Table I. Rates of Zinc Porphyrin Formation as a Function of Porphyrin Type

Compound	$10^3 k_0$,[a,b] sec^{-1}
Mesoporphyrin IX DME[c]	3.46
Deuteroporphyrin DME	2.66
Hematoporphyrin DME	2.20
Protoporphyrin DME	3.01
Dibromodeuteroporphyrin DME	3.85
Porphine	1.92
Etioporphyrin III	3.01
Uroporphyrin I OME[d]	2.77
Tetraphenylporphine	6.65
p-OCH_3, TPP[e]	10.2
p-CH_3, TPP	5.54
p-Cl, TPP	9.49

[a] Concentration of $ZnCl_2$ is 7.44×10^{-2} *F*. [b] Solvent is 11% water in pyridine, 55.4°. [c] DME is dimethyl ester. [d] OME is octamethyl ester. [e] *p*-Methoxy derivative of tetraphenylporphine.

of copper acetate incorporation, data were not taken over a wide enough range, and this could have led to a mistake in reaction order.

The kinetics of nickel acetate reacting with hematoporphyrin in acetic acid is half order in total nickel.[1] The explanation was that $Ni(OAc)^+$ (from $Ni(OAc)_2$) was the reactant. The observation that monomeric copper acetate produced by the addition of LiOAc to copper dimers shows first-order rate behavior might argue against, for example, $Cu_2(OAc)_3^+$ being a reactant in our system. In related work, the incorporation of copper into TPyP in 8.3% acetic acid, pH 1.92, showed a first-order dependence on total copper. Under these conditions, the copper monomer would be predominant.

The acidity of acetic acid has been used to rank the inherent basicity of porphyrins toward proton acceptance.[10] In this study, the order would be tetrapyridylporphine and diacetyldeuteroporphyrin (primarily PH_2), hematoporphyrin (primarily PH_2 and PH_3^+), and etioporphyrin (PH_2, PH_3^+ and PH_4^{2+}). The observation that all of the porphyrins incorporate copper, except when the porphyrin is almost exclusively in the diacid form with HCl, suggests that the diacid is extremely unreactive compared to the free base and monocation porphyrins. Since the hydrogen ion concentration is by necessity constant in this study, the reactions of monomeric copper with either the monocation or the free base porphyrin, or both, give the same empirical rate law. In aqueous solution, however, only the free base has shown appreciable reactivity.[3,9]

Along similar lines, Table I is a list of rate constants found for zinc incorporation into 12 porphyrins in a mixed pyridine–water solvent. All of the porphyrins are in the free base form. While explored in detail with mesoporphyrin,[8] the rates are assumed to be half order in total zinc. Figure 3 is a linear plot of $\Delta H^\ddagger$ *vs.* $\Delta S^\ddagger$ for three of these reactions, and this suggests that a common mechanism may be followed. The isokinetic temperature is 160°, over 100° above the temperature at which the measurements were taken. While a detailed mechanism cannot be postulated, it is quite interesting to note that, regardless of the porphyrin type or basicity, the rates of incorporation are quite similar. In general, it appears that it is the charge on the periphery of the porphyrin, and not the porphyrin basicity with respect to the four central nitrogen atoms, which influences the rate of metal ion incorporation.[11] This is in contrast to the results found for three porphyrins in aqueous solution,[12] and further work is needed to clarify this discrepancy.[13]

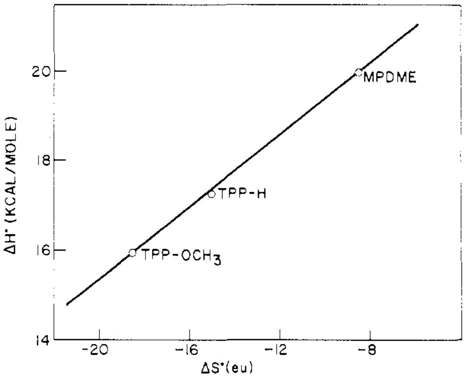

Figure 3. Plot of the activation parameters for three porphyrins for the formation of the zinc porphyrins in a pyridine–water solvent.

