

common outer-sphere mechanism differences in the intrinsic self-exchange barriers in the ground and excited states may be large, reflecting differences in the shapes of the potential energy surfaces in the two states. The intersections of the ground- and excited-state potential surfaces with that for the reaction products may also be so different that effects due to the differences in ΔG° for the reactions of the two states cannot necessarily be discussed in simple terms for the extrinsic barriers of the Marcus theory³⁰ of electron-transfer rates.

Tris(bipyridyl)ruthenium complexes are nonlabile and their electron-transfer reactions (such as that between Fe^{2+} and $\text{Ru}(\text{bipy})_3^{3+}$) are outer sphere. The reaction between Tl^{3+} and ${}^3\text{CT Ru}(\text{bipy})_3^{2+}$ is also outer sphere, and the rate constant is very much greater than that for the thermal reaction between ground state $\text{Ru}(\text{bipy})_3^{2+}$ and Tl^{3+} , $1.9 \times 10^{-1} M^{-1} \text{sec}^{-1}$.¹² The standard one-electron reduction potential of Tl^{3+} is +0.3 V,¹³ and if E° for the reduction of $\text{Ru}(\text{bipy})_3^{3+}$ to ${}^3\text{CT Ru}(\text{bipy})_3^{2+}$ is ca. -1 V, the standard free energy changes for the reactions of the ground and the triplet charge-transfer states will be +22 and -28 kcal mol⁻¹. Such large differences in ΔG° would be more than sufficient to account for the difference of a factor of 10^9 in the reaction rates, but as we have pointed out above, such an interpretation may be

(30) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); **72**, 891 (1968).

too simplistic. The quenching by Fe^{3+} is also due to an electron-transfer process,²⁸ and ΔG° is ca. -38 kcal mol⁻¹, again very much more favorable than ΔG° for the ground-state reaction, +11.5 kcal mol⁻¹. The rate constant for the ground-state reaction can be calculated from the rate of the reverse reaction¹⁶ and is $2.6 \times 10^{-3} M^{-1} \text{sec}^{-1}$. Once again the increase in the rate of the reaction with ${}^3\text{CT Ru}(\text{bipy})_3^{2+}$ cannot be assigned definitely to the change in the thermodynamic barrier for the electron transfer.

The ratio of the rate constants for the reactions of Tl^{2+} with $\text{Ru}(\text{bipy})_3^{2+}$ and $\text{Ru}(\text{bipy})_3^{3+}$ is 1.6. The reactions have almost the same ΔG° (-21.8 and -22.1 kcal mol⁻¹, respectively, which are the same within the experimental errors in the E° values for the couples involving Tl^{2+})¹³ and the near identity of the rate constants is not surprising, as the reactions are outer sphere and the self-exchange rates for $\text{Tl}^{\text{III}}-\text{Tl}^{\text{II}}$ and $\text{Tl}^{\text{II}}-\text{Tl}^{\text{I}}$ are probably very similar. From the correlation between ΔG° and ΔG^\ddagger for other outer-sphere electron-transfer reactions of Tl^{2+} ,¹⁵ for $\Delta G^\circ = -22$ kcal mol⁻¹, k_9 and k_{10} are expected to be of the order of $10^6-10^7 M^{-1} \text{sec}^{-1}$.

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Registry No. $\text{Ru}(\text{bipy})_3^{2+}$, 15158-62-0; Fe^{3+} , 20074-52-6; Tl^{3+} , 14627-67-9; Fe^{2+} , 15438-31-0; Tl^+ , 22537-56-0.

