This is consistent with photolabilization of CO followed by reaction of the transient photoproduct II with free CO,[5] e.g.

$$Ru_3(CO)_{12} \xrightarrow[S]{h\nu} \underset{\text{II}}{Ru_3(CO)_{11}S} + CO \qquad (3)$$

$$\text{II} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} Ru_3(CO)_{11} + S \qquad (4)$$

$$Ru_3(CO)_{11} + CO \xrightarrow{k_c} Ru_3(CO)_{12} \qquad (5)$$

If CO loss (eq 3) were a primary photoprocess at higher energy, then photosubstitution should occur readily in the presence of other ligands. In confirmation of this expectation, 313-nm continuous photolysis of $Ru_3(CO)_{12}$ in octane containing $P(OCH_3)_3$ led to the formation of the substituted clusters $Ru_3(CO)_{12-n}L_n$ (n = 1–4) in competition with photofragmentation to mononuclear species as determined from electronic and IR spectra of the product mixtures.[6] The patterns of spectral changes indicate that formation of the n = 2–4 products is the result of sequential substitution of CO by $P(OCH_3)_3$. In the THF solution, 313-nm photolysis in the presence of added $P(OCH_3)_3$ was shown to give substituted triruthenium clusters with a quantum yield comparable to that seen in octane solution (below). However, competing photofragmentation was largely supressed owing to the quenching mechanism noted above.

That the observed photosubstitution was not just the result of cluster fragmentation followed by secondary photoreactions of the primary products as $Ru(CO)_4P(OCH_3)_3$ was tested by studying the photoreactions of this mononuclear species. Direct 313-nm photolysis of $Ru(CO)_4P(OCH_3)_3$ (0.001 M) in octane containing 0.012 M $P(OCH_3)_3$ leads only to the further substitution of $P(OCH_3)_3$ for CO on the mononuclear complex as confirmed by IR spectroscopy.[7] In addition, photolysis of $Ru(CO)_4L$ (0.001 M) in the presence of $Ru_3(CO)_{12}$ (0.0002 M) gave no substitution clusters.

Quantum yields for cluster fragmentation (Φ_f) and for the formation of $Ru_3(CO)_{11}P(OCH_3)_3$ (Φ_s) were determined spectrally and are indicated in Figure 1. Note that Φ_f is essentially wavelength independent, whereas Φ_s increases dramatically for the shorter wavelengths. Carrying out the 313-nm photolysis under a CO atmosphere ($[P(OCH_3)_3]$ = 0.012 M) had opposite effects on the two photoreactions; Φ_s decreased from 0.086 to 0.043, and Φ_f increased from 0.021 to 0.029 relative to the experiment under argon. Increasing $[P(OCH_3)_3]$ to 0.1 M had the effect of increasing the yields of both reaction pathways: substitution by a factor of 2, fragmentation by 50%.

The continuous and kinetic flash photolysis results described here indicate the presence of two reactive intermediates, each key to independent pathways, leading respectively to photofragmentation or to ligand photosubstitution of $Ru_3(CO)_{12}$. The intermediate for photosubstitution appears to be $Ru_3(CO)_{11}$ or $Ru_3(CO)_{11}S$ (S = solvent); however, the current evidence does not differentiate between formation of II via simple dissociation from a cluster excited state or via a more complex mechanism.[8] In addition, these observations further emphasize the important roles played by the reaction medium and excitation energy in directing the course of this photochemistry. Studies in progress are focused on the further elucidation of the quantitative aspects of the reaction dynamics of the observed intermediates.

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Registry No. THF, 109-99-9; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(CO)_{11}P(OCH_3)_3$, 82532-25-0; $Ru_3(CO)_{11}$, 93862-52-3; $P(OCH_3)_3$, 121-45-9; PPh_3, 603-35-0; cyclohexene, 110-83-8.

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(5) Over this monitoring wavelength range, the intermediate I′ has no absorbance. However, when the transient behavior resulting from short-wavelength flash photolysis in the presence of various ligands was monitored at 390 nm, temporal absorbance changes consistent with the behavior expected for the simultaneous formation of both I′ and II were observed.