Registry No. Mesoporphyrin IX dimethyl ester, 1263-63-4; deuteroporphyrin dimethyl ester, 10589-94-3; hematoporphyrin dimethyl ester, 32562-61-1; protoporphyrin dimethyl ester, 6164-53-0; dibromodeuteroporphyrin dimethyl ester, 14196-91-9; porphine, 101-60-0; etioporphyrin III, 531-16-8; uroporphyrin I octamethyl ester, 10170-03-3; tetraphenylporphine, 917-23-7; tetra-*p*-anisylporphine, 22112-78-3; tetra-*p*-tolylporphine, 14527-51-6; tetrakis(*p*-chlorophenyl)porphine, 22112-77-2; tetrapyridylporphine, 16834-13-2; diacetyldeuteroporphyrin, 7265-15-8; copper, 7440-50-8; zinc, 7440-66-6; acetic acid, 64-19-7.

Acknowledgments. We thank the USAEC, Contract No. AT-(40-1)-4047, and the Gulf Educational Foundation for financial support.

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(11) P. Hambright, *Coord. Chem. Rev.*, 6, 247 (1971).

(12) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964, p 35.

(13) Note Added in Proof. D. A. Brisbin and G. D. Richards (*Inorg. Chem.*, 11, 2849 (1972)) have recently come to similar conclusions concerning the rate law for copper incorporation in acetic acid. Their observed half-order rate constant for protoporphyrin IX DME is in agreement with our data for similar ligands.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Kinetics of Tertiary Phosphine Substitution on Di-μ-nitrosyl-decacarbonylruthenium

Jack R. Norton and James P. Collman*

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The kinetics of substitution on mononuclear nitrosylcarbonyl complexes such as $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ have been the subject of much recent study.[1,2] They display rate laws dominated by terms first order in the entering ligand as well as in the metal complex

$$\text{rate} = [M(NO)_n(CO)_{4-n}][L]$$

In contrast the isoelectronic $Ni(CO)_4$ undergoes substitu-

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(1) F. Basolo, *Chem. Brit.*, 5, 505 (1969), and references therein.

(2) J. P. Day, D. Diamente, and F. Basolo, *Inorg. Chim. Acta*, 3, 363 (1969).

tion at a very rapid rate independent of the concentration of the entering ligand

rate = $[Ni(CO)_4]$

Although it is possible that a second-order term is present with nickel carbonyl but experimentally undetectable due to the rapid first-order reaction,[1,2] it has frequently been suggested that the nitrosyl ligand functions as an "electron well" to stabilize coordinatively supersaturated transition states.[1-4] It was clearly of interest to see whether the anomalous kinetic behavior of nitrosyl complexes extended to polynuclear species containing nitrosyl bridges such as the recently characterized $Ru_3(CO)_{10}(NO)_2$.[5]

Experimental Section

Materials. The $Ru_3(CO)_{10}(NO)_2$ employed was prepared as previously described.[5] $Rh_4(CO)_{12}$ was made by the method of Stone[6] and stored at −30°. Other materials used were obtained commercially. Triphenylphosphine was recrystallized from ethanol. The solvent cyclohexane was Matheson Coleman and Bell Spectroquality. All solutions were deoxygenated with nitrogen before use.

Kinetics. The rates of the phosphine substitution reactions of $Ru_3(CO)_{10}(NO)_2$ in cyclohexane solution were obtained by monitoring the disappearance of its sharp infrared absorption at 2038 cm^{-1} using a Perkin-Elmer 457 spectrometer. Pseudo-first-order conditions were employed, with the initial concentration of entering phosphine always being at least 10 times that of the ruthenium cluster. Solutions were placed in a controlled-temperature bath (±0.1°) for 30 min before mixing. At appropriate intervals aliquots were withdrawn under a countercurrent of argon and placed in a 1-mm KBr cell, and their carbonyl region infrared spectrum was then recorded. Control experiments established that the progress of the reaction was negligible during the scanning period. Examination of the spectrum after 1 hr showed that the reaction of triphenylphosphine (1.6×10^{-3} *M*) and $Ru_3(CO)_{10}(NO)_2$ (1.6×10^{-4} *M*) was almost completely suppressed by 65 psi of carbon monoxide.

