obtained from the absorbance change over the first half-time. The third stage was not very reproducible but showed first-order dependence on c_0 and k_{obsd} increased with [ICl] roughly according to eq 4.

Reaction of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ with I_2 and Br_2. Reaction with I_2 and Br_2 led to final products showing IR bands at 2160 m, 2060 s, and 2030 s cm^{-1} and 2160 m, 2075 s, and 2030 m cm^{-1}, respectively. Both reactions showed an increase in absorbance at 360 nm during the first stage followed by a substantial decrease. The first stage of reaction with Br_2 was too fast to measure with the stopped-flow apparatus even when $[Br_2]$ was as low as 2.7×10^{-4} M. The first stage of reaction with I_2 showed half-times of 5–90 ms over the range of conditions used (Table III) while the second stages of reaction with I_2 and Br_2 showed half-times over the ranges 100–400 and 0.3–7 s, respectively. The first stage of reaction with I_2 showed clear first-order dependence on c_0 and $[I_2]$. The second stage was also first order in c_0, but the $[I_2]$ dependence followed eq 6. The second stage of reaction with Br_2 was also first order in c_0, and the $[Br_2]$ dependence was in very good agreement with eq 7. This was shown first by graphical analysis and then by the use of the VA04A program.[4,10]

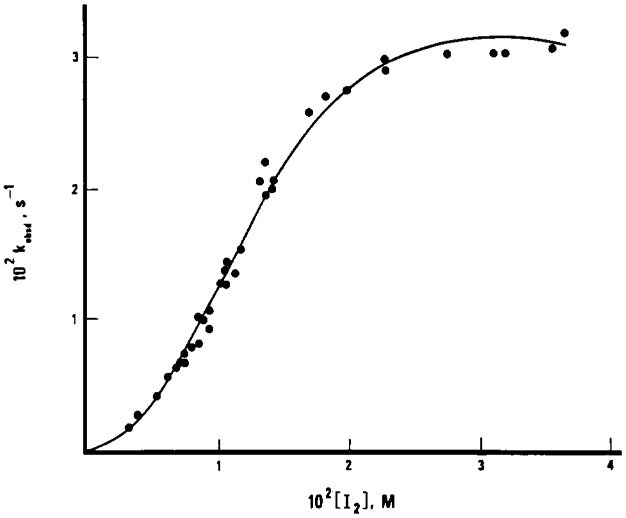

Figure 3. Dependence of k_{obsd} on $[I_2]$ for stage II of reaction of I_2 with $Ru_3(CO)_9[P(OPh)_3]_3$.

Reaction of $Ru_3(CO)_9[P(OPh)_3]_3$ with I_2 and Br_2. Reactions with I_2 and Br_2 both occurred in two stages, and addition of a large excess of halogen led to final products with IR bands at 2105 m, 2080 vs, 2055 m, and 2030 m cm^{-1} and 2078 s, 2055 m, and 2035 m cm^{-1}, respectively.

The first stage of reaction with I_2 was shown (Table IV) to be first order in c_0 over a wide range of concentrations. The dependence of k_{obsd} on $[I_2]$ followed eq 6 very closely with half-times in the range 0.1–6 s. The slower stage also showed first-order dependence on c_0 and the $[I_2]$ dependence showed

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excellent agreement with eq 8. Graphical analysis showed initially that terms $k_2[I_2]$ in the numerator and $\beta_1[I_2]$ in the denominator were negligible and the parameters in Table IV were obtained by using the program VA04A.[10] A plot of k_{obsd} against $[I_2]$ is shown in Figure 3, the continuous line being the one calculated by using the parameters in Table IV.

The first stage of reaction with Br_2 was too fast to measure even with the stopped-flow apparatus. The second stage of reaction showed half-times of 2–8 s and was closely first order in c_0 (Table IV). The dependence of k_{obsd} on $[Br_2]$ was in good agreement with eq 3.

