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

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

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 $H_2O\text{---}Co(NH_3)_5{}^{3+}\text{---}X$, 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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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

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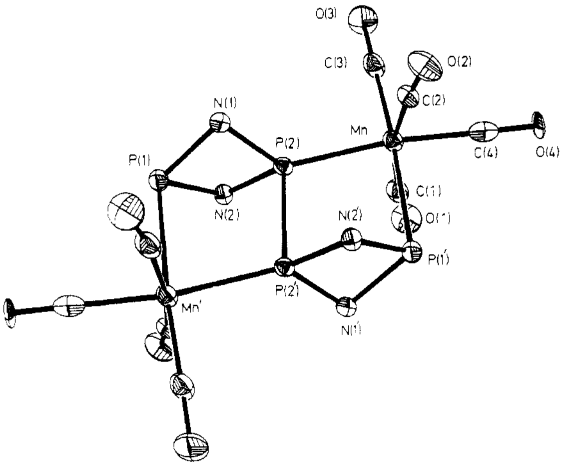

Figure 1. Molecular geometry and atom-labeling scheme for $\mathrm{Mn_2(CO)_8[P_2}(t\text{-}\mathrm{BuN})_2\mathrm{P_2}(t\text{-}\mathrm{BuN})_2]$ with t-Bu groups on N(1), N(2), N(1'), and N(2') removed.

routes to a host of new P–N cage species.[2,3] In this regard we have recently reported[3] that reduction of the parent chlorocyclodiphosphazane, $\mathrm{Cl}\overline{\mathrm{P}(t\text{-}\mathrm{BuN})\mathrm{P}(t\text{-}\mathrm{BuN})}(\mathrm{Cl})$ (**1**), by Mg or sodium naphthalide results in a sequence of P–P bond forming and P–N bond breaking and re-forming processes with the subsequent generation of a new cage $\mathrm{P_4}(t\text{-}\mathrm{BuN})_4$ (**2**). This molecule has two geometrical isomers, one of which closely resembles $\mathrm{S_4N_4}$.

Transition-metal nucleophiles such as $\mathrm{CpMo(CO)_3^-}$ and $\mathrm{CpFe(CO)_2^-}$ might be expected to induce related reductive phosphorus coupling reactions of **1** with or without metal fragment incorporation or heterolytic P–Cl bond cleavage. The last course would result in the formation of metallaphosphenium ion complexes as established with reactions of several metal carbonylates and simple chlorophosphites,[4] phosphorus trihalides,[4] and aminochlorophosphines.[5] In fact, heterolytic P–Cl bond cleavage has now been demonstrated[6-8] with **1** in the presence of $\mathrm{Cp^*Mo(CO)_3^-}$ and $\mathrm{Cp^*Fe(CO)_2^-}$. In addition, we have observed that $\mathrm{Na_2Fe(CO)_4}$ induces P–Cl bond cleavage, the formation of metallaphosphenium ion complexes, and under some conditions the formation of a unique phosphine complex,[9] $\mathrm{(CO)_4Fe[(H)\overline{P}(}t\text{-}\mathrm{BuN)P(}t\text{-}\mathrm{Bu\overline{N})(H)]Fe(CO)_4}$ (**3**). In the present report we describe the first characterized example of cyclodiphosphazane coupling in which metal fragments are incorporated into the resulting cage structure.

$\mathrm{NaMn(CO)_5}$ (1.5 mmol) and **1** (1.5 mmol) were combined in THF and stirred for 10 h at −78 °C.[10] The mixture was then warmed to 25 °C and refluxed for 10 h. Evolved CO was quantitatively determined, the solution filtered to remove NaCl, and the solvent and $\mathrm{Mn_2(CO)_{10}}$ evaporated in vacuo. The resulting green solid (**4**) was redissolved in a minimum of THF, and crystals were obtained at 0 °C from this solution.