Observed rate constants were obtained from the slope of a plot of $\ln (A - A_\infty)$ against time as determined by standard least-squares methods on an IBM 360 computer. Values of activation parameters were also calculated by a least-squares program. Uncertainties given are the least-squares standard deviations.

With triphenylphosphine as entering ligand the observed infrared spectrum after a sufficient number of half-lives was identical with that of pure $Ru_3(CO)_8(NO)_2((C_6H_5)_3P)_2$ prepared as described below. However, an intermediate (characterized by distinct bands at 2095 and 2055 cm^{-1} and overlapping absorptions elsewhere) appeared and disappeared during the course of the disubstitution. At a given temperature the time $t_{\max}$ of maximum concentration of the intermediate was independent of the concentration of triphenylphosphine. Thus an estimate of the second rate constant was obtained by treating the situation as a series of two first-order reactions with rates k_1 and k_2 where

$$t_{\max} = \frac{1}{k_1 - k_2} \ln\frac{k_1}{k_2}$$

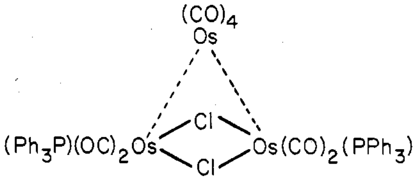
With methyldiphenylphosphine a similar intermediate was observed and in addition a band at 1900 cm^{-1}, characteristic of $Ru(CO)_3L_2$,[7] began to appear before the substitution reactions were entirely complete.

Preliminary experiments with $Ir_4(CO)_{12}$ and $Rh_4(CO)_{12}$ showed that the iridium carbonyl had a substitution half-life of at least 2 days in refluxing cyclohexane, whereas substitution on the rhodium carbonyl[8] occurred upon mixing solutions at room temperature (as indicated by the immediate evolution of bubbles of carbon monoxide). Assuming a temperature dependence of the former reaction comparable to that of other metal carbonyl cluster substitution reactions,[9,10] a very conservative estimate of a rate difference of 10^7 at room temperature can be obtained.

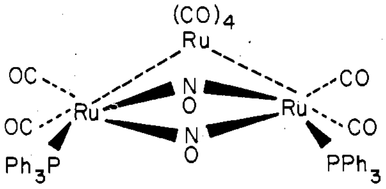
Di-μ-nitrosyl-octacarbonylbis(triphenylphosphine)triruthenium-Benzene, $Ru_3(CO)_8((C_6H_5)_3P)_2(NO)_2 \cdot C_6H_6$. Di-μ-nitrosyl-decacarbonyltriruthenium (26 mg) and triphenylphosphine (31 mg) were stirred for 12 hr at room temperature in 10 ml of benzene under nitrogen. Heptane was then added and solvent removed under vacuum until an orange-brown powder precipitated. The product was filtered and washed three times with pentane under a blanket of nitrogen. *Anal.* Calcd for $Ru_3C_{50}H_{36}N_2P_2O_{10}$: C, 50.47; H, 3.05; N, 2.35; P, 5.21; mol wt 1190. Found: C, 50.55; H, 3.11; N, 2.28; P, 5.02; mol wt 1226 (osmometric in benzene). Infrared: ν_{CO} (in cyclohexane) 2077 (s), 2018 (s), 2008 (vs), 1998 (m), and 1975 (m, br) cm^{-1}; ν_{NO} (in KBr) 1445 and 1470 cm^{-1} (partially obscured by overlapping triphenylphosphine bands).