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Reaction Mechanisms of Metal-Metal Bonded Carbonyls. IX.¹ Reaction of Tri-*n*-butylphosphine with Dodecacarbonyltriruthenium and Tetracarbonyl(tri-*n*-butylphosphine)ruthenium

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Tri-*n*-butylphosphine reacts with dodecacarbonyltriruthenium according to the rate equation $k_{\text{obsd}} = k_1 + k_2 [\text{PBu}_3]$. $\Delta H_2^\ddagger = 50.43 \pm 0.80$ kJ mol⁻¹, $\Delta S_2^\ddagger = -115.0 \pm 2.5$ J K⁻¹ mol⁻¹, and $10^2 k_2(50^\circ) = 4.56 \pm 0.17$ l. mol⁻¹ sec⁻¹. The products of the reaction are the complexes $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$, $\text{Ru}(\text{CO})_4\text{PBu}_3$, and *trans*- $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ in ratios that depend on the relative initial concentrations of complex and phosphine, high values of $[\text{Ru}_3(\text{CO})_{12}]/[\text{PBu}_3]$ leading to more trinuclear product and low values to more mononuclear products. When mainly mononuclear products are formed, the ratio $[\text{Ru}(\text{CO})_4\text{PBu}_3]/[\text{Ru}(\text{CO})_3(\text{PBu}_3)_2]$ in the product solutions is 2:1 suggesting that fission of the Ru_3 cluster occurs mainly in $\text{Ru}_3(\text{CO})_{11}\text{PBu}_3$. The $\text{Ru}(\text{CO})_4$ and $\text{Ru}(\text{CO})_3\text{PBu}_3$ products of this fission show a strong tendency to trimerize rather than to add an additional ligand. The substitution reaction of tri-*n*-butylphosphine with the complex $\text{Ru}(\text{CO})_4\text{PBu}_3$ proceeds by a dissociative mechanism and is much more rapid than that of $\text{Fe}(\text{CO})_2\text{PPh}_3$. Reaction under an atmosphere of carbon monoxide shows that carbon monoxide is about 6 times more nucleophilic than tri-*n*-butylphosphine toward the intermediate $\text{Ru}(\text{CO})_3\text{PBu}_3$.

Introduction

Reactions of dodecacarbonyltriruthenium with simple phosphorus-donor nucleophiles are generally believed²⁻⁴ to proceed in a stepwise manner to form the trisubstituted complexes $\text{Ru}_3(\text{CO})_9\text{L}_3$ in which one ligand L is attached to

each ruthenium atom in the triangular metal cluster. Whether intermediate, less substituted complexes are formed in detectable amounts during the course of the reaction depends on the particular nucleophile employed. Thus with triphenylphosphine no intermediates are detected although the complex $\text{Ru}_3(\text{CO})_{11}\text{PPh}_3$ has been isolated after reaction of the dodecacarbonyl with triphenylphosphine in hexane.⁴ With triphenyl phosphite and ETPB ($\text{P}(\text{OCH}_2)_3\text{CEt}$) ir bands assignable to mono- and disubstituted intermediates are seen to rise and fall in intensity during the reaction, the trisubstituted complex being the final product.^{1a}

Reactions with $\text{P}(\text{OPh})_3$,¹ PPh_3 ,¹ $\text{P}(\text{OCH}_2)_3\text{CEt}$,¹ $\text{P}(\text{OMe})_3$,¹ PMePh_2 ,⁵ PET_2Ph ,² PET_3 ,² and $\text{P}(n\text{-Bu})_3$ ^{1,2} all proceed by

(1) (a) Part VIII: A. J. Poë and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, in press; (b) A. J. Poë and M. V. Twigg, *J. Organometal. Chem.*, **50**, C39 (1973).

(2) J. P. Candlin and A. C. Shortland, *J. Organometal. Chem.*, **16**, 289 (1969), and references therein.

(3) M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, **7**, 427 (1968).

(4) M. I. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 2094 (1972).

Table I. Products of Reaction of Tri-*n*-butylphosphine with Dodecacarbonyltriruthenium