Discussion

Reaction Sequence. The reactions of these trinuclear clusters with halogens might be expected to go through three stages as in eq 9–11. Unsubstituted analogues, $Os_3(CO)_{12}I_2$ and

$$Ru_3(CO)_9L_3 + X_2 \rightarrow Ru_3(CO)_9L_3X_2 \qquad (9)$$

$$Ru_3(CO)_9L_3X_2 + X_2 \rightarrow Ru_2(CO)_6L_2X_2 + Ru(CO)_3LX_2 \qquad (10)$$

$$Ru_2(CO)_6L_2X_2 + X_2 \rightarrow 2Ru(CO)_3LX_2 \qquad (11)$$

$Os_2(CO)_8I_2$, of the intermediates are known[11] and are formed with increasing difficulty by direct reaction with $Os_3(CO)_{12}$. $Os(CO)_4I_2$ does not appear to be formed at all easily[11] by reaction of I_2 with $Os_2(CO)_6I_2$, so the sequence of three reactions of $Os_3(CO)_{12}$ with I_2 involves steadily decreasing rates. Only two kinetically distinguishable stages are observed for reactions of the substituted ruthenium clusters with I_2 and Br_2. If the above scheme is correct this implies either that reaction 11 is much faster than (10) (in which case $Ru_3(CO)_{12}L_3X_2$ would be the product of the first stage) or that reaction 10 is much faster than (9) and (11) (in which case the product of the first stage would be an equimolar mixture of $Ru_2(CO)_6L_2X_2$ and $Ru(CO)_3LX_2$). In either case one would expect substantial absorbances in the metal–metal-bonding region of the electronic spectrum at the end of the first stage. Whether these would be lower than the initial absorbances (as is the case for one reaction) or higher (as is the case for all the other reactions) would depend on the detailed spectra of the individual complexes and the particular wavelength at which the reactions were monitored.[12]

The changes in IR spectra observed throughout those reactions that proceed sufficiently slowly at low halogen concentrations are quite complex and do not allow characterization of the intermediates. One clear feature was evident in the reactions of $Ru_3(CO)_9(PPh_3)_3$ with I_2 and Br_2 and of $Ru_3(CO)_9[P(OPh)_3]_3$ with I_2. The spectra measured ca. 1 min after addition of 1 molar equiv of halogen showed strong, clearly resolved bands at 1970–1980 cm^{-1} characteristic of unreacted starting complex,[6] but the intensity was reduced by ca. 50%. Addition of 2 molar equiv was required for all the initial complex to react, and the intensities of the new bands were then twice as great as when only 1 equiv was added. This strongly suggests that 2 molecules of halogen are consumed in the first stage and that reaction 10 is much faster than (9); i.e., the second stage involves reaction of $Ru_2(CO)_6L_2X_2$. While we did not show this to be the case also for the reactions of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ with I_2 and Br_2 and of $Ru_3(CO)_9[P(OPh)_3]_3$ with Br_2, we consider it to be reasonable to conclude by analogy that the same applies.

The IR spectra after completion of reactions of $Ru_3(CO)_9(PPh_3)_3$ with large excess of I_2 and Br_2 are identical with those published[9] for the isolated complexes $Ru(CO)_3(PPh_3)X_2$ (X = I and Br) and which can be concluded to be fac isomers. The final IR spectra after reactions of $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$ with I_2 and Br_2 and of $Ru_3(CO)_9[P(OPh)_3]_3$ with Br_2 show very similar three-band spectra, and the products can therefore be concluded to be *fac*-$Ru(CO)_3LX_2$ by analogy. The product of the reaction of $Ru_3(CO)_9[P(OPh)_3]_3$ with I_2 shows four bands as do the complexes $Os(CO)_3(PPh_3)X_2$ (X = Cl and Br) formed from similar reactions of $Os_3(CO)_9(PPh_3)_3$.[14,15] The spectra showed no evidence for formation of halogen-bridged complexes $[Ru(CO)_2LX_2]_2$ of the type known to be formed under more stringent conditions.[9]

The final products all showed significant but relatively low absorbance in the range 350–450 nm. The products of reaction of $Ru_3(CO)_9(PPh_3)_3$ with I_2 and Br_2 showed maxima at 360 and 395 nm (both with $\epsilon \approx 3 \times 10^3$ L mol^{-1} cm^{-1}) and 440 nm ($\epsilon \approx 10^3$ L mol^{-1} cm^{-1}), respectively. Bands with energies and molar absorption coefficients such as these have been observed with other mononuclear halogeno metal carbonyls and have been assigned to transitions from a π orbital on the halogen to an M–X antibonding σ orbital.[16]

The data for reactions of I_2 and Br_2 with these complexes are, therefore, fully consistent with the final products being mononuclear $Ru(CO)_3LX_2$ complexes, stage I of the reaction involving formation of equimolar mixtures of $Ru_2(CO)_6L_2X_2$ and $Ru(CO)_3LX_2$ and stage II involving further reaction of $Ru_2(CO)_6L_2X_2$. The final products of reaction of $Ru_3(CO)_9(PPh_3)_3$ with ICl are not clearly defined. The IR spectrum is not in agreement with those after reaction with either I_2 or Cl_2[9] nor is it intermediate between the two. The reaction proceeds in three stages, but nothing can be said at this time about the sequence of reactions involved.

