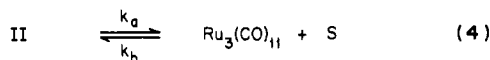
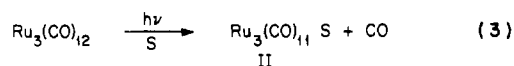


This is consistent with photolabilization of CO followed by reaction of the transient photoproduct II with free CO,<sup>5</sup> e.g.



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  $\text{Ru}_3(\text{CO})_{12}$  in octane containing  $\text{P}(\text{OCH}_3)_3$  led to the formation of the substituted clusters  $\text{Ru}_3(\text{CO})_{12-n}\text{L}_n$  ( $n = 1-4$ ) in competition with photofragmentation to mononuclear species as determined from electronic and IR spectra of the product mixtures.<sup>6</sup> The patterns of spectral changes indicate that formation of the  $n = 2-4$  products is the result of sequential substitution of CO by  $\text{P}(\text{OCH}_3)_3$ . In the THF solution, 313-nm photolysis in the presence of added  $\text{P}(\text{OCH}_3)_3$  was shown to give substituted triruthenium clusters with a quantum yield comparable to that seen in octane solution (below). However, competing photofragmentation was largely suppressed 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  $\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_3)_3$  was tested by studying the photoreactions of this mononuclear species. Direct 313-nm photolysis of  $\text{Ru}(\text{CO})_4\text{P}(\text{OCH}_3)_3$  (0.001 M) in octane containing 0.012 M  $\text{P}(\text{OCH}_3)_3$  leads only to the further substitution of  $\text{P}(\text{OCH}_3)_3$  for CO on the mononuclear complex as confirmed by IR spectroscopy.<sup>7</sup> In addition, photolysis of  $\text{Ru}(\text{CO})_4\text{L}$  (0.001 M) in the presence of  $\text{Ru}_3(\text{CO})_{12}$  (0.0002 M) gave no substitution clusters.

Quantum yields for cluster fragmentation ( $\Phi_f$ ) and for the formation of  $\text{Ru}_3(\text{CO})_{11}\text{P}(\text{OCH}_3)_3$  ( $\Phi_s$ ) were determined spectrally and are indicated in Figure 1. Note that  $\Phi_f$  is essentially wavelength independent, whereas  $\Phi_s$  increases dramatically for the shorter wavelengths. Carrying out the 313-nm photolysis under a CO atmosphere ( $[\text{P}(\text{OCH}_3)_3] = 0.012$  M) had opposite effects on the two photoreactions;  $\Phi_s$  decreased from 0.086 to 0.043, and  $\Phi_f$  increased from 0.021 to 0.029 relative to the experiment under argon. Increasing  $[\text{P}(\text{OCH}_3)_3]$  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  $\text{Ru}_3(\text{CO})_{12}$ . The intermediate for photosubstitution appears to be  $\text{Ru}_3(\text{CO})_{11}$  or  $\text{Ru}_3(\text{CO})_{11}\text{S}$  ( $\text{S} = \text{solvent}$ ); 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.<sup>8</sup> 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.

**Acknowledgment.** This research was supported by the National Science Foundation. Ruthenium used in these studies was provided on loan by Johnson Matthey, Inc.

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

(8) However, Wrighton and co-workers have identified (via FTIR techniques) a species equivalent to II in the low-temperature (77 K) photoreactions of  $\text{Ru}_3(\text{CO})_{12}$  in hydrocarbon matrices containing the donor ligand 2- $\text{CH}_3$ -THF (private communication from M. S. Wrighton).

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### Failure of Stranks' Postulate and the Volume Profile for the Aquation of $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$

Sir:

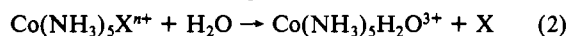
In summary, it can be shown that (i) eq 1 is incorrect, (ii) eq 3 is correct, but this does not justify eq 1, and (iii) in reaction 2, the entering  $\text{H}_2\text{O}$  and the leaving X almost equally participate in the transition state.

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

$$\bar{V}_{\text{int}}(\text{ML}_5\text{X}^{n+}) \approx \bar{V}_{\text{int}}(\text{ML}_5\text{X}^{n+}) \quad (1)$$

where  $\bar{V}_{\text{int}} = \bar{V} - \bar{V}_{\text{el}}$  and  $\bar{V}_{\text{el}}$  is the contribution from the electrostatic interaction of the charged complex ion with the solvent.<sup>1</sup> Since the magnitude of  $\bar{V}_{\text{el}}$  should be similar for octahedral complexes of the same charge,<sup>4</sup> eq 1 automatically means that  $\bar{V}(\text{ML}_5\text{X}^{n+})$  is approximately constant throughout a series of  $\text{ML}_5\text{X}^{n+}$  complexes with a fixed  $n$  value. However,  $\bar{V}(\text{Co}(\text{NH}_3)_5\text{X}^{2+})$  ranges from 63.6  $\text{cm}^3 \text{mol}^{-1}$  for  $\text{X} = \text{F}^-$  to 94.8  $\text{cm}^3 \text{mol}^{-1}$  for  $\text{X} = \text{I}^-$  and  $\bar{V}(\text{Co}(\text{NH}_3)_5\text{X}^{3+})$  ranges from 60.3  $\text{cm}^3 \text{mol}^{-1}$  for  $\text{X} = \text{H}_2\text{O}$  to 122.9  $\text{cm}^3 \text{mol}^{-1}$  for  $\text{X} = \text{OC}(\text{NHCH}_3)_2$ .<sup>5</sup> When it is considered that the magnitudes of  $\Delta V^\ddagger$  or reaction volume ( $\Delta V$ ) in water are in a range from  $-30$  to  $+30 \text{ cm}^3 \text{mol}^{-1}$ , eq 1 is obviously incorrect.<sup>6</sup>

