

The spectra for ( $\eta^5$ -cyclopentadienyl)( $\eta^3$ -allyl)molybdenum and tungsten dicarbonyls (C and D, respectively) are quite similar. For both C and D the band assignments are as follows:  $I_1$  at 7.14 or 7.08 eV and  $I_2$  at 7.67 or 7.65 eV, metal d orbital ionization components;  $I_3$  at 8.71 or 8.80 eV, allyl  $\pi$  HOMO;  $I_4$  at 9.52 or 9.66 eV and  $I_5$  at 9.75 or 9.97 eV, cyclopentadienyl  $\pi$  orbitals;  $I_6$  at 10.71 or 10.75 eV, second allyl  $\pi$  orbital. Lichtenberger and Fenske<sup>68</sup> have reported the UPS of ( $\eta^5$ -cyclopentadienyl)manganese tricarbonyl, and Lichtenberger has recently obtained the UPS of ( $\eta^5$ -methylcyclopentadienyl)manganese tricarbonyl, ethylenedicarbonyl, and propylenedicarbonyl.<sup>11</sup> In contrast to the intriguing observations that the  $\pi$  orbitals of the ethylene and propylene ligands are destabilized by complexation with manganese, the  $\pi$  orbitals of the cyclopentadienyl ligand are stabilized (relative to cyclopentadiene at an  $I_1$  of 8.57 eV).<sup>12</sup> The degeneracy of the  $\pi$  HOMO of the ligand is broken by complexation, giving rise to ionization band components at ca. 9.6 and 9.9 eV in the spectrum of ( $\eta^5$ -methylcyclopentadienyl)manganese tricarbonyl. The  $I_4$  and  $I_5$  band components for complexes C and D are very similar in energy and shape to those observed by Lichtenberger which leaves very little doubt in our band assignments. The  $I_6$  component for C and D is rather broad relative to the analogous  $\pi$  allyl component for A and B. This could indicate that the lower  $\pi$  cyclopentadienyl orbital ionization component also lies in this region of the spectrum (the second  $\pi$  ionization energy for cyclopentadiene is 10.62 eV).<sup>12</sup> However, Lichtenberger has observed that the most stable  $\pi$  component for the cyclopentadienyl ligand for manganese complexes occurs at an ionization energy above 12 eV.<sup>11</sup> One notes that the perturbations introduced by the transition metal to the allyl  $\pi$  orbitals are smaller for C and D than they were for A and B. It is possible that this is caused by the presence of the  $\eta^5$ -cyclopentadienyl ligand for C and D rather than by alteration of the transition metal (see earlier discussion).

Finally, it is of interest to compare the current results for  $\eta^3$ -allyl complexes with those obtained by Green et al. for ( $\eta^3$ -allyl)bis( $\eta^5$ -cyclopentadienyl)niobium<sup>13</sup> and more recently by Fehlner et al. for ( $\eta^5$ -cyclopentadienyl)( $\eta^1$ -allyl)iron dicarbonyl.<sup>14</sup> For the former complex UPS bands at 8.0 and 8.6 eV were assigned to ionization of the perturbed allyl  $\pi$  orbital and metal/cyclopentadienyl orbitals, respectively; the current work suggests that these assignments should be reversed. For the latter  $\eta^1$ -allyl complex, a band at 9.78 eV is assigned to ionization of the isolated  $\pi$  orbital (analogous to free propylene), while a band at 8.54 eV is assigned to ionization of the Fe-C  $\sigma$  orbital. Thus it would appear that the  $\pi$  HOMO for the  $\eta^3$ -allyl complexes is slightly more stable than is the  $\sigma$  HOMO for the  $\eta^1$ -allyl complex and that the same is true for the lower ligand orbital for the two types of complexes. A reasonable conclusion which might be drawn from this observation is that an  $\eta^3$ -allyl complex should be somewhat more stable than its  $\eta^1$  analogue, a conclusion that is amply substantiated by experimental observations.<sup>15</sup>