Rate Equations. The kinetics of these reactions are generally quite well behaved although they sometimes became rather irreproducible when concentrations outside the ranges listed in Tables II–IV were used. The rate equations observed for these reactions can all be encompassed by eq 12. This is

$$k_{obsd} = \frac{k_2[X_2] + k_3[X_2]^2 + k_4[X_2]^3}{1 + \beta_1[X_2] + \beta_2[X_2]^2 + \beta_3[X_2]^3} \qquad (12)$$

characteristic of the mechanism proposed[2,4] for reactions of I_2 and Br_2 with some group 7 dimetal carbonyls, which can be summarized by eq 13 and 14. In the reactions reported here formation of adducts containing up to three halogen

$$\text{complex} + nX_2 \xrightleftharpoons{\beta_n'} \text{complex}\cdot nX_2 \qquad (13)$$

$$\text{complex}\cdot nX_2 \xrightarrow{k_n'} \text{products} \qquad (14)$$

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(11) Bruce, M. I.; Cooke, M.; Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1969**, 987.

(12) When $Os_3(CO)_{12}$ reacts with Br_2 to form $Os_3(CO)_{12}Br_2$, the absorbance at 400 nm falls by a factor of 5, but that at 350 nm more than doubles.[5] Reaction with I_2 to form $Os_2(CO)_8I_2$ would lead to a decrease of absorbance of ca. 30% at 337 nm.[11] $Ru_2(CO)_8(SiMe_3)_2$ shows a strong band ($\epsilon \approx 9 \times 10^3$ L mol^{-1} cm^{-1}) at 353 nm[13] as compared with the strongest band in the near-UV spectrum of $Ru_3(CO)_{12}$ at 390 nm ($\epsilon = 6 \times 10^3$ L mol^{-1} cm^{-1}).[8] Direct formation of this dinuclear complex from $Ru_3(CO)_{12}$ (and it is prepared by this direct reaction in high yield)[13] would therefore be accompanied by pronounced increases or decreases in absorbance depending on the wavelength.

(13) Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 2559.

(14) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Chem. Commun.* **1967**, 384.

(15) These products must presumably exist as mixtures of geometrical isomers of which one *fac* and two *mer* are possible. This question has not been investigated either by those who synthesised the complexes originally or by ourselves. Mixtures of the isomers *cis*- and *trans*-$M(CO)_4LX$ were also formed on reaction of Br_2 and I_2 with $M_2(CO)_6L_2$ (M = Mn, Re; L = P donor (see ref 2 and 4)). The detailed steric course of these reactions remains an open question which we have not yet attempted to answer. A related observation is that reaction of $Ru_3(CO)_9(PPh_3)_3$ with small excesses of I_2 leads to a final product showing four bands at wavelengths close to those shown by the product of reacting $Ru_3(CO)_9[P(OPh)_3]_3$ with I_2. It seems reasonable to suppose that the steric course of such reactions may depend on the particular rate path followed. In view of the complicated kinetics shown by many of these reactions this would generally be difficult to investigate, and we shall be concerned here only with the kinetic form of the reactions.

(16) McLean, R. A. N. *J. Chem. Soc., Dalton Trans.* **1974**, 1568.

Table V. Kinetic Parameters[a] Assigned to Reactions of Some Halogens with $Ru_3(CO)_9L_3$ and $Ru_2(CO)_6L_2X_2$[b] in Cyclohexane at 25 °C

reacn no.[c]	L	X_2	k_1', s^{-1}	$\beta_2'k_2'/\beta_1'$, M^{-1} s^{-1}	$\beta_3'k_3'/\beta_1'$, M^{-2} s^{-1}	β_1',[d] M^{-1}
			Reaction with $Ru_3(CO)_9L_3$			
iii	PBu_3	I_2		1.7×10^5		$\gtrsim 10^5$
i	PPh_3	I_2		7.5×10^4		$\gtrsim 10^4$
xi	$P(OPh)_3$	I_2	8×10^{-2}	4×10^2	1×10^5	$\gtrsim 5 \times 10^4$
v	PPh_3	Br_2	20^e			5.2×10^3
ix	PPh_3	ICl	2	9×10^4		$\gtrsim 2 \times 10^5$
			Reaction with $Ru_2(CO)_6L_2X_2$[b]			
x	PBu_3	I_2	1.6×10^{-3}	1.5×10^{-1}	6	$\gtrsim 10^4$
viii	PPh_3	I_2	2.1×10^{-3}	1.9×10^{-1}		3×10^4[f]
xii	PBu_3	Br_2	8×10^{-2}	9×10^1		$\gtrsim 3 \times 10^4$
ii	PPh_3	Br_2		2.7		$\gtrsim 5 \times 10^2$
vi	$P(OPh)_3$	Br_2	0.3^e			1.6×10^3