(6) These products' spectra were compared to the spectra of authentic samples of $Ru_3(CO)_{12-n}(P(OCH_3)_3)_n$ (n = 1–3) prepared by Dr. R. Trautman and D. Taube of this laboratory. The cluster n = 4, previously unreported, is presumed present from the shift in the band maximum with increased subsitution; for n = 1–3, the λ_{max} is 402, 416, and 426 nm, respectively. From the reaction mixture a fourth cluster was isolated with a λ_{max} at 445 nm. The $Ru_3(CO)_{11}(P(OCH_3)_3)$ cluster has been reported: Bruce, M. I.; Keheo, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442–444.

(7) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1982**, *1*, 453–459.

(8) However, Wrighton and co-workers have identified (via FTIR techniques) a species equivalent to II in the low-temperature (77 K) photoreactions of $Ru_3(CO)_{12}$ in hydrocarbon matrices containing the donor ligand 2-CH_3-THF (private communication from M. S. Wrighton).

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Failure of Stranks' Postulate and the Volume Profile for the Aquation of $Co(NH_3)_5X^{n+}$

Sir:

In summary, it can be shown that (i) eq 1 is incorrect, (ii) eq 3 is correct, but this does not justify eq 1, and (iii) in reaction 2, the entering H_2O and the leaving X almost equally participate in the transition state.

In 1974 Stranks made a postulate concerning the partial molal volume ($\bar{V}$) of complex ion in its transition state of ligand substitution.[1] Activation volumes (ΔV^{*}) for many complex ion reactions were interpreted on the basis of this postulate.[2,3] He has assumed that the intrinsic component ($\bar{V}_{int}$) of $\bar{V}$ of a five-coordinate intermediate is approximately equal to that of its six-coordinate precursor

$$\bar{V}_{int}(ML_5{}^{m+}) \simeq \bar{V}_{int}(ML_5X^{n+}) \qquad (1)$$

where $\bar{V}_{int} = \bar{V} - \bar{V}_{el}$ and $\bar{V}_{el}$ is the contribution from the electrostatic interaction of the charged complex ion with the solvent.[1] Since the magnitude of $\bar{V}_{el}$ should be similar for octahedral complexes of the same charge,[4] eq 1 automatically means that $\bar{V}(ML_5X^{n+})$ is approximately constant throughout a series of ML_5X^{n+} complexes with a fixed n value. However, $\bar{V}(Co(NH_3)_5X^{2+})$ ranges from 63.6 cm³ mol⁻¹ for X = F^- to 94.8 cm³ mol⁻¹ for X = I^- and $\bar{V}(Co(NH_3)_5X^{3+})$ ranges from 60.3 cm³ mol⁻¹ for X = H_2O to 122.9 cm³ mol⁻¹ for X = $OC(NHCH_3)_2$.[5] When it is considered that the magnitudes of ΔV^{*} or reaction volume (ΔV) in water are in a range from −30 to +30 cm³ mol⁻¹, eq 1 is obviously incorrect.[6]

Later, Palmer and Kelm assumed the existence of $Co(NH_3)_5{}^{3+}$ in the transition state of the aquation

$$Co(NH_3)_5X^{n+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + X \qquad (2)$$

and demonstrated that

$$\bar{V}(Co(NH_3)_5{}^{3+}) = \bar{V}(Co(NH_3)_6{}^{3+}) \qquad (3)$$

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(1) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303–323.

(2) Lawrance, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979**, *12*, 403–409.

(3) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89–153.

(4) Kitamura, Y.; van Eldik, R. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 418–422.

(5) Throughout this report, $\bar{V}$ is expressed by assuming $\bar{V}(H^+)$ = −4.5 cm³ mol⁻¹.

(6) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407–489.