### Experimental Section

The photoelectron spectra discussed in this work were obtained on a Perkin-Elmer PS 18 spectrometer. A volatile-inlet probe was employed for complexes A and B, but the solid-inlet probe was used for C and D because temperatures near 70 °C were necessary to obtain suitable spectra. The spectra in Figure 1 represent the average of

several runs for each sample. Xenon and argon were always employed as internal calibrants. Compounds A-C were prepared by phase-transfer catalysis;<sup>16</sup> compound D was prepared by the method of Faller et al.<sup>17</sup>

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**Registry No.** A, 33307-28-7; B, 33307-32-3; C, 12128-87-9; D, 31811-41-3.

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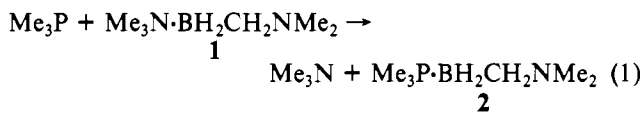
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### Trimethylphosphine-((Dimethylamino)methyl)borane

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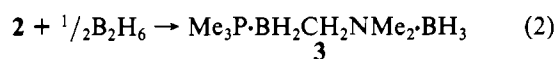
The anomalous greater basicity of trimethylphosphine than trimethylamine relative to borane<sup>1</sup> was used to advantage in the preparation of a new borane-derived base, trimethylphosphine-((dimethylamino)methyl)borane (**2**) (eq 1). The



known amine analogue, **1**, is prepared from the reaction of *tert*-butyllithium and bis(trimethylamine)dihydroboron(1+) chloride.<sup>2</sup> After 12 h in hexane solution, the reaction with 1:1 to 1.5:1 stoichiometry yields nearly 50% of product which is separated as a clear, colorless liquid, mp -31 to -33 °C, by fractional condensation in a -35 °C trap.

Like **1**, **2** is simultaneously a strong Lewis base and an adduct of another strong Lewis base, this time trimethylphosphine. This feature is the cause of inherent thermal instability toward loss of the  $\text{BH}_2\text{CH}_2\text{NMe}_2$  fragment (and its concomitant dimerization) on standing at room temperature. Any process such as bonding to an acid or dissolution in a protonic solvent (water, ethanol) that effectively removes the basic site markedly improves the thermal stability. Under comparable conditions, however, **2** is observably much more stable than **1**. Even toward acid hydrolysis, **2** is also more stable.

An interesting compound of **2** is the borane adduct prepared by contact with diborane in hexane at -78 °C (eq 2). The



adduct forms as an insoluble solid and is purified by sublimation without decomposition, at 60 °C under high vacuum. This adduct, like the analogous adduct of **1**, has two different dative bonds in the same molecule and does not rearrange to the supposedly stabler adducts  $\text{Me}_3\text{P}\cdot\text{BH}_3$  and  $[(\text{BH}_2\text{CH}_2\text{NMe}_2)_2]$ .

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Table I. Characterization Data