[a] As defined in eq 13 and 14. [b] For assignment of stage II to reaction of this complex see text. [c] See Table I. [d] All limiting values for β_1' are those required for $\beta_1'[X_2]$ to have been $\gg 1$ for all values of $[X_2]$ used. [e] Obtained from k_2/β_1 and not directly from the kinetics. [f] Obtained from the dependence on $[I_2]$ of the absorbance at the end of stage I and not from the kinetics.

molecules occurs very rapidly and sometimes quite extensively. This is followed by relatively slow, first-order, intramolecular reaction of the adducts.

At first sight one would assign the derived, experimental rate constants k_2, k_3, etc. to $\beta_1'k_1'$, $\beta_2'k_2'$, etc., as defined in eq 13 and 14, and the kinetically derived, experimental equilibrium constants β_1, β_2, etc. to β_1', β_2', etc. However, there are certain limiting situations where this would be incorrect. Most of the reactions studied here do, in fact, show evidence for the incorrectness of such simple assignments of the rate constants although the assignments $\beta_1 = \beta_1'$, etc. seem to be generally correct.

Significance of k_1. Reactions viii–xi in Table I all have empirical rate equations that contain a term k_1. It is most unlikely that these terms correspond to spontaneous, unimolecular reactions of the complexes themselves since they are all quite stable, thermally and photochemically, even in the presence of O_2.[6] It is much more likely that k_1 arises because $\beta_1'[X_2] \gg 1$ for all the values of $[X_2]$ used. Provided $\beta_2'[X_2]^2$ and $\beta_3'[X_2]^3$ are both much less than $\beta_1'[X_2]$, rate equation 15 would be followed, and k_1 could then be assigned to k_1'.

$$k_{\text{obsd}} = k_1' + (\beta_2'k_2'/\beta_1')[X_2] + (\beta_3'k_3'/\beta_1')[X_2]^2 \qquad (15)$$

For reaction viii there is independent evidence showing that this is almost certainly the case. The variation (Figure 1) with $[I_2]$ of the absorbance at the end of the first stage of reaction of $Ru_3(CO)_9(PPh_3)_3$ with I_2 can be interpreted most simply in terms of an equilibrium such as that shown in eq 16, and

$$Ru_2(CO)_6(PPh_3)_2I_2 + I_2 \overset{\beta_1'}{\rightleftharpoons} Ru_2(CO)_6(PPh_3)_2I_2{\cdot}I_2 \qquad (16)$$

a value of β_1' = ca. 3×10^4 M^{-1} can be obtained. The kinetics were all measured at values of $[I_2]$ that were high enough for this equilibrium to lie completely to the right, i.e., $\beta_1'[I_2] \gg 1$ and $k_1 = k_1'$. The limiting values for β_1' that would be required for this assignment to be correct for reactions ix–xi are shown in Table V together with the values assigned to k_1'. The values of β_1' for reaction with I_2 are close to those for reaction 16.

Reaction xii differs from reactions viii–xi in that the empirical rate equation contains a term $\beta_1[X_2]$ *as well as* a term k_1. The value of β_1 derived from the data is only 17 M^{-1} (Table III) which is very much lower than the other value of β_1 (5×10^3 M^{-1}) found for a reaction with Br_2 (reaction v). We suggest that $\beta_1'[Br_2]$ was always much greater than unity in this reaction as well and that $\beta_2'[Br_2]^2$ was also significant. This would result in the assignments $k_1 = k_1'$ and $\beta_1 = \beta_2'/\beta_1'$. The lower limit for β_1' for this to be possible is shown in Table V. This is the only reaction for which there is any evidence that the experimentally derived β_1 is assignable to anything other than β_1'.