$10^3[\text{Ru}_3(\text{CO})_{12}], M$	$[\text{PBu}_3], M$	Solvent	Temp, °C	Reaction time	Products
100	0.5	Acetone or hexane	Reflux	2 hr	Ru_3L_3^a with a little RuL_2^b
30	1.5	Acetone or hexane	Reflux	10 min	RuL^c and RuL_2 ; more of latter when reaction time increased
~4	0.013	Heptane	60	3 hr	Mainly Ru_3L_3 but some RuL and RuL_2
~4	0.2	Heptane	60	25 min	Mainly RuL and RuL_2 but significant amounts of Ru_3L_3
0.5	≥ 0.1	Decalin	40	20 min	Only RuL and RuL_2 in mole ratio 2:1
0.1	0.01-0.08	Decalin	~25	25 hr	Mainly RuL and RuL_2 with some Ru_3L_3 ; $[\text{RuL}_2]/[\text{RuL}]$ increases with $[\text{L}]$; $[\text{Ru}_3\text{L}_3]$ increases with decreasing $[\text{L}]$
5-10	0.2	CH_2Cl_2 or acetone	~25	12 hr	Mainly RuL and RuL_2 in mole ratio 2:1; some Ru_3L_3 .
0.1	0.2	CH_2Cl_2 or acetone	~25	12 hr	RuL and RuL_2 ; no Ru_3L_3

^a $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ (ir bands at 1961 (s) and 1925 (m) cm^{-1} ; cf. ref 6). ^b *trans*- $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ (ir bands at 1883 and 1879 cm^{-1} ; cf. ref 6). ^c $\text{Ru}(\text{CO})_4\text{PBu}_3$ [ir bands at 2061 (s), 1980 (m), and 1945 (vs) cm^{-1} ; cf. 2060 (s), 1980 (m), 1940 (vs), and 1906 (vw) cm^{-1} for $\text{Ru}(\text{CO})_4\text{PPh}_3$ (F. Piacenti, *et al.*, *Inorg. Chem.*, 7, 1815 (1968))].

paths that are of mixed zero and first order in [nucleophile]. Monitoring the reaction with $\text{P}(\text{OMe})_3$ and $\text{P}(n\text{-Bu})_3$ by ir techniques showed that mononuclear substituted carbonyls were formed in large amounts; *i.e.*, fission of the Ru_3 cluster had readily occurred at some stage during the substitution process.^{1a} Since a knowledge of such fission processes should cast light on the strength and nature of the metal-metal bonding in such clusters, we have studied the reaction of $\text{Ru}_3(\text{CO})_{12}$ with tri-*n*-butylphosphine in some detail and also the reaction of tributylphosphine with $\text{Ru}(\text{CO})_4\text{PBu}_3$, one of the products of the former reaction.

Experimental Section

Chemicals were obtained and purified, and kinetic studies were performed, exactly as described previously,^{1a} especial care being taken to exclude oxygen when making up solutions of tributylphosphine.

Reaction of Tri-*n*-butylphosphine with Dodecacarbonyltriruthenium. Piacenti, *et al.*,⁶ reported the preparation of the complex $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ from a 1:4 mole ratio of carbonyl to phosphine in methanol or acetone at 50-60° but no further experimental details were given. We carried out the reaction under a wide variety of conditions and the results are summarized in Table I. Reactions were carried out under an atmosphere of nitrogen and the more concentrated solutions of complex were diluted with suitable amounts of decalin before measurement of their ir spectra. The $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ product, when formed, was found to react smoothly at 110° with an excess of phosphine to form *trans*- $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ with a half-life of 1-2 hr. An attempt was made to isolate pure samples of $\text{Ru}(\text{CO})_4\text{-PBu}_3$ and $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ from some of the product solutions by column chromatography on silica gel but, although dilute solutions of pure $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ were obtainable, isolation of larger amounts failed owing to extensive decomposition on the column.

In following the kinetics of the reaction, in decalin at 40-50°, of $\text{Ru}_3(\text{CO})_{12}$ (*ca.* $5 \times 10^{-4} M$) with phosphine ($\geq 0.1 M$) when no $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ product was observed the infinite-time spectra were characteristic of mixtures of the complexes $\text{Ru}(\text{CO})_2\text{PBu}_3$ and *trans*- $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$. On heating these mixtures at 70° all the $\text{Ru}(\text{CO})_4\text{-PBu}_3$ was converted to $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$, the intensity of the ir bands of the latter increasing in four runs by a factor of 3.08 with a mean deviation of ± 0.15 . Since $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ is quite stable under these conditions, this implies that the mono- and bisphosphine products of the reaction at 40-50° were formed in the mole ratio of 2:1, a ratio that was also observed for similar reactions at room temperature in dichloromethane or acetone.