A single-crystal X-ray diffraction[11] analysis of **4** revealed its precise stoichiometry, and a view of the molecular structure with the t-Bu groups removed from the nitrogen atoms for clarity is shown in Figure 1. The molecule possesses a center of symmetry at the midpoint of the P–P bond. The structure contains two slightly puckered cyclodiphosphazane rings having the exo chlorine atoms removed and two of the four phosphorus atoms, P(2) and P(2'), joined by a single bond, 2.234 (2) Å. This distance compares favorably with the typical range of P–P single-bond distances found in diphosphines,[12] 2.12–2.25 Å, and it is considerably shorter than the P–P distances in $\mathrm{P_4}(t\text{-}\mathrm{BuN})_4$ (**2**), 2.330 (1) and 2.340 (1) Å.[3] The P(1)···P(2) separation is 2.486 (1) Å, which is similar to the related nonbonded distance in the starting ligand **1**, 2.53 Å.[13] The P–N bond distances fall in interesting short and long sets. The short distances are associated with the internal P–P-bonded atoms P(2) and P(2'): P(2)–N(1) = 1.694 (3) Å; P(2)–N(2) = 1.720 (3) Å. These compare with the P–N distances in $\mathrm{Cp_2Mo_2(CO)_4[\overline{P(}}t\text{-}\mathrm{BuN)P(}t\text{-}\mathrm{Bu\overline{N})]}$ (**5**), 1.716 (3) Å, and **1** 1.689 (4) Å, and the short distances in $\mathrm{P_4}(t\text{-}\mathrm{BuN})_4$, 1.708 (3) Å (average), and in **3**, 1.702 (2) and 1.709 (2) Å. The P–N distances associated with the external, metal-coordinated phosphorus atoms, P(1) and P(1'), are considerably longer: P(1)–N(1) = 1.761 (3) Å; P(1)–N(2) = 1.802 (3) Å. These are notably longer than the long set of P–N distances in **2**, 1.742 (3) Å (average). The N(1)–P(1)–N(2) angle, 82.3 (1)°, is smaller than the N(1)–P(2)–N(2) angle, 86.8 (1)°, and the latter is similar to the NPN angles in **1**, **3**, and **5**. The P–N–P angles in **4** are 92.0 (2) and 89.8 (1)° about N(1) and N(2), respectively.

Examining the main group framework in **4** suggests that it may represent an early intermediate in the formation of $\mathrm{P_4}(t\text{-}\mathrm{BuN})_4$, which has been trapped by two $\mathrm{Mn(CO)_4}$ fragments before P–N bond breaking and making processes have occurred. The $\mathrm{Mn(CO)_4X_2}$ fragments have a distorted octahedral geometry, with phosphorus atoms occupying cis positions. It is important to notice that the Mn–P distances are very asymmetric. The P–P-coupled phosphorus atoms display a short Mn–P(2) distance, 2.293 (1) Å, which can be compared with a range of distances found in Mn–phosphine complexes,[12,14] 2.24–2.40 Å. The P(1')–Mn dis-

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(10) Stirring of the initially yellow reaction mixture at −78 °C results in the formation of NaCl and a green solution. When it is warmed to room temperature, the color changes to yellow-red and then to dark green upon reflux. A total of 90% of 2 equiv of CO based upon the amount of $\mathrm{NaMn(CO)_5}$ added was recovered with a Toepler pump. The final yield of isolated **4** was approximately 40%. The compound is air and moisture sensitive.

(11) A green crystal of dimensions 0.161 × 0.345 × 0.554 mm was mounted in a glass capillary on a Syntex P3/F automated diffractometer. With Mo$K\alpha$ radiation (λ = 0.71069 Å) the following crystal data were obtained at 20 °C: monoclinic space group $P2_1/n$, with a = 10.231 (3) Å, b = 14.927 (4) Å, c = 11.260 (2) Å, β = 106.42 (2)°, Z = 4, V = 1649.5 (7) Å^3, ρ_{calcd} = 1.49 g cm^{-3}, μ = 9.7 cm^{-1}. Empirical absorption correction R_{merge} on ψ scans before 3.59, after 3.29; maximum transmission 0.636, minimum transmission 0.581. The 2θ limits on the ω-scan data set were $1 \le \pm h,\pm k,+l \le 55°$. A total of 7939 reflections were collected, yielding 3804 unique reflections, of which 2692 unique data with $F \ge 4\sigma(F)$ were used. The structure was solved by heavy-atom methods (SHELXTL-81) and blocked least-squares refinement of all non-hydrogen atoms isotropically converged with R = 0.090. Anisotropic refinement led to R = 0.064. Hydrogen atoms were included in fixed idealized positions and their individual U_{iso}'s were fixed at 1.2 times the last U_{equiv} of their parent atom. Refinement on 190 parameters converged to R_F = 0.055 and R_{wF} = 0.041 and GOF = 1.815. A final difference map showed no peak larger than 0.55 e Å^{-3}.

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tance, 2.507 (1) Å, on the other hand, is quite long.[15] The long P(1′)–Mn interactions occur approximately perpendicular to the $P_2(t\text{-BuN})_2$ rings while the short interactions are more in-plane. In this regard the P(1), P(2), Mn, C(1), C(2), and C(4) atoms nearly lie in a plane that is perpendicular to the C(3)–Mn–P(1′) vector.[16] The Mn–CO bond distances, Mn–C(1) = 1.842 (4) Å, Mn–C(2) = 1.831 (5) Å, Mn–C(3) = 1.822 (5) Å, and Mn–C(4) = 1.850 (4) Å offer some evidence for the differing donor qualities of P(2) and P(1′) sites. The Mn–C(4) distance is long and trans to the short Mn–P(2) distance while Mn–C(3) is short and trans to the long Mn–P(1′) distance.