Significance of k_2. Since rections viii–xii have been concluded to have $\beta_1'[X_2] \gg 1$ and $k_1 = k_1'$ it follows that $k_2 = \beta_2'k_2'/\beta_1'$; i.e., k_2 is the observed second-order rate constant for attack by X_2 on the adduct complex·I_2.

There are three other reactions (i, iii, and vii) for which the same assignment of k_2 can be made even though there is no term k_1 in the observed rate equation. For reaction i β_1' would have to be $\gtrsim 10^4$ M^{-1} for $\beta_1'[I_2]$ to have been $\gg 1$ for all values of $[I_2]$ used. This is quite compatible with all the other values of β_1' in Table V and is quite reasonable in view of the fact $\beta_1' = 5 \times 10^3$ M^{-1} for the reaction of this complex with Br_2. A larger value of β_1' for reaction with I_2 would be expected compared with that for reaction with Br_2.[2,17] A value of β_1' of only $\gtrsim 5 \times 10^2$ M^{-1} would be needed for the same to apply to reaction ii, and this is quite reasonable in view of the value $\beta_1' = 3 \times 10^4$ M^{-1} for the reaction of the same complex with I_2. A value $\beta_1' \gtrsim 10^5$ M^{-1} would be needed for reaction iii, and this is compatible with the other values for I_2-adduct formation since it has been found before[2] that this is most pronounced for P-*n*-Bu_3 complexes.

It therefore appears that it is only for reactions v and vi, where k_2 and β_1 are the only terms in the rate equations, that it is likely that k_2 can be truly equated with $\beta_1'k_1'$.

Significance of k_3. Reactions x and xi are ones for which $\beta_1'[X_2] \gg 1$ so that $k_3 = \beta_3'k_3'/\beta_1'$. However, there seems to be no reason why k_3 for reaction xiii cannot be straightforwardly assigned to $\beta_2'k_2'$ although the absence of a detectable β_1 term in the rate equation is puzzling. However, a very similar rate equation (with terms $\beta_2[I_2]^2$ and $\beta_3[I_2]^3$ but no term $\beta_1[I_2]$) was obtained for reaction of $Mn_2(CO)_8[P(OPh)_3]_2$.[2] The only other reactions which show a term k_3 are stages II and III for reaction of $Ru_3(CO)_9(PPh_3)_3$ with ICl. Since it has not been possible to assign these observed kinetics to particular reactions, no further comment is justified.

Trends in Kinetic Parameters and the Intimate Mechanism. The sequence of reactivities inferred for all the reactions with I_2 and Br_2, namely, $Ru_3(CO)_9(PPh_3)_3X_2 \gg Ru_3(CO)_9L_3 > Ru_2(CO)_6L_2X_2$, is different from that shown by the reactions of $Os_3(CO)_{12}$ with halogens.[5,13] However, in the absence of any other examples it is not clear whether this is a function of the different metals involved or of the presence of substituents.

The values of $\beta_2'k_2'/\beta_1'$ for stage I of reaction with I_2 show a steady increase as the substituent changes along the series $P(OPh)_3 < PPh_3 < PBu_3$ while the change is $PPh_3 < PBu_3$ for stage II of reaction with Br_2. These trends are similar to, though less pronounced than, those for reactions of Mn_2-

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(17) Andrews, J. J.; Keefer, R. M. *Adv. Inorg. Chem. Radiochem.* **1961**, *3*, 91.

$(CO)_8L_2$.[2,4] The only comparable values of k_1' for different substituents show that $P(OPh)_3 > PBu_3$ for stage II of reaction with Br_2 and $PPh_3 \gtrsim PBu_3$ for stage II of reaction with I_2. This suggests that the substituent effect may be fully manifested in the rapid preequilibrium formation of the adducts complex·X_2 rather than in the slow stage of the reactions. In all reactions for which comparison is possible the rate constants for reaction with Br_2 are greater than for reaction with I_2 or ICl. Finally, the values of β_1' are generally much greater than those observed for reactions of $Mn_2(CO)_8L_2$.[2,4]

While the trends shown in some of these reactions are not as clear-cut or pronounced as those shown by the reactions of $Mn_2(CO)_8L_2$,[2,4] the general form of the kinetic behavior leads us to propose that the same mechanism is operating, namely, that there is a rapid preassembly of one or more halogen molecules around the surface of the complex and that these weaken the metal–metal bonds by attracting electron density from the metal–metal-bonding orbitals (which are the HOMO).[8] This attraction is probably transmitted through the CO ligands.[2,4] When the metal–metal bonds have been sufficiently weakened (by either the number or strength of the interactions with the halogen molecules), they undergo spontaneous fission (homolytic or heterolytic),[2] and halogen molecules are present to react very rapidly with the fragments formed. There is no evidence (for or against) as to whether the attraction of electrons from the HOMOs is quantized, i.e., whether a single electron is transferred to form $(\text{complex}^{+}\cdot)(X_2^{-}\cdot)(X_2)_{n-1}$, and this remains a distinct possibility.[18]