Later, Palmer and Kelm assumed the existence of  $\text{Co}(\text{NH}_3)_5^{3+}$  in the transition state of the aquation



and demonstrated that

$$\bar{V}(\text{Co}(\text{NH}_3)_5^{3+}) = \bar{V}(\text{Co}(\text{NH}_3)_6^{3+}) \quad (3)$$

(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  $\text{Ru}_3(\text{CO})_{12-n}(\text{P}(\text{OCH}_3)_3)_n$  ( $n = 1-3$ ) 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 substitution; for  $n = 1-3$ , the  $\lambda_{\text{max}}$  is 402, 416, and 426 nm, respectively. From the reaction mixture a fourth cluster was isolated with a  $\lambda_{\text{max}}$  at 445 nm. The  $\text{Ru}_3(\text{CO})_{11}(\text{P}(\text{OCH}_3)_3)_2$  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.

(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  $\bar{V}(\text{H}^+) = -4.5 \text{ cm}^3 \text{mol}^{-1}$ .

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

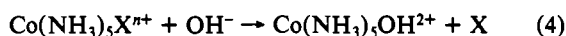
Table I. Volume Profile ( $\text{cm}^3 \text{mol}^{-1}$ ) for the Aquation of  $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ 

X	$\bar{V}_c^a$	$\bar{V}_x$	$\Delta V$	$\Delta V_{\text{exptl}}^\ddagger$	$\Delta V_{\text{calcd}}^{\ddagger h}$
$\text{F}^-$	63.6 <sup>b</sup>	3.3 <sup>b</sup>			
$\text{Cl}^-$	83.5 <sup>b</sup>	22.3 <sup>b</sup>	-15.6 <sup>d</sup>	-7.9 <sup>e</sup>	0.5
$\text{Br}^-$	88.5 <sup>b</sup>	29.2 <sup>b</sup>	-14.4 <sup>d</sup>	-6.7 <sup>e</sup>	2.4
$\text{I}^-$	94.8 <sup>b</sup>	40.7 <sup>b</sup>	-10.0 <sup>d</sup>		
$\text{NO}_3^-$	85.4 <sup>b</sup>	33.5 <sup>b</sup>	-12.3 <sup>d</sup>	-4.9 <sup>e</sup>	9.8
$\text{SO}_4^{2-}$	94.6 <sup>b</sup>	23.0 <sup>b</sup>	-29.4 <sup>d</sup>	-13.0 <sup>e</sup>	-9.9
$\text{Me}_2\text{SO}$	112.2 <sup>b</sup>	68.8 <sup>b</sup>	-4.3 <sup>d</sup>	-1.7 <sup>f</sup>	18.3
$\text{H}_2\text{O}$	60.3 <sup>b</sup>	18.1 <sup>b</sup>	0	1.2 <sup>g</sup>	19.5
$\text{OHCH}_3^c$	78.8	38.1	1.6	2.2	21.0
$\text{OHCH}_2\text{CH}_3^c$	95.2	55.1	2.2	2.9	21.6
$\text{OHCH}(\text{CH}_3)_2^c$	111.3	71.9	2.9	3.8	22.3
$\text{OC}(\text{NH}_3)_2^c$	85.3	44.2	1.2	1.3	20.6
$\text{OC}(\text{NH}_3)(\text{NHCH}_3)^c$	106.0	62.1	-1.6	0.3	17.8
$\text{OC}(\text{NHCH}_3)_2^c$	122.9	80.0	-0.6	1.5	18.8
$\text{OCH}(\text{NH}_3)^c$	81.0	39.2	0.5	1.1	19.9
$\text{OCH}(\text{NHCH}_3)^c$	98.3	57.5	1.5	1.7	20.9
$\text{OCH}(\text{N}(\text{CH}_3)_2)^c$	115.4	76.0	2.9	2.6	22.3

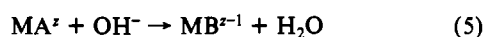
<sup>a</sup>  $\bar{V}(\text{Co}(\text{NH}_3)_5\text{X}^{n+})$ . <sup>b</sup> Taken from ref 10 and references therein. <sup>c</sup> Taken from ref 9 and references therein. <sup>d</sup> Reference 4. <sup>e</sup> Calculated by fitting the kinetic data up to 2.03 kbar in ref 13 to  $\ln k_p = aP + b$ . <sup>f</sup> Reference 7. <sup>g</sup> Reference 14. <sup>h</sup> See text.