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Table I. Volume Profile ($cm^3\ mol^{-1}$) for the Aquation of $Co(NH_3)_5X^{n+}$

X	$\bar{V}_c{}^a$	$\bar{V}_x$	ΔV	$\Delta V^{\ddagger}{}_{exptl}$	$\Delta V^{\ddagger}{}_{calcd}{}^h$
F^-	63.6[b]	3.3[b]			
Cl^-	83.5[b]	22.3[b]	−15.6[d]	−7.9[e]	0.5
Br^-	88.5[b]	29.2[b]	−14.4[d]	−6.7[e]	2.4
I^-	94.8[b]	40.7[b]	−10.0[d]		
NO_3^-	85.4[b]	33.5[b]	−12.3[d]	−4.9[e]	9.8
SO_4^{2-}	94.6[b]	23.0[b]	−29.4[d]	−13.0[e]	−9.9
Me_2SO	112.2[b]	68.8[b]	−4.3[d]	−1.7[f]	18.3
H_2O	60.3[b]	18.1[b]	0	1.2[g]	19.5
$OHCH_3$[c]	78.8	38.1	1.6	2.2	21.0
$OHCH_2CH_3$[c]	95.2	55.1	2.2	2.9	21.6
$OHCH(CH_3)_2$[c]	111.3	71.9	2.9	3.8	22.3
$OC(NH_2)_2$[c]	85.3	44.2	1.2	1.3	20.6
$OC(NH_2)(NHCH_3)$[c]	106.0	62.1	−1.6	0.3	17.8
$OC(NHCH_3)_2$[c]	122.9	80.0	−0.6	1.5	18.8
$OCH(NH_2)$[c]	81.0	39.2	0.5	1.1	19.9
$OCH(NHCH_3)$[c]	98.3	57.5	1.5	1.7	20.9
$OCH(N(CH_3)_2)$[c]	115.4	76.0	2.9	2.6	22.3

[a] $\bar{V}(Co(NH_3)_5X^{n+})$. [b] Taken from ref 10 and references therein. [c] Taken from ref 9 and references therein. [d] Reference 4. [e] Calculated by fitting the kinetic data up to 2.03 kbar in ref 13 to $\ln k_p = aP + b$. [f] Reference 7. [g] Reference 14. [h] See text.

as experimental evidence in favor of eq 1.[7] Sisley and Swaddle indicated that the conclusion by Palmer and Kelm was erroneously obtained from some error in the value of $\bar{V}(Co(NH_3)_5X^{n+})$.[8] Sisley and Swaddle arbitrary assumed the existence of $Co(NH_3)_5{}^{3+}$ in the transition state of the aquo-exchange reaction of $Co(NH_3)_5H_2O^{3+}$ and demonstrated that $\bar{V}(Co(NH_3)_5{}^{3+})$ should be smaller by 17–20 $cm^3\ mol^{-1}$ than $\bar{V}(Co(NH_3)_6{}^{3+})$.[8] Lawrance further investigated that the $\bar{V}$ of the assumed five-coordinate intermediate for reaction 2 depends significantly on the charge of X.[9] His result essentially means the nonexistence of independent $Co(NH_3)_5{}^{3+}$ species in the transition state of reaction 2.

Recently, our investigation on the volume profile for the base hydrolysis reaction

$$Co(NH_3)_5X^{n+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X \qquad (4)$$

enabled us to estimate $\bar{V}(Co(NH_3)_4(NH_2)^{2+}) = 71.1 \pm 3.9\ cm^3\ mol^{-1}$.[10] In another work, ΔV's were measured for a series of reactions:[4]

$$MA^z + OH^- \rightarrow MB^{z-1} + H_2O \qquad (5)$$

where MA^z is an octahedral transition-metal complex with ligand A = OH_2, NH_3, $C_2O_4H^-$ and MB^{z-1} is the corresponding conjugate base complex with ligand B = OH^-, NH_2^-, $C_2O_4^{2-}$. The results were expressed as

$$\Delta V\ (cm^3\ mol^{-1}) = (14.5 \pm 0.8) - (2.5 \pm 0.2)\Delta Z^2 \qquad (6)$$

where $\Delta Z^2 = (z-1)^2 - z^2$. One can predict by use of eq 6 ΔV for the hypothetical reaction

