

Figure 1. Electronic spectrum of  $[\text{Cr}^{\text{V}}(\text{bpb})\text{N}]$  in dimethylformamide.

$[\text{Cr}^{\text{V}}(\text{salen})\text{N}]$  ( $\text{H}_2\text{salen} = N,N'$ -bis(salicylidene)ethylenediamine)<sup>10</sup> involving photolysis of chromium(III) azides. The  $[\text{Cr}^{\text{V}}(\text{bpb})\text{N}]$  complex is only slightly soluble in most common organic solvents and hence easily separated out from  $\text{Na}[\text{Cr}^{\text{III}}(\text{bpb})(\text{N}_3)_2]$ . It is stable in the solid state and in fluid solution. Its IR spectrum shows the absence of  $\nu(\text{N-H})$  stretch in the 3000–3500- $\text{cm}^{-1}$  region, indicating that the coordinated amide is in the deprotonated form. An extra intense peak at 1015  $\text{cm}^{-1}$ , which is absent in the IR spectrum of  $\text{Na}[\text{Cr}(\text{bpb})(\text{N}_3)_2]$ , is attributed to the  $\nu(\text{C}\equiv\text{N})$  stretch. For the  $[\text{Cr}^{\text{V}}(\text{TPP})\text{N}]$  and  $[\text{Cr}^{\text{V}}(\text{salen})\text{N}]$  complexes, the corresponding  $\nu(\text{C}\equiv\text{N})$  stretches are at 1017  $\text{cm}^{-1}$ .<sup>6,10</sup> As expected for the  $d^1$ -metal system, it is paramagnetic with a  $\mu_{\text{eff}}$  of 1.93  $\mu_{\text{B}}$ , which is slightly higher than the spin-only value of one unpaired electron. The optical spectrum (Figure 1) of the Cr(V) complex in dimethylformamide shows intense absorption bands in the 400–250-nm region, possibly arising from the ligand (bpb) to metal (Cr(V)) charge-transfer transitions.

There are relatively few structures of chromium(V) complexes in the literature.<sup>6,11</sup> Figure 2 shows the atomic numbering scheme and the ORTEP drawing of the  $[\text{Cr}^{\text{V}}(\text{bpb})\text{N}]$  molecule. The structure features the first example of a chromium(V) complex with organic amide ligands. The complex is five-coordinated, as a consequence of the large  $\sigma$ -trans effect of the  $\text{N}^{3-}$  group. The salient feature of the structure is that the chromium atom is located 0.508 Å above the mean plane of the four nitrogen atoms. This is likely attributed to the large Coulombic repulsive effect between the  $\text{Cr}\equiv\text{N}$  group and bpb ligand. A similar structural feature has also been found with other Cr(V) complexes such as  $[\text{Cr}(\text{TTP})\text{N}]$ <sup>6</sup> and  $[\text{OCr}(\text{O}_2\text{CCOMeEt})_2]\cdot\text{H}_2\text{O}$ .<sup>11</sup> Consistent with that of a formal triple bond, the measured  $\text{Cr}\equiv\text{N}$  bond distance of 1.560 (2) Å is very short and virtually identical with that found in  $[\text{Cr}^{\text{V}}(\text{TTP})\text{N}]$  (1.565 Å).<sup>6</sup> The average  $\text{Cr-N}(\text{amide})$  bond distance is 1.961 (2) Å, which is comparable to the  $\text{Cr-N}(\text{peptide})$  bond distance of 1.956 (7) Å in  $[\text{Cr}(\text{Gly-H}_1\text{Gly})_2]^{-}$ <sup>12</sup> but slightly shorter than that in  $[\text{Cr}(\text{H}(\text{chba-Et}))(\text{py})_2]_2\cdot 2\text{py}$  (2.030 Å).<sup>13</sup> The average  $\text{Cr-N}(\text{pyridine})$  bond length is ca 0.07 Å longer than the average  $\text{Cr-N}(\text{amide})$  bond length, in agreement with the fact that the deprotonated amide group is a very strong  $\sigma$ -donor. As