Results and Discussion

In the presence of triphenylphosphine $Ru_3(CO)_{10}(NO)_2$ (**1**) undergoes disubstitution to form $Ru_3(CO)_8((C_6H_5)_3P)_2(NO)_2$ (**3**). The formation and disappearance of an intermediate, presumably the monosubstituted cluster $Ru_3(CO)_9((C_6H_5)_3P)(NO)_2$ (**2**), are plainly observed. The fact that these are consecutive first-order reactions of comparable rate (see below) suggests consecutive substitutions at either end of the nitrosyl bridge of **1**, as does the strong resemblance of the carbonyl region infrared spectrum of the product **3** to that reported for the similar complex[11]



Thus the disubstituted complex **3** seems likely to have the structure



(The proposed stereochemistry around ruthenium is based solely on that observed in X-ray crystallographic studies of structurally related $Fe_3(CO)_{12}$ derivatives.[12,13])

The rates observed for the first substitution step in cyclohexane solution are given in Table I. They obey the law

rate = $k_1 [Ru_3(CO)_{10}(NO)_2]$

where $k_1 = (10.0 \pm 0.2) \times 10^{-5}$ sec^{-1} at 22.1°. There is no dependence on the concentration of triphenylphosphine over a 50-fold range. With more alkylated phosphines such as $CH_3(C_6H_5)_2P$ the disubstituted product is slowly

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(3) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 9, 1105 (1970).

(4) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 91, 5659 (1969).

(5) J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 11, 382 (1972).

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

(10) G. Cetini, O. Gambino, E. Sappa, and G. A. Vaglio, *Atti Accad. Sci. Torino, Cl. Sci Fis., Mat. Natur.*, 101, 855 (1966-1967).

(11) A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 897 (1970).

(12) D. J. Dahm and R. A. Jacobson, *J. Amer. Chem. Soc.*, 90, 5106 (1968).

(13) W. S. McDonald, J. R. Moss, G. Raper, B. L. Shaw, R. Greatrex, and N. N. Greenwood, *Chem. Commun.*, 1295 (1969).

Table I. Kinetic Data for the Disappearance of $Ru_3(CO)_{10}(NO)_2$ by Phosphine Substitution in Cyclohexane Solution

Temp, °C	10^3[L], *M*	$10^4[Ru_3(CO)_{10}(NO)_2]_0$, *M*	$10^5 k_{obsd}$,[a] sec^{-1}
	$L = (C_6H_5)_3P$		
22.1	1.6	1.6	9.7 (4)
22.1	4.0	4.0	9.6 (2)
22.1	8.0	4.0	10.1 (2)
22.1	16.0	4.0	9.8 (3)
22.1	32.0	4.0	10.1 (2)
22.1	80.0	4.0	10.1 (3)
10.1	16.0	4.0	1.27 (3)
15.9	16.0	4.0	3.52 (12)
28.1	16.0	4.0	26.4 (5)
	$L = CH_3(C_6H_5)_2P$		
22.1	16.0	4.0	9.6 (2)
22.1	32.0	4.0	10.7 (2)
22.1	80.0	4.0	10.1 (2)

[a] Least-squares standard deviation in the least significant digit is in parentheses.

cleaved to monomeric species such as $Ru(CO)_3L_2$;[7] however, the rate of the primary substitution reaction remains essentially the same and is hence independent of the nature as well as of the concentration of entering ligand. This evidence, along with the observation of inhibition by carbon monoxide, supports a dissociative mechanism

$$Ru_3(CO)_{10}(NO)_2 \xrightarrow{k_1} Ru_3(CO)_9(NO)_2 + CO \quad \text{(slow)}$$

$$Ru_3(CO)_9(NO)_2 + L \rightarrow \text{products} \quad \text{(fast)}$$

The rates for both substitution steps with triphenylphosphine and the activation parameters for the first step and related reactions are given in Table II. Comparison with the values reported for first-order substitution[9] and exchange[10] on $Ru_3(CO)_{12}$ (also in Table II) shows that the data are quite consistent with the operation of dissociative mechanisms in both cases. The Ru–C bond broken in the rate-determining step of the reaction appears to be somewhat weaker in **1** than in $Ru_3(CO)_{12}$, resulting in a slightly smaller $\Delta H^{\ddagger}$ and a slightly faster rate of substitution.