as experimental evidence in favor of eq 1.<sup>7</sup> Sisley and Swaddle indicated that the conclusion by Palmer and Kelm was erroneously obtained from some error in the value of  $\bar{V}(\text{Co}(\text{NH}_3)_5\text{X}^{n+})$ .<sup>8</sup> Sisley and Swaddle arbitrarily assumed the existence of  $\text{Co}(\text{NH}_3)_5^{3+}$  in the transition state of the aquo-exchange reaction of  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$  and demonstrated that  $\bar{V}(\text{Co}(\text{NH}_3)_5^{3+})$  should be smaller by 17–20  $\text{cm}^3 \text{mol}^{-1}$  than  $\bar{V}(\text{Co}(\text{NH}_3)_6^{3+})$ .<sup>8</sup> Lawrance further investigated that the  $\bar{V}$  of the assumed five-coordinate intermediate for reaction 2 depends significantly on the charge of X.<sup>9</sup> His result essentially means the nonexistence of independent  $\text{Co}(\text{NH}_3)_5^{3+}$  species in the transition state of reaction 2.

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



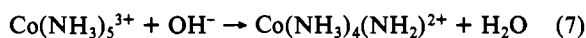
enabled us to estimate  $\bar{V}(\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+}) = 71.1 \pm 3.9 \text{ cm}^3 \text{mol}^{-1}$ .<sup>10</sup> In another work,  $\Delta V$ 's were measured for a series of reactions:<sup>4</sup>



where  $\text{MA}^z$  is an octahedral transition-metal complex with ligand  $\text{A} = \text{OH}_2, \text{NH}_3, \text{C}_2\text{O}_4\text{H}^-$  and  $\text{MB}^{z-1}$  is the corresponding conjugate base complex with ligand  $\text{B} = \text{OH}^-, \text{NH}_2^-, \text{C}_2\text{O}_4^{2-}$ . The results were expressed as

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

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



as  $27 \pm 1.8 \text{ cm}^3 \text{mol}^{-1}$ . Then,  $\bar{V}(\text{Co}(\text{NH}_3)_5^{3+})$  can be obtained by

$$\begin{aligned} \bar{V}(\text{Co}(\text{NH}_3)_5^{3+}) &= \bar{V}(\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+}) + \bar{V}(\text{H}_2\text{O}) - \\ &\quad \bar{V}(\text{OH}^-) - (\Delta V \text{ of reaction 7}) \\ &= (71.1 \pm 3.9) + 18.1 - 0.5 - (27 \pm 1.8) \\ &= 61.7 \pm 5.7 \text{ cm}^3 \text{mol}^{-1} \end{aligned} \quad (8)$$

This value of  $\bar{V}(\text{Co}(\text{NH}_3)_5^{3+})$  is quite close to the value  $\bar{V} = 61.3 \text{ cm}^3 \text{mol}^{-1}$  of  $\text{Co}(\text{NH}_3)_6^{3+}$ .<sup>10</sup> This result may be interpreted that there are crevices between adjacent monodentate  $\text{NH}_3$  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  $\bar{V}_{\text{int}}$ .<sup>11,12</sup>

On the other hand, using  $\bar{V}(\text{Co}(\text{NH}_3)_5^{3+}) = 61.7 \pm 5.7 \text{ cm}^3 \text{mol}^{-1}$ , one can calculate  $\Delta V^\ddagger$  for reaction 2 in the limit of dissociative mechanism by

$$\Delta V_{\text{calcd}}^\ddagger = \bar{V}(\text{Co}(\text{NH}_3)_5^{3+}) + \bar{V}(\text{X}) - \bar{V}(\text{Co}(\text{NH}_3)_5\text{X}^{n+}) \quad (9)$$

As shown in Table I, the resulting  $\Delta V_{\text{calcd}}^\ddagger$  differs significantly from  $\Delta V_{\text{exptl}}^\ddagger$  and this discrepancy denies the existence of a common intermediate of  $\text{Co}(\text{NH}_3)_5^{3+}$  in the transition state of reaction 2. Instead, there is a good correlation (correlation coefficient 0.99) between  $\Delta V_{\text{exptl}}^\ddagger$  and  $\Delta V$ :

$$\Delta V_{\text{exptl}}^\ddagger = (0.51 \pm 0.02)\Delta V + (1.2 \pm 0.2) \quad (10)$$

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  $\text{cm}^3 \text{mol}^{-1}$  than this mean). In other words, the entering  $\text{H}_2\text{O}$  and the leaving X almost equally take part in the transition state. The transition state may be depicted as  $\text{H}_2\text{O} \cdots \text{Co}(\text{NH}_3)_5^{3+} \cdots \text{X}$ , where the dashed line stands for a weak coordination bond.

Registry No.  $\text{Co}(\text{NH}_3)_5^{3+}$ , 44236-77-3; Co, 7440-48-4.

(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,<sup>1</sup> now appears to offer unanticipated

(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.