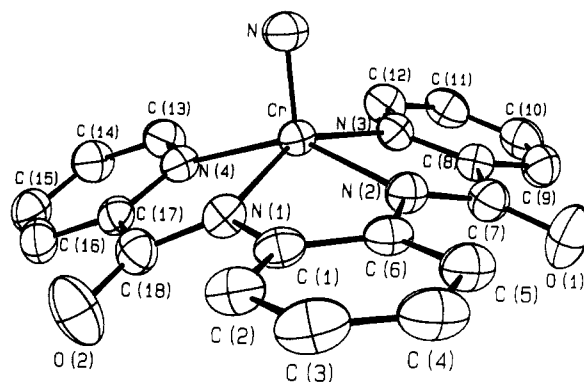


Figure 2. ORTEP drawing of the  $[\text{Cr}^{\text{V}}(\text{bpb})\text{N}]$  molecule showing the atomic numbering scheme.

with other metal-bpb complexes,<sup>5</sup> the N(amide) atoms, N(1) and N(2), are  $\text{sp}^2$  hybridized with the C(18)–N(1)–C(1) and C(6)–N(2)–C(7) bond angles being 124.5 (2) and 124.6 (2)°, respectively. The bond angles and bond distances of the bpb ligand are normal.

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**Registry No.**  $\text{Na}[\text{Cr}(\text{bpb})(\text{N}_3)_2]$ , 114720-38-6;  $\text{Cr}^{\text{V}}(\text{bpb})\text{N}$ , 114720-39-7;  $\text{Cr}(\text{bpb})\text{Cl}$ , 114720-40-0;  $\text{N}_3^-$ , 14343-69-2.

**Supplementary Material Available:** Tables of hydrogen atomic coordinates, anisotropic thermal parameters, bond lengths and angles for non-hydrogen atoms, and the least-squares plane (4 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

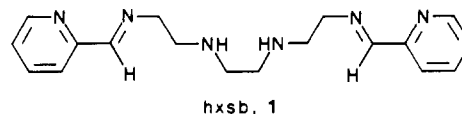
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### Reactivity Trends and Volumes of Activation for Dissociation of [1,8-Bis((2-pyridylmethylene)amino)-3,6-diazaoctane]iron(II) by Hydroxide Ion in Aqueous Alcohols and Aqueous Acetone

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There are many examples of Schiff-base, low-spin complexes of iron(II).<sup>2,3</sup> The hexadentate ligand 1,8-bis((2-pyridylmethylene)amino)-3,6-diazaoctane (hxsb, 1) forms with iron(II)



a complex<sup>3</sup> that is particularly inert to dissociation by nucleophiles.<sup>4</sup> Kinetic studies of the dissociation of  $\text{Fe}(\text{hxsb})^{2+}$  by hydroxide ion in aqueous solution over a range of pressure yielded a volume of activation,  $\Delta V^\ddagger$ , of +13  $\text{cm}^3 \text{mol}^{-1}$  at 298.2 K.<sup>4b,5</sup> The expected value of  $\Delta V^\ddagger$  for the bimolecular reaction in the absence of a solvent, i.e. intrinsic, is –10  $\text{cm}^3 \text{mol}^{-1}$ .<sup>6</sup> Desolvation of electrostricted water from the hydroxide ion as it attacks the iron

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Table I. Dissociation of  $\text{Fe}^{\text{II}}(\text{hxs})\text{Cl}_2$  by Hydroxide Ions in Aqueous Alcohols at 298.2 K and 1 atm

Ethanol											
% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$				% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$			
		0.050 <sup>a</sup>	0.10	0.20	0.33			0.050 <sup>a</sup>	0.10	0.20	0.33
10	0.033				1.45	35	0.14			2.67	12.6
20	0.062			0.729	3.50	40	0.170			3.43	19.7
25	0.091			1.04	5.77	50	0.235	3.53		6.38	43.2
30	0.117			1.67	8.10	60	0.316			12.8	115