The kinetics of this reaction were followed under high-purity nitrogen or argon by monitoring the decreasing intensity of the ir band at 2065 cm^{-1} due to the dodecacarbonyl. Pseudo-first-order rate plots were obtained in the usual way and were linear for at least 80% reaction. Values of k_{obsd} are given in Table II and were found to be linearly dependent on $[\text{PBu}_3]$. A suitably weighted least-squares analysis^{1a} was applied, assuming the rate equation to be $k_{\text{obsd}} = k_1 +$

Table II. Kinetic Data for the Reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{P}(n\text{-Bu})_3$ in Decalin ($[\text{Complex}] = \text{ca. } 5 \times 10^{-4} M$)

Temp, °C	$10^3[\text{P-Bu}_3], M$	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$	Temp, °C	$10^3[\text{P-Bu}_3], M$	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
30.0	15.8	1.73	50.0	14.0	7.17
	27.8	3.18		26.5	12.0
	40.9	5.12		36.9	18.1
	51.2	6.02		50.6	24.3
	56.1	6.66		68.6	31.1
	67.9	8.15		73.1	35.4
40.0	81.7	10.0	60.0	108	48.9
	97.5	11.9		2.1	2.04
	127	16.4		5.7	5.61
	29.5	7.48		8.1	7.34
	38.7	10.1		13.9	12.8
	60.0	16.2		24.3	19.9
50.0	84.5	21.8	32.0	27.4	
	105	28.3	39.4	32.6	
	119	32.2	43.2	34.8	
			51.2	43.1	

Table III. Kinetic Parameters for the Reaction of $\text{Ru}_3(\text{CO})_{12}$ with PBu_3 Obtained by a Least-Squares Analysis According to the Rate Equation $k_{\text{obsd}} = k_1 + k_2[\text{PBu}_3]^a$

Temp, °C	$10^4 k_1, \text{sec}^{-1}$	$10^2 k_2, \text{l. mol}^{-1} \text{sec}^{-1}$	$\sigma(k_{\text{obsd}}), \%$
30.0	-0.27 ± 0.08	1.26 ± 0.02	3.4
40.0	-5.19 ± 0.34	2.73 ± 0.07	3.0
50.0	0.66 ± 0.51	4.56 ± 0.17	5.4
60.0	0.36 ± 0.14	8.38 ± 0.22	6.1

^a $\Delta H_2^\ddagger = 50.43 \pm 0.80 \text{ kJ mol}^{-1}$ ($12.05 \pm 0.19 \text{ kcal mol}^{-1}$); $\Delta S_2^\ddagger = -115.0 \pm 2.5 \text{ J K}^{-1} \text{ mol}^{-1}$ ($-27.5 \pm 0.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$).

$k_2[\text{PBu}_3]$, and values of k_1 and k_2 are shown in Table III. The uncertainties in k_1 and k_2 are standard deviations corrected for the number of degrees of freedom so that any chosen confidence limits can be obtained by multiplying by the appropriate *t* factor for an infinite number of degrees of freedom. The quoted values of $\sigma(k_{\text{obsd}})$, the standard deviation of an individual measurement of k_{obsd} in any given set of values, have been similarly corrected. The values of ΔH_2^\ddagger and ΔS_2^\ddagger given in Table III were calculated by an appropriately weighted linear least-squares analysis of the dependence of $\log(k_2/T)$ on $1/T$.

The kinetics of the reaction of tributylphosphine with the complex $\text{Ru}(\text{CO})_4\text{PBu}_3$ were studied by allowing the dodecacarbonyl to react with tributylphosphine in decalin at room temperature under conditions such that $\text{Ru}(\text{CO})_4\text{PBu}_3$ and $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ were the only products. The product solutions were thoroughly degassed by one or more freeze-pump-thaw cycles and the space above the solutions in the reaction vessels filled with pure nitrogen or, in some cases, carbon monoxide. The temperature was then raised to a convenient value and the conversion of the mono- to the bisphosphine complex was followed by monitoring the decreasing intensity of the ir band at 1945 cm^{-1} characteristic of the former complex. Excellent pseudo-first-order rate plots, linear for *ca.* 90% reaction, were obtained and values of k_{obsd} are reported in Table IV. Those obtained from reactions under nitrogen are independent of $[\text{PBu}_3]$ and the quoted values

(5) M. V. Twigg, unpublished observations.