The infrared spectrum (benzene) of **4** shows four bands in the terminal carbonyl stretching region, 2043, 1995 (s), 1960 (s), and 1943 (m) cm^{-1}, which is consistent with local C_s symmetry for the *cis*-$Mn(CO)_4$ P_2 fragment. The $^{31}P\{^1H\}$ NMR spectrum (H_3PO_4 reference) shows two resonances at 345 [P(1), P(1′)] and 0.9 ppm [P(2), P(2′)], and no P(1)–P(2) coupling has been resolved. The spectrum is consistent with two uniquely differing phosphorus environments as found in the crystal structure determination. The $^{13}C\{^1H\}$ NMR spectrum (Me_4Si reference) shows two resonances at 56.8 (J_{PNC} = 9 Hz, $(CH_3)_3C$) and 31.1 ppm ($(CH_3)_3C$).

The process by which **4** is formed appears to be complex. Sodium chloride appears with some CO evolution at −78 °C followed by additional CO evolution and $Mn_2(CO)_{10}$ generation at THF reflux. Accompanying color and spectroscopic changes suggest formation of at least three species prior to the appearance of **4**, and these are under study at this time. It appears that this complex offers a starting point for a new family of main-group–transition-metal clusters whose chemistry should be intriguing.

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Registry No. **1**, 24335-35-1; **4**, 93841-99-7; $NaMn(CO)_5$, 13859-41-1.

Supplementary Material Available: Details of the crystal structure determination and listings of crystal structure data, positional parameters, anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(14) Some typical Mn–phosphine Mn–P distances: $[Mn(CO)_4PEt_3]_2$, 2.247 (7) Å;[14a] $ClMn(CO)_4(PPh_3)$, 2.398 (4) Å;[14b] $(CO)_4Mn(H)(PPh_2)Mn(CO)_4$, 2.284 (6) Å;[14c] $[Ph_4P][Mn(CO)_4PPh_3]$, 2.248 (2) Å.[14d] (a) Bennett, M. J.; Mason, R. *J. Chem. Soc. A* **1968**, 75. (b) Vahrenkamp, H. *Chem. Ber.* **1971**, *104*, 449. (c) Doedens, R. J.; Robinson, W. T.; Ibers, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4323. (d) Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159.

(15) This distance is longer than the Mn–P distances found in several manganese phosphides,[12] 2.36–2.41 Å.

(16) Deviations (Å) from this approximate plane: P(1), +0.029; P(2), −0.070; Mn, 0.130; C(1), −0.041; C(2), 0.041; C(4), −0.006. Nitrogen atom deviations: N(1), 0.453; N(2), 0.186.

Articles

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Cobaltocene Reductions of Multiply Bonded Dirhenium Complexes: Isolation, Characterization, and Reactivity Studies of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$, $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PR_3)_2]$, and $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PR_3)_3]$

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The quadruply bonded dirhenium(III) complexes $Re_2Cl_6(PR_3)_2$ (PR_3 = PEt_3, P-*n*-Pr_3, $PMePh_2$, $PEtPh_2$) and $Re_2(O_2CR)_4Cl_2$ (R = C_3H_7, CMe_3, Ph) are reduced by cobaltocene in acetone to give the paramagnetic salts $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_6(PR_3)_2]$ and $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(O_2CR)_4Cl_2]$, respectively, complexes which are derivatives of the Re_2^{5+} core. The cobaltocene reduction of $Re_2Cl_5(PMePh_2)_3$ to give $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$ and its oxidation to $[Re_2Cl_5(PMePh_2)_3]PF_6$ by $NO^+PF_6^-$ have also been accomplished. These results demonstrate that mixed halide–phosphine complexes of Re_2^{n+} (n = 6, 5, 4) exhibit the most extensive redox chemistry of any class of multiply bonded dimetal species. The nonredox substitution chemistry of $[Re_2Cl_6(PR_3)_2]^-$ with PR_3 and of $[Re_2Cl_5(PR_3)_3]^-$ with PR_3 has been shown to lead to the formation of $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_4(PR_3)_4$, respectively.

Introduction

The redox properties of compounds that possess multiple metal–metal bonds are developing into an important facet of the chemistry of this class of molecules.[1] Dirhenium complexes have proved especially interesting because of their ability to undergo multiple-electron oxidations or reductions without disruption of the dimetal unit. One such example is that of the net four-electron reduction of the Re(IV) anion $[Re_2Cl_9]^-$, possessing a Re–Re triple bond ($\sigma^2\pi^4$ configuration), to give the Re(II) complex $Re_2Cl_4(PEt_3)_4$, also possessing a formal bond order of 3 ($\sigma^2\pi^4\delta^2\delta^{*2}$).[2] Previous studies on the electrochemistry of $Re_2X_4(PR_3)_4$ and $Re_2X_4(LL)_2$ (X = Cl, Br, I; LL = 1,2-bis(diphenylphosphino)ethane or 1-(diphenylphosphino)-2-(diphenylarsino)ethane)[3,4] led to the discovery of a novel series of coupled electrochemical–chemical reactions and the isolation of the paramagnetic monocations of these complexes.[5-7] More recently,[8] the isolation and

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