Isopropyl Alcohol										
% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$					% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$	
		0.050	0.10	0.15	0.20	0.25			0.30	0.33
10	0.026									2.44
20	0.056				1.11					5.19
25					1.94					7.94
30	0.092				2.72					14.6
35					5.02					19.8
40	0.136				5.77					38.4
45					7.59					
50					12.3					91.5
55					16.2					
60	0.262	8.46			21.0	33.3	66.7	126	200	254
65					35.1					
70					41.9					

<i>tert</i> -Butyl Alcohol														
% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$					% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$					
		0.10	0.15	0.20	0.25	0.30			0.33	0.10	0.15	0.20	0.25	0.30
10	0.021					2.60	30	0.076						18.9
17	0.038					5.09	38	0.105	3.74	6.08	10.1	18.4	24.2	36.1
24	0.057	1.37				14.0	50	0.161	4.35	10.8	17.3	31.0		61.2

Acetone														
% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$					% v/v	$x_2$	$10^5 k_{\text{obsd}}, \text{s}^{-1}$					
		0.05	0.10	0.15	0.20	0.25			0.33	0.05	0.10	0.15	0.20	0.25
10	0.027		0.89				40	0.141		14.6				133
20	0.058		2.24			9.9	50	0.196		47				552
30	0.095	2.55	4.81	8.49	13.8	20.4	33.1	60	0.270	141				

<sup>a</sup> Hydroxide ion concentration (mol dm<sup>-3</sup>).

complex is considered to dominate over the intrinsic volume change occurring upon formation of the activated complex. Addition of methanol causes an increase in the dissociation rate of  $\text{Fe}(\text{hxs})^{2+}$  due to the increase in chemical potential of the hydroxide ion. A modest decrease in  $\Delta V^\ddagger$  (to +6 cm<sup>3</sup> mol<sup>-1</sup>) occurs upon addition of methanol at a mole fraction,  $x_2$ , of methanol of 0.57. This result<sup>4b</sup> can be understood as arising from contributions to  $\Delta V^\ddagger$  from solvation by methanol of the activated complex of +1 charge and from less dehydration/desolvation of hydroxide on entering the transition state. Support for this conclusion comes from the finding of little preferential solvation of the initial state,  $\text{Fe}(\text{hxs})^{2+}$ , by methanol in increasing concentrations of methanol cosolvent.<sup>5</sup> The chemical potential for transfer,  $\delta_m \mu^\theta$ , of  $\text{Fe}(\text{hxs})^{2+}$  from water to aqueous methanol ( $x_2 = 0.57$ ) is only about -4 kJ mol<sup>-1</sup>. An examination of a molecular model of  $\text{Fe}(\text{hxs})^{2+}$  based upon the structure of the complex ion obtained from an X-ray diffraction study<sup>7</sup> shows that a significant fraction of the total periphery of the ion is relatively hydrophilic. Therefore, the kinetics results at elevated pressure and equilibrium measurements upon the reacting metal complex ion are mutually consistent and are revealing of the roles of solvent components in solvation and rate control.

The present report is concerned with the effect of the cosolvents ethanol, isopropyl alcohol, *tert*-butyl alcohol, and acetone upon

the dissociation rate constant and the effect of increasing the organic moiety of the alcohol (with isopropyl alcohol and *tert*-butyl alcohol) upon the volume of activation. It is anticipated that the dissociation will be accelerated. A probable virtually common contribution to  $\Delta V^\ddagger$  from desolvating water from hydroxide allows the contribution from any solvation of the incipient activated complex by cosolvent to be observed. On the basis of the earlier considerations a further decrease in  $\Delta V^\ddagger$  (relative to that in aqueous solution and aqueous methanol) is predicted upon more favorable solvation by the cosolvents isopropyl alcohol and *tert*-butyl alcohol, as the transition state is reached.