$$Co(NH_3)_5{}^{3+} + OH^- \rightarrow Co(NH_3)_4(NH_2)^{2+} + H_2O \qquad (7)$$

as 27 ± 1.8 $cm^3\ mol^{-1}$. Then, $\bar{V}(Co(NH_3)_5{}^{3+})$ can be obtained by

$$\begin{aligned}\bar{V}(Co(NH_3)_5{}^{3+}) &= \bar{V}(Co(NH_3)_4(NH_2)^{2+}) + \bar{V}(H_2O) - \\ &\quad \bar{V}(OH^-) - (\Delta V \text{ of reaction 7}) \\ &= (71.1 \pm 3.9) + 18.1 - 0.5 - (27 \pm 1.8) \\ &= 61.7 \pm 5.7\ cm^3\ mol^{-1} \qquad (8)\end{aligned}$$

This value of $\bar{V}(Co(NH_3)_5{}^{3+})$ is quite close to the value $\bar{V} = 61.3\ cm^3\ mol^{-1}$ of $Co(NH_3)_6{}^{3+}$.[10] This result may be interpreted that there are crevices between adjacent monodentate NH_3 ligands and hence the contraction or expansion of the Co–N bonds due to the change of the coordination number does not cause significant change in $\bar{V}_{int}$.[11,12]

On the other hand, using $\bar{V}(Co(NH_3)_5{}^{3+}) = 61.7 \pm 5.7\ cm^3\ mol^{-1}$, one can calculate $\Delta V^{\ddagger}$ for reaction 2 in the limit of dissociative mechanism by

$$\Delta V^{\ddagger}{}_{calcd} = \bar{V}(Co(NH_3)_5{}^{3+}) + \bar{V}(X) - \bar{V}(Co(NH_3)_5X^{n+}) \qquad (9)$$

As shown in Table I, the resulting $\Delta V^{\ddagger}{}_{calcd}$ differs significantly from $\Delta V^{\ddagger}{}_{exptl}$ and this discrepancy denies the existence of a common intermediate of $Co(NH_3)_5{}^{3+}$ in the transition state of reaction 2. Instead, there is a good correlation (correlation coefficient 0.99) between $\Delta V^{\ddagger}{}_{exptl}$ and ΔV:

$$\Delta V^{\ddagger}{}_{exptl} = (0.51 \pm 0.02)\Delta V + (1.2 \pm 0.2) \qquad (10)$$

This fact indicates that in reaction 2 the partial molal volume of the transition state is very close to the corresponding mean $\bar{V}$ of the initial and the final state (larger only by 1.2 $cm^3\ mol^{-1}$ than this mean). In other words, the entering H_2O and the leaving X almost equally take part in the transition state. The transition state may be depicted as $H_2O{\cdots}Co(NH_3)_5{}^{3+}{\cdots}X$, where the dashed line stands for a weak coordination bond.

Registry No. $Co(NH_3)_5{}^{3+}$, 44236-77-3; Co, 7440-48-4.

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(7) Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1977**, *16*, 3139–3143.
(8) Sisley, M. J.; Swaddle, T. W. *Inorg. Chem.* **1981**, *20*, 2799–2803.
(9) Lawrance, G. A. *Inorg. Chem.* **1982**, *21*, 3687–3691.
(10) Kitamura, Y.; van Eldik, R.; Kelm, H. *Inorg. Chem.* **1984**, *23*, 2038–2043.
(11) Kitamura, Y.; Ito, T.; Kato, M. *Inorg. Chem.* **1984**, *23*, 3836–3838.
(12) Kitamura, Y.; Ida, K. *Inorg. Chim. Acta* **1984**, *88*, 161–163.
(13) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972**, *50*, 2739–2746.
(14) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642–2646.

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Formation and X-ray Crystal Structure Determination of an Unusual Phosphorus–Phosphorus Coupled Bicyclodiphosphazane Complex

Sir:

The chemistry of main-group element rings and cages continues to attract wide attention, and a class of four-membered P–N rings, the cyclodiphosphazanes,[1] now appears to offer unanticipated