The bridging nitrosyl ligands present in **1** in place of the terminal carbonyl ligands in $Ru_3(CO)_{12}$ have no substantial effect on the mechanism of the substitution reaction. They do not serve as "electron wells" and cause **1** to show a relative preference for a second-order rate law. The roughly octahedral geometry around the ruthenium atoms in **1** is important in this respect, since the mononuclear nitrosyl complexes where second-order terms have been shown to be important[1,2] can have less crowded associative transition states.

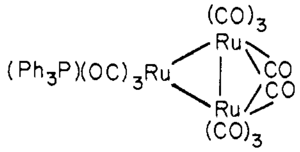
The nitrosyl bridges in **1** also do not produce a rate enhancement of the magnitude which results from the introduction of carbonyl bridges into molecules of this sort. A striking example of the latter effect is provided by the comparison between nonbridged $Ir_4(CO)_{12}$ and its bridged periodic analog $Rh_4(CO)_{12}$. At room temperature the substitution rate of the latter is at least 10^7 times faster, far too great an increase to be explained by metal-carbon bond strength differences. Presumably carbonyl-bridged complexes can undergo substitution by some mechanism other than a purely dissociative one—a mechanism not available to the nitrosyl-bridged **1**.

Table II. Rate Constants and Activation Parameters for the Substitution of Ruthenium Carbonyl Clusters at 22.1°

Compd	Entering ligand	$10^5 k_1$,[a] sec^{-1}	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[a] eu
$Ru_3(CO)_{10}(NO)_2$	$(C_6H_5)_3P$	10.0 (2) 7 (1)[b]	27.9 (5)	18 (2)
$Ru_3(CO)_{12}$	$(C_6H_5)_3P$	0.09[c,d]	32 (2)[d]	23 (4)[d]
$Ru_3(CO)_{12}$	CO	0.09[c,e]	32 (1)[e]	21[e]

[a] Numbers in parentheses are the least-squares standard deviations in the least significant digit. [b] Approximate first-order rate constant observed for the disappearance of an intermediate. [c] Extrapolated from higher temperature data. [d] Data of Candlin and Shortland.[9] [e] Data of Cetini, Gambino, Sappa, and Vaglio.[10]

The observation of a rate constant for the second substitution on $Ru_3(CO)_{10}(NO)_2$ ($2 + L \rightarrow 3$) comparable to that of the first ($1 + L \rightarrow 2$) is worthy of comment because only *one* rate constant is observed for trisubstitution on $Ru_3(CO)_{12}$ (no mono- or disubstituted cluster can be isolated or detected).[9] It would appear that a "long-range" effect is at work across the $Ru_3(CO)_{12}$ cluster. Monosubstitution must produce some change in the reactivity of the initially unsubstituted ruthenium atoms, perhaps by inducing transient formation of a labile (see above) carbonyl-bridged structure such as



Registry No. $Ru_3(CO)_{10}(NO)_2$, 36583-24-1; $(C_6H_5)_3P$, 603-35-0; $CH_3(C_6H_5)_2P$, 1486-28-8; $Ru_3(CO)_8((C_6H_5)_3P)_2(NO)_2 \cdot C_6H_6$, 36631-36-4.

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Contribution from the Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069

High-Pressure Interaction of Phosphorus Trifluoride with Oxygen, Sulfur, Selenium, and Tellurium[1]

Arnulf P. Hagen* and Eugene A. Elphingstone

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The use of high pressures (4000 atm) in the synthesis of volatile inorganic substances has not received the general acceptance that this technique has received in organic synthesis and mechanistic studies.[2-6] This communication further demonstrates[7,8] the versatility of combining the

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(1) This report is based on portions of a dissertation submitted by E. A. E. to the Graduate College of the University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
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(3) R. C. Neuman, Jr., *J. Org. Chem.*, 37, 495 (1972).
(4) W. J. Le Noble, *Progr. Phys. Org. Chem.*, 5, 207 (1967).
(5) S. D. Hamann, *High Pressure Phys. Chem.*, 2, 163 (1963).
(6) C. Walling and T. A. Augurt, *J. Amer. Chem. Soc.*, 88, 4163 (1966).