### Experimental Section

**Materials.** Solvents and solutes except for ethanol (pure dehydrated U.S.1-USP, U.S. Industrial Chemicals Co., Tuscola, IL) and isopropyl alcohol (Gold Label spectrophotometric grade, supplied by Aldrich Chemical Co.) were those reported earlier.<sup>4,5</sup>

**Methods.** Kinetic measurements at atmospheric pressure were made on the chloride salt of  $\text{Fe}(\text{hxs})^{2+}$  by using either a Unicam SP 8-100 or a Cary 219 spectrophotometer. The dissociation by hydroxide ion followed by loss of absorbance at 595 nm gave good first-order plots. All solvent percentages quoted are for volume percent before mixing, and all measurements were made at 298.2 K. Kinetics at elevated pressures were measured by using the aliquot sampling apparatus described previously;<sup>8</sup> in each case a portion of the reacting solution was retained for study of the room-pressure kinetics, for comparison. Solutions were maintained at a constant ionic strength (0.33 mol dm<sup>-3</sup>) by using sodium chloride.

### Results and Discussion

Values of  $k_{\text{obsd}}$ , the first-order rate constant for dissociation of  $\text{Fe}(\text{hxs})^{2+}$  by hydroxide ion in aqueous ethanol, aqueous isopropyl

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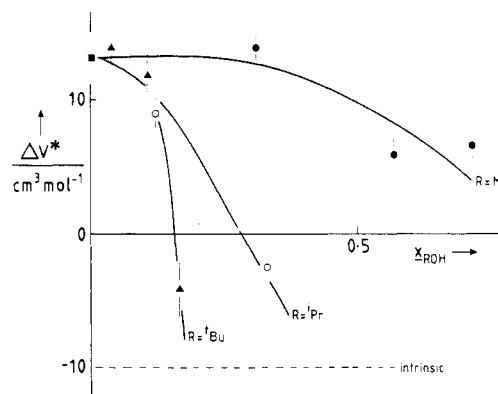
**Table II.** Dissociation of  $\text{Fe}^{\text{II}}(\text{hxsb})\text{Cl}_2$  by Hydroxide Ions in Aqueous Alcohols at 298 K

alcohol	% v/v	$x_2$	$[\text{OH}^-]^b$ mol dm <sup>-3</sup>	$k_p/k_0^a$								$\Delta V^*$ , cm <sup>3</sup> mol <sup>-1</sup>
				$p = 0.34$	$p = 0.51$	$p = 0.68$	$p = 0.85$	$p = 1.01$	$p = 1.18$	$p = 1.34$		
none <sup>c</sup>	0		0.33	0.76		0.65		0.56		0.49	13.3 ± 1.9	
methyl <sup>c</sup>	50	0.308	0.33		0.62	0.67		0.58		0.46	14.0	
	75	0.37	0.33	0.93		0.84		0.79		0.70	6.2 ± 0.6	
	75	0.57	0.10				0.83		0.76	0.74	5.5 ± 1.2	
	85	0.72	0.33			0.82		0.76		0.65	6.8	
isopropyl	35	~0.12	0.10			0.78		0.67			9	
	66.7	~0.33	0.10			1.08		1.11			-2.5	
<i>tert</i> -butyl	17	0.038	0.33			0.68		0.55		0.51	14.1 ± 1.1	
	38	0.105	0.10			0.72					~12	
	50	0.161	0.10			1.13			1.23		-4.2	

<sup>a</sup>  $k_p/k_0$  is the ratio of the observed first-order rate constant at pressure  $p$  (in kbar) to that at atmospheric pressure at the specified hydroxide ion concentration. <sup>b</sup> The  $[\text{OH}^-]$  value is that prior to pressure application. <sup>c</sup> See ref 4.