(6) F. Piacenti, M. Bianchi, E. Benedetti, and G. Sbrana, *J. Inorg. Nucl. Chem.*, 29, 1389 (1967).

Table IV. Kinetic Data for the Reaction of $\text{Ru}(\text{CO})_4\text{PBu}_3$ with PBu_3 in Decalin ($[\text{Complex}] = ca. 5 \times 10^{-4} M$)^a

Temp, °C	$10^3 [\text{P-Bu}_3], M$	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$	Temp, °C	$10^3 [\text{P-Bu}_3], M$	$10^4 k_{\text{obsd}}, \text{sec}^{-1}$
60.0	190	1.30	90.0	504	77.6
	255	1.34		720	78.0
	286	1.35		753	74.5
65.0	358	2.88	Under 1 atm of carbon monoxide		
	399	2.90			
70.0	96	5.50	80.0	19	7.39
	194	5.58		25	8.56
	483	5.69		35	13.2
75.0	377	11.2	61	15.1	
	411	11.6	89	16.2	
80.0	177	20.4	151	18.3	
	218	22.2	173	18.6	
	382	21.4	320	19.3	
85.0	344	40.2	422	20.0	
	421	39.4			

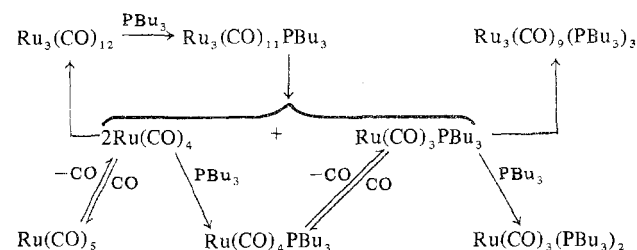
^a $\Delta H^\ddagger = 132.13 \pm 0.74 \text{ kJ mol}^{-1}$ ($31.57 \pm 0.18 \text{ kcal mol}^{-1}$); $\Delta S^\ddagger = 76.6 \pm 2.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ($18.3 \pm 0.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$); $\sigma(k_{\text{obsd}}) = \pm 3.2\%$.

of ΔH^\ddagger and ΔS^\ddagger were obtained by a nonweighted linear least-squares analysis of the dependence of $\log(k_{\text{obsd}}/T)$ on $1/T$, the assumption being made that there was a constant percentage uncertainty in each value of k_{obsd} . The uncertainties quoted are standard deviations corrected as before for the number of degrees of freedom.

Discussion

The results can be described most simply in terms of Scheme I. The relative yields (2:1) of $\text{Ru}(\text{CO})_4\text{PBu}_3$ and $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$

Scheme I



$(\text{PBu}_3)_2$ when the concentration of complex is low suggest that it is the monosubstituted complex $\text{Ru}_3(\text{CO})_{11}\text{PBu}_3$ that undergoes fission of the Ru_3 cluster. If $\text{Ru}_3(\text{CO})_{12}$ itself undergoes fission, then the only mononuclear products formed would be $\text{Ru}(\text{CO})_4\text{PBu}_3$ since the latter does not undergo substitution under these conditions. Equally, if it were $\text{Ru}_3(\text{CO})_{10}(\text{PBu}_3)_2$ that underwent fission, then $\text{Ru}(\text{CO})_4\text{PBu}_3$ and $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ would be formed in the ratio 1:2. It is, however, possible that the observed ratio 2:1 could result accidentally from Ru_3 fission of $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{11}\text{PBu}_3$, and $\text{Ru}_3(\text{CO})_{10}(\text{PBu}_3)_2$ in appropriate proportions but we believe this to be improbable.