The ease with which some of these metal–metal-bonded carbonyls can attract several halogen molecules shows that they can act as quite strong polydentate Lewis bases[2,17] toward halogens. In the Ru_3 complexes, as with the Mn_2 complexes, it is those that are substituted with $P(OPh)_3$ that show the formation of adducts with the highest number of halogen molecules.[2,4] The reason for this is not clear.

The activation parameters (Table II) for bimolecular attack of I_2 on $Ru_3(CO)_9(PPh_3)_3\cdot I_2$ are quite compatible with the mechanism being proposed, but little can be said until further values are available.

The kinetics of stages II and III of reaction of ICl with $Ru_3(CO)_9(PPh_3)_3$ have not been discussed in detail because it is not clear exactly what the reactant complexes are. It is interesting, however, that stage II involves a path that is clearly *second* order in [complex]. Similar behavior is shown at high values of c_0 in the first stage of reaction of Br_2 with this complex and in the reaction[19] of I_2 with $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$. It therefore seems that in some cases activation of the metal–metal bonds can be accomplished by bringing two molecules of complex together, though a halogen molecule, sandwiched between them, may be a requirement for this.

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Registry No. $Ru_3(CO)_9(PPh_3)_3$, 15663-31-7; $Ru_3(CO)_9(P\text{-}n\text{-}Bu_3)_3$, 12258-07-0; $Ru_3(CO)_9[P(OPh)_3]_3$, 50661-53-5; I_2, 7553-56-2; Br_2, 7726-95-6; ICl, 7790-99-0; $Ru(CO)_3(PPh_3)I_2$, 76648-27-6; $Ru(CO)_3(PPh_3)Br_2$, 76648-28-7; $Ru(CO)_3(P\text{-}n\text{-}Bu_3)I_2$, 76613-62-2; $Ru(CO)_3(P\text{-}n\text{-}Bu_3)Br_2$, 76613-63-3; $Ru(CO)_3[P(OPh)_3]I_2$, 76613-64-4; $Ru(CO)_3[P(OPh)_3]Br_2$, 76613-65-5.

Supplementary Material Available: A table of kinetic data (6 pages). Ordering information is given on any current masthead page.

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Low Oxidation State, σ-Bonded Organometallic Derivatives of Indium(I)

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The organoindium compounds $NaIn(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe$, whose formulas indicate indium in the +1 oxidation state, have been prepared and characterized by elemental analyses, cryoscopic molecular weight measurements in benzene solution, and infrared and ^1H NMR spectral data. The novel indium(I) compounds were prepared from $In(CH_2SiMe_3)_3$ and NaH in the appropriate solvent by an apparent reductive elimination reaction. The nature of the specific indium(I) product was dependent on the reaction solvent. When either aromatic or hydrocarbon solvents were used, a hexameric species, $[NaIn(CH_2SiMe_3)_2]_6$, was formed. The product from dimethoxyethane, $[NaIn(CH_2SiMe_3)_2\cdot MeOC_2H_4OMe]_x$, exhibited an association which was concentration dependent. Structures which involve indium–indium bonds are proposed to account for the observed molecular association as well as the chemical and spectral properties.

Introduction

The organometallic derivatives of the main-group metals in low oxidation states provide unique synthetic challenges and opportunities. Cyclopentadienylindium(I), $In(C_5H_5)$,[1,2] represents the only previously known organometallic, low oxidation state compound of indium. The preparative reaction invovles the reagents $InCl_3$ and NaC_5H_5 in ether solution. The indium(I) product was believed to be formed by the reduction of $In(C_5H_5)_3$ by the cyclopentadienyl anion.[2] Unfortunately, little more is known about the nature of the apparent reduction reaction. An X-ray structural study[3] of $In(C_5H_5)$ has shown the compound to exist as a linear polymer with the cyclopentadienyl ring exhibiting η^5 coordination, rather than as a simple σ-bonded organometallic species.

The initial goal of our synthetic studies in indium chemistry was the preparation of a kinetically stable, σ-bonded, low

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