alcohol, aqueous *tert*-butyl alcohol, and aqueous acetone at the various hydroxide ion concentrations, are compiled in Table I. As previously noted for methanol as cosolvent,<sup>4b</sup> addition of alcohol is accompanied by a considerable increase in the rate constant of dissociation, which may be ascribed to the increase in the chemical potential of the hydroxide ion, thus reducing the free energy of activation. The rate law, which has a negligible solvolysis term (zero intercept in a plot of  $k_{\text{obsd}}$  vs  $[\text{OH}^-]$ ), is second order, first order in each reactant, at low hydroxide ion concentrations but includes higher order terms in hydroxide ion as the latter concentration is increased.<sup>9</sup> The occurrence of these higher order terms appears at lower hydroxide concentration as  $x_2$  is increased. Consequently, the reactivity trends considered as  $k_{\text{obsd}}$  values at 0.10 mol dm<sup>-3</sup> hydroxide are broadly indicative rather than exactly quantitative since small contributions from higher order terms may be present even at this concentration. The slowness of the reaction at 298.2 K at low concentrations (<0.10 mol dm<sup>-3</sup>) of hydroxide ion makes a comprehensive study in this concentration region impractical. When  $x_2 = 0.15$ , the extent of rate acceleration is not widely different for each alcohol. At higher mole fractions, for example 0.26, ethanol and methanol have fairly similar kinetic influences, compared with that of isopropyl alcohol, which almost triples the rate enhancement shown by the lower molecular weight alcohols. Practical limitations prevent *tert*-butyl alcohol from being used at the higher mole fractions, but the indication is that the effect of increasing the organic moiety of the cosolvent is optimized with isopropyl alcohol. Higher mole fractions of alcohols are not used, thus limiting the possible complications from ion pairing. Where direct comparison is possible,<sup>10</sup> the effect of cosolvents is similar to that reported for dissociation of  $\text{Fe}(\text{phen})_3^{2+}$ . The acceleration of dissociation of  $\text{Fe}(\text{hxsb})^{2+}$  is greater with added acetone than with any alcohols used. It could be presumed that isopropyl alcohol and acetone would interact somewhat similarly with the iron(II) cation; therefore, the bigger effect of added acetone is upon the chemical potential of hydroxide ion. This is consistent with values of  $\delta_{\text{m}\mu}^\theta(\text{OH}^-)$  recently established;<sup>11</sup> for example at  $x_2$ (isopropyl alcohol) values of 0.136 and 0.262,  $\delta_{\text{m}\mu}^\theta(\text{OH}^-)$  is 6.2 and 10.2 kJ mol<sup>-1</sup>, respectively, whereas at an  $x_2$ (acetone) value of 0.109,  $\delta_{\text{m}\mu}^\theta(\text{OH}^-)$  is +12 kJ mol<sup>-1</sup>, rising to +21 kJ mol<sup>-1</sup> at  $x_2$ (acetone) = 0.196.

Values of  $k_{\text{obsd}}$  for dissociation at elevated pressure ( $k_p$ ), expressed as a ratio with respect to the dissociation rate constant for the corresponding system at room pressure ( $k_0$ ), together with the derived values of  $\Delta V^*$  are listed in Table II. The uncertainties in these values are typically 10–15%, but the differences with variation in cosolvent are so dramatic that the trends are readily



**Figure 1.** Dissociation of  $\text{Fe}(\text{hxsb})^{2+}$  by hydroxide ions at 298.2 K and ionic strength 0.33 mol dm<sup>-3</sup>:  $\Delta V^*$  vs mole fraction of added alcohol,  $x_{\text{ROH}}$ .

discerned and are illustrated in Figure 1. The modest decrease in  $\Delta V^*$  that occurs at high mole fractions of methanol (a reduction from 13 cm<sup>3</sup> mol<sup>-1</sup> in aqueous solution to 6 and 7 cm<sup>3</sup> mol<sup>-1</sup> at  $x_2 = 0.57$  and 0.72, respectively<sup>4b,5</sup>) is indicative of some solvation by methanol of the incipient activated complex of +1 charge, although the desolvation of electrostricted water from hydroxide still appears to be the dominant influence. It is expected that the methanol molecules will solvate by means of the methyl group with the peripheral part of the complex ion that is hydrophobic. The 2-pyridyl moieties are bound at adjacent coordination sites; consequently, solvent association is projected to be concentrated in this region of the solute species (that is, solvation that is different in the transition state from that of the initial state). From Table II it is evident that the reduction of  $\Delta V^*$  is even more strikingly shown for the reactions in aqueous isopropyl alcohol and aqueous *tert*-butyl alcohol, to the extent that  $\Delta V^*$  assumes progressively smaller positive values, and indeed (by interpolation) the rate is accelerated by pressure application at  $x_2 = 0.3$  (isopropyl alcohol) and  $x_2 \approx 0.15$  (*tert*-butyl alcohol). In fact  $\Delta V^* = -2.5$  cm<sup>3</sup> mol<sup>-1</sup> at  $x_2 = 0.33$  and  $-4.2$  cm<sup>3</sup> mol<sup>-1</sup> at  $x_2 = 0.16$  for isopropyl alcohol and *tert*-butyl alcohol, respectively. The cosolvent range over which the change occurs from  $\Delta V^*$  values close to that for the reaction in water to the small negative values is quite small. Whether these different trends of  $\Delta V^*$  reflect a greater volume reduction per molecule of alcohol solvating the complex or reflect a greater number of solvating molecules cannot be answered definitively. But given that the fraction of the complex ion surface area which is hydrophobic is not high, then from steric considerations it is unlikely that very large numbers of the higher molecular weight alcohols would be able to participate in the association. For a given alcohol the profile of  $\Delta V^*$  and  $x_2$  is probably a consequence of a combination of alcohol concentration and solvent structure reorganization as  $x_2$  increases. It is noteworthy that the profiles develop significantly greater changes in  $\Delta V^*$  with lower  $x_2$  values as the molecular weight of the alcohol increases. This parallels the two solvent structure reorganization mole