It is not clear from the data whether the fission process occurs in a spontaneous way or as the result of bimolecular attack by the phosphine. The former has been assumed in the scheme solely for simplicity. The pronounced increase in the proportion of $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ in the product solutions as the initial concentration of the complex is increased is in accord with the kinetic order expected for the formation of clusters from the mononuclear intermediates but it is not possible to distinguish whether the clustering proceeds *via* slow second-order dimerization followed by rapid addition of the third fragment or *via* a slow, one-step termolecular reaction. The competition between formation of mono- and trinuclear products is also clearly dependent on the concentration of phosphine in the way expected. Significant cluster formation occurs even when the initial concentration

of complex is as low as $10^{-4} M$ provided that the concentration of the phosphine complex is not much greater than *ca.* $10^{-2} M$. This implies that the rate of recombination of the four-coordinate intermediates with each other must be *at least* 10^2 times greater than that of simple addition of a phosphine ligand. The instability of $\text{Ru}(\text{CO})_5$ with respect to $\text{Ru}_3(\text{CO})_{12}$ is well known^{7,8} and this is especially true⁵ in the light and under low pressures of CO so that trimerization of $\text{Ru}(\text{CO})_4$ is a highly favored process although no quantitative data are available. $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ is also formed to some extent in the CO-dissociative reaction of $\text{Ru}(\text{CO})_4\text{PBu}_3$ with low concentrations of tributylphosphine so that trimerization of $\text{Ru}(\text{CO})_3\text{PBu}_3$ is also favored. There is some evidence that $\text{Ru}(\text{CO})_4$ trimerizes more readily than $\text{Ru}(\text{CO})_3\text{PBu}_3$ in that when tri- and mononuclear products are formed together, the ratio of $\text{Ru}(\text{CO})_3(\text{PBu}_3)_2$ to $\text{Ru}(\text{CO})_4\text{PBu}_3$ in the product mixture increases with $[\text{PBu}_3]$. The trimerization of $\text{Ru}(\text{CO})_3\text{PBu}_3$ under our conditions must be essentially irreversible since $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ undergoes ring fission with tributylphosphine at appreciable rates only above *ca.* 100° .

There is no evidence for formation of significant amounts of $\text{Ru}_3(\text{CO})_{10}(\text{PBu}_3)_2$ in the sequence of reactions and it would therefore appear that while $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ are both quite stable, kinetically and thermodynamically, toward Ru_3 fission the mono- and disubstituted cluster complexes are both relatively quite unstable. This suggests that electronic asymmetry in the Ru-Ru bonds must result in instability since the steric effects even in $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ are evidently not particularly large. Our results contrast with those of Udovich, *et al.*,⁹ who found that up to six carbonyl groups can be replaced by trifluorophosphine before ring fission occurs. They do bear some resemblance, however, to photochemical reaction of $\text{Ru}_3(\text{CO})_{12}$ with triphenylphosphine in *n*-heptane which, in the absence of carbon monoxide, produces $\text{Ru}(\text{CO})_4\text{PPh}_3$ and *trans*- $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ in the molar ratio *ca.* 2:1.¹⁰ Under these conditions, therefore, it appears that $\text{Ru}_3(\text{CO})_{11}\text{PPh}_3$ is also very susceptible to ring fission.

The kinetics of the reaction of tributylphosphine with $\text{Ru}_3(\text{CO})_{12}$ follow the typical rate equation¹ $k_{\text{obsd}} = k_1 + k_2 \cdot [\text{PBu}_3]$ where k_1 is characteristic of a CO-dissociative path. However, the values of k_1 in Table III do not agree with those found, for instance, from the reaction with the much less air-sensitive nucleophile triphenylphosphine. Preliminary results led to significantly negative values of k_1 at all temperatures, but as more extreme care was taken to exclude oxygen, the values of k_1 increased and the data in Table II represent the best sets obtained. Candlin and Shortland's data² for reaction of $\text{Ru}_3(\text{CO})_{12}$ with highly nucleophilic, air-sensitive nucleophiles also show very inconsistent values of k_1 , and negative intercepts are also found from plots of k_{obsd} against $[\text{PBu}_3]$ for the reaction with $(\text{C}_8\text{H}_8)\text{Fe}(\text{CO})_3$ to form $\text{Fe}(\text{CO})_3(\text{PBu}_3)_2$.¹¹ This problem does not affect at all significantly the values of the kinetic parameters found for bimolecular attack of tributylphosphine on $\text{Ru}_3(\text{CO})_{12}$ that have been discussed elsewhere.¹ It is, however, unfortunate since it prevents a check being made on one implication of the proposed scheme. Thus, if the fission of $\text{Ru}_3(\text{CO})_{11}\text{PBu}_3$ is

(7) F. Piacenti, M. Bianchi, E. Benedetti, and G. Braca, *Inorg. Chem.*, **7**, 1815 (1968).

(8) F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, **6**, 1220 (1967).

(9) C. A. Udovich and R. J. Clark, *J. Organometal. Chem.*, **36**, 355 (1972).

(10) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organometal. Chem.*, **67**, C75 (1974).

(11) F. Faraone, F. Zingales, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, **7**, 2362 (1968).

independent of $[\text{PBu}_3]$ and if all the $\text{Ru}(\text{CO})_4$ formed reverts to $\text{Ru}_3(\text{CO})_{12}$ at very low values of $[\text{PBu}_3]$, then k_{obsd} should approach $k_1/3$ as $[\text{PBu}_3]$ approaches zero. If the fission is caused by bimolecular attack by phosphine, then formation of $\text{Ru}_3(\text{CO})_9(\text{PBu}_3)_3$ under these conditions should proceed without formation of mononuclear intermediates and k_{obsd} would approach k_1 . Bimolecular attack by phosphines on $\text{Ru}_3(\text{CO})_{12}$ has been shown most probably to occur at or close to a metal atom¹ since the selectivity between different phosphines is characteristic of similar attack at mononuclear carbonyls. Since there are no comparable data for attack on $\text{Ru}_3(\text{CO})_{11}\text{L}$ complexes, one cannot exclude the possibility that bimolecular reactions, if they occur, might proceed by highly reversible fission of one Ru-Ru bond followed by phosphine attack on the "ring-opened" intermediate. Such a mechanism would result in a much lower selectivity between different phosphines because of the reactivity of the intermediate but could very easily lead to complete ring fission.

The data in Table III show that the substitution reaction of $\text{Ru}(\text{CO})_4\text{PBu}_3$ with tributylphosphine is first order in [complex] and independent of $[\text{PBu}_3]$ and that it therefore most probably proceeds *via* a CO-dissociative mechanism. The values of ΔH^\ddagger and ΔS^\ddagger are consistent with this and can be compared with the values $\Delta H^\ddagger = 178 \pm 5 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 77 \pm 12 \text{ J K}^{-1} \text{ mol}^{-1}$, and $k(170^\circ) = 1.1 \times 10^{-4} \text{ sec}^{-1}$ for the CO-dissociative reaction of $\text{Fe}(\text{CO})_4\text{PPh}_3$ in decalin.¹² This greater reactivity of the second-row metal carbonyl is similar to that shown by $\text{Mo}(\text{CO})_6$ compared with $\text{Cr}(\text{CO})_6$, the former having an activation enthalpy 35 kJ mol^{-1} less than the first-row metal carbonyl¹³ although there is an additional activation entropy difference in this case that is not apparent in the reactions of $\text{Fe}(\text{CO})_4\text{PPh}_3$ and $\text{Ru}(\text{CO})_4\text{PBu}_3$.