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fraction points that are postulated on the basis of several properties.<sup>12</sup> Knowledge of the partial molar volume,  $\bar{V}$ , of the hydroxide ion in the solvent mixtures used would be valuable.<sup>13</sup> But a much better basis for analysis and interpretation of  $\Delta V^*$  would be possible if  $\bar{V}$  were also available for the iron(II) complex cations.

Data cannot be acquired with sufficient accuracy to permit quantitative correlation with solvent properties and solvent structure as they change with composition. However, it is evident that the magnitude of  $\Delta V^*$  variation is greatest when alcohol cosolvent causes water structure change and breakdown for the lowest values of  $x_2$  (among the alcohols studied) where these changes occur; that is, when *tert*-butyl alcohol is used as a solvent. The smaller effects seen in aqueous methanol reflect findings that the solvent structure reorganization positions are less well defined with the binary system.

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**Registry No.** Fe(hxsb)<sup>2+</sup>, 88686-51-5; OH<sup>-</sup>, 14280-30-9.

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### Synthesis and Crystal Structure of $[\text{Et}_4\text{N}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Pd}(\text{C}_9\text{H}_9)]$ ( $\text{C}_9\text{H}_9 = \eta^3\text{-1-Phenylallyl}$ ). An Example of a Non-"Slipped" Palladium(II) Capping Moiety

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In a previous paper<sup>1</sup> we noted the similarity of the cluster  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{2-}$  to cyclopentadienide,  $[\text{C}_5\text{H}_5]^-$ , and the dicarbollide ion,  $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ . We described the synthesis and characterization of a number of compounds of the general formula  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{ML}_n]^{2-}$ , where  $\text{ML}_n$  is a platinum-metal-based fragment. Variable-temperature <sup>13</sup>C NMR studies showed that these complexes adopt a (1,4)-bicapped octahedral geometry<sup>2</sup> in solution; a crystal structure of  $[\text{PPN}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Pt}(\eta^3\text{-2-methylallyl})]$  agreed with this assignment. Unfortunately, a detailed analysis of this structure was not possible due to disorder. In this note we describe the preparation and full crystallographic characterization of the mixed-metal cluster  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Pd}(\eta^3\text{-1-phenylallyl})]^{2-}$ . (The phenylallyl ligand will hereafter be referred to as  $\text{C}_9\text{H}_9$ .)

When a late-transition-metal-based moiety caps a carborane, the resulting cluster often exhibits a "slip" distortion, where the metal cap asymmetrically bridges the carborane face. The most thoroughly studied of these metallocarborane complexes are those of  $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ . In these compounds, the degree of slippage is defined as  $\Delta$ , the distance between the perpendicular from the

**Table I.** Crystal Data for  $[\text{Et}_4\text{N}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Pd}(\text{C}_9\text{H}_9)]\cdot\text{CHCl}_3$

formula	$\text{C}_{48}\text{H}_{50}\text{Cl}_3\text{N}_2\text{O}_{21}\text{PdRe}_7$
fw	2506.08
cryst dims, mm	$0.2 \times 0.3 \times 0.4$
system	monoclinic
space group	$P2_1$
<i>a</i> , Å	14.406 (5)
<i>b</i> , Å	19.988 (10)
<i>c</i> , Å	11.603 (6)
$\beta$ , deg	112.08 (3)
<i>V</i> , Å <sup>3</sup>	3096 (2)
<i>Z</i>	2
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	2.688
diffractometer	Syntex P2 <sub>1</sub>
monochromator	graphite
scan range, deg	$3.0 < 2\theta < 54.0$
data collected	$\pm h, +k, +l$
$\lambda(\text{K}\alpha)$ of Mo radiation, Å	0.71073
<i>T</i> , K	300
no. of obsd reflns	7611
no. of unique reflns	7011
<i>R</i>	0.044
<i>R<sub>w</sub></i>	0.048

**Table II.** Selected Bond Distances (Å) and Angles (deg) for  $[\text{Et}_4\text{N}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Pd}(\text{C}_9\text{H}_9)]\cdot\text{CHCl}_3$

Distances			
Re1-Re2	2.967 (2)	Re1-Re3	2.936 (1)
Re2-Re3	2.959 (2)	Re1-Re4	2.964 (2)
Re2-Re4	2.963 (2)	Re3-Re4	2.953 (2)
Re2-Re5	2.969 (2)	Re3-Re5	3.017 (2)
Re3-Re6	3.009 (2)	Re4-Re6	3.001 (1)
Re5-Re6	3.081 (2)	Re2-Re7	2.968 (2)
Re4-Re7	2.978 (2)	Re5-Re7	3.016 (2)
Re6-Re7	3.067 (2)	Re5-Pd	2.879 (3)
Re6-Pd	2.952 (3)	Re7-Pd	2.786 (3)
Pd-C(1)	2.16 (3)	Pd-C2	2.01 (5)
Pd-C3	2.27 (5)	C1-C2	1.57 (7)
C2-C3	1.11 (7)	av Re-C <sub>carbide</sub>	2.13 (3)
Angles <sup>a</sup>			
Re5-Pd-Re6	63.78 (7)	Re5-Pd-Re7	64.31 (7)
Re6-Pd-Re7	64.53 (6)	C1-C2-C3	128 (5)

<sup>a</sup>All angles within 1.0° of those required for a regular octahedron for Re2 to Re7 and a regular tetrahedron for the Re1 cap.

capping metal to the mean pentagonal  $\text{C}_2\text{B}_3$  plane and the pentagon centroid.<sup>3</sup> This quantity depends on the capping metal and the ligands on the metal; for example, the fragment  $\text{Rh}(\text{PPh}_3)_2$  symmetrically caps the carborane, whereas  $\text{Pd}(\text{PMe}_3)_2$ ,  $\text{Pd}(\text{C}_2\text{H}_4(\text{NMe}_2)_2)$ , and  $\text{Au}(\text{S}_2\text{CNET}_2)$  display more open structures.<sup>4-6</sup> The electronic factors responsible for the slip distortion have been elucidated in a theoretical study by Mingos.<sup>3</sup> Similar distortions have been observed in cyclopentadienyl complexes of late transition metals. We were therefore interested in determining whether the slip distortion observed in many metallocarboranes and cyclopentadienyl compounds is also seen in our mixed-metal clusters.

### Results and Discussion

$[\text{Et}_4\text{N}]_2[\text{Re}_7\text{C}(\text{CO})_{21}\text{Pd}(\text{C}_9\text{H}_9)]$  is easily prepared from  $[\text{Et}_4\text{N}]_3[\text{Re}_7\text{C}(\text{CO})_{21}]$  and  $[\text{Pd}(\text{C}_9\text{H}_9)\text{Cl}]_2$ ; X-ray-quality crystals were grown from an acetone/chloroform solution. Tables I and II contain crystallographic data and pertinent bond distances and angles for this compound, respectively. Figure 1 shows a view of the entire mixed-metal dianion. The complex crystallizes with one molecule of chloroform of solvation per formula unit. The

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