The behavior of the substitution reaction of $\text{Ru}(\text{CO})_4\text{PBu}_3$ under an atmosphere of carbon monoxide is also consistent with the CO-dissociative mechanism, the rate being increasingly retarded as $[\text{PBu}_3]$ is lowered although the reaction still goes to completion. The rate equation characteristic of a CO-dissociative reaction under such conditions is $k_{\text{obsd}} = \{k_1 k_2 [\text{PBu}_3] / k_{-1} [\text{CO}]\} / \{1 + k_2 [\text{PBu}_3] / k_{-1} [\text{CO}]\}$ where k_1 is the rate constant for the dissociative loss of carbon monoxide and k_{-1} and k_2 are the second-order rate constants for nucleophilic attack by carbon monoxide and tributylphosphine, respectively, on the four-coordinate intermediate $\text{Ru}(\text{CO})_3\text{PBu}_3$. The plot of $1/k_{\text{obsd}}$ against $1/[\text{PBu}_3]$ is linear as expected (Figure 1) and the value $k_1 = (22.2 \pm 1.4) \times 10^{-4} \text{ sec}^{-1}$, obtained from the intercept at $1/[\text{PBu}_3] = 0$ by a weighted linear least-squares analysis, is in excellent agreement with the values found in the absence of carbon monoxide. The value of $[\text{CO}]$ is $5.4 \times 10^{-3} \text{ M}$ under these condi-

(12) E. E. Siefert and R. J. Angelici, *J. Organometal. Chem.*, **8**, 374 (1967).

(13) H. Werner, *Angew. Chem., Int. Ed. Engl.*, **7**, 930 (1968).

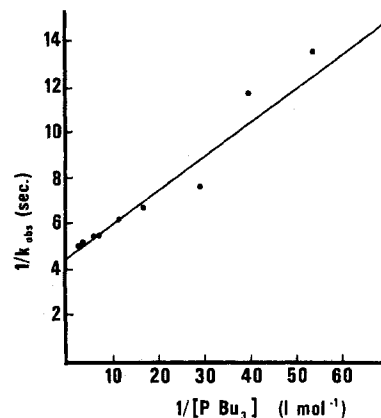


Figure 1. $1/k_{\text{obsd}}$ vs. $1/[\text{PBu}_3]$ for the reaction of $\text{Ru}(\text{CO})_4\text{PBu}_3$ with PBu_3 in decalin at 80.0° under an atmosphere of carbon monoxide.

tions¹⁴ and the ratio of the gradient to the intercept leads to a value of 0.17 ± 0.04 for k_2/k_{-1} . This value is rather low when compared with corresponding values for some four-coordinate d^8 cobalt carbonyl complexes^{1a,14} and even with the five-coordinate d^6 intermediate $\text{Mo}(\text{CO})_4\text{PPh}_3$.¹⁵ This suggests that the intermediate $\text{Ru}(\text{CO})_3\text{PBu}_3$ may be quite discriminating and, therefore, relatively unreactive, a conclusion already indicated by the relatively high rate of trimerization even in the presence of quite significant amounts of free phosphine. An extension of such studies to a series of different nucleophiles would clearly be of interest as a means of characterizing this four-coordinate d^8 complex. Cardaci¹⁶ has shown that triphenylphosphine is about 6 times more nucleophilic than carbon monoxide toward $\text{Fe}(\text{CO})_4$ in distinct contrast to the value $k(+\text{PBu}_3)/k(+\text{CO}) = 0.17$ for attack at $\text{Ru}(\text{CO})_3\text{PBu}_3$. He has further postulated that $\text{Fe}(\text{CO})_4$ occurs in two forms, one of which reacts with triphenylphosphine to form $\text{Fe}(\text{CO})_4\text{PPh}_3$, the other forming $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$. Darensbourg and Condor¹⁷ have shown that the carbene intermediate $\text{Fe}(\text{CO})_3\text{C}(\text{OEt})\text{Me}$ is also quite discriminating toward phosphorus-donor nucleophiles and it is evident that such competition studies provide a powerful means of investigating the nature of coordinatively unsaturated intermediates.

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Registry No. $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{Ru}(\text{CO})_4\text{PBu}_3$, 52699-23-7; PBu_3 , 998-40-3.

(14) M. Basato, J. P. Fawcett, and A. J. Poë, *J. Chem. Soc., Dalton Trans.*, 1350 (1974).

(15) C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1286 (1973).

(16) G. Cardaci, *Inorg. Chem.*, **13**, 368 (1974).

(17) D. J. Darensbourg and H. L. Condor, *Inorg. Chem.*, **13**, 374 (1974).