compd	% C		% H		% N		IR absorption, <sup>a</sup> cm <sup>-1</sup>
	calcd	found	calcd	found	calcd	found	
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> H <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	24.6	25.4	6.9	7.0	4.8	4.4	3257 s; 2364 s; 2283 w; 1340 w; 1300 s; 1163 m; 1148 m; 1134 w; 1056 m; 1120 w; 990 s; 970 s; 948 s; 840 s b; 760 w; 753 w; 740 w; 705 m
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> ·BH <sub>3</sub>	44.8	45.2	13.8	13.7	8.7	8.8	2350 m; 2310 m; 2260 m; 1305 w; 1294 w; 1167 m; 1140 w; 1005 w; 990 w; 960 m; 950 w; 927 w; 893 w; 840 w b; 810 w; 760 w; 750 w; 720 w; 700 w
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> C <sub>16</sub> H <sub>33</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	51.1	52.4	10.1	10.9	2.7	3.3	2345 w b; 2285 w; 1320 vw; 1301 w; 1155 w; 969 s; 955 m; 930 m; 840 s b; 868 m; 770 w; 720 w
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> (2)							2980 w; 2960 w; 2940 m; 2900 vw; 2840 vw; 2818 w; 2804 m; 2750 s; 2323 s; 2270 w; 1490 w; 1470, 1450, 1440, 1420 m mltp; 1310 w, 1290 w; 1260 vw; 1250 m; 1183 m; 1170 m; 1155 w; 1140 w; 1100 w; 1160 w; 1040 vw; 1125 m; 1000 vw; 960 s b; 910 w d; 880 w; 860 w; 840 w; 770 w; 750 m; 695 w
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> BH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>							2470 m; 2240 vw; 2420 w; 2375 m; 2340 m; 2290 w; 1320 w; 1302 m; 1245 m; 1218 m; 1203 m; 1195 m; 1185, 1180 vw; 1160 w; 1140 vw; 1120 vw; 1110 w; 1060 w; 1007 w; 995 w; 975 m; 952 m; 925 w; 900 w; 840 s b; 760 w mltp
[Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> ] <sub>2</sub> BH <sub>2</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>							2470 w; 2350 m; 2290 w; 1318 w; 1298 m; 1232 w; 1216 m; 1193 m; 1180 w; 1160 w; 1147 w; 1136 vw; 1128 w; 1102 w; 1060 w; 1050 w; 1010 w; 956 s, 990 sh, 974 sh; 925 w; 900 w; 840 s b; 760 w; 755 w; 705 w
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> BH <sub>2</sub> NMe <sub>2</sub> CH <sub>2</sub> BH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>							2450 w; 2330 m b; 2280 w; 1315 w; 1295 m; 1240 w, 1250 sh; 1210 m; 1190 m; 1170 vw, 1158 m, 1135 sh; 1125 vw; 1095 w; 1060 w; 955 m b; 915 w; 830 s b; 755 w; 720 w

<sup>a</sup> Run on Beckman 4240, as mineral oil mulls, except for 2. Absorptions common to those of mineral oil are not included. Key: s, strong; m, medium; w, weak; vw, very weak; d, doublet; b, broad; sh, shoulder; mltp, multiplet.

Table II. High-Resolution Mass Spectral Data,<sup>a</sup> Molecular Ion Region,<sup>b</sup> for Me<sub>3</sub>P·BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>·BH<sub>3</sub>

m/e	assignt	Δ(m/e), mmu from theor
161.16322	C <sub>5</sub> <sup>13</sup> CH <sub>21</sub> N <sup>11</sup> B <sub>2</sub> P	0.1
160.1598	C <sub>6</sub> H <sub>21</sub> N <sup>11</sup> B <sub>2</sub> P (Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> ·BH <sub>2</sub> )	0.0
159.16335	C <sub>6</sub> H <sub>21</sub> N <sup>10</sup> B <sup>11</sup> BP	0.1
159.15201	C <sub>6</sub> H <sub>21</sub> N <sup>10</sup> B <sup>11</sup> BP	0.0
158.16706	C <sub>6</sub> H <sub>21</sub> N <sup>10</sup> B <sub>2</sub> P	0.0
158.15556	C <sub>6</sub> H <sub>20</sub> N <sup>10</sup> B <sup>11</sup> BP	0.0
158.14406	C <sub>6</sub> H <sub>19</sub> N <sup>11</sup> B <sub>2</sub> P	0.1

<sup>a</sup> Midwest Center for Mass Spectroscopy, University of Nebraska, Lincoln, NE. <sup>b</sup> Resolving power, 17 000.

A class of adduct-bases, base-BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, is thus established wherein "base" should be stronger toward borane than trimethylamine. Indeed, when considered this way, the previously reported<sup>2</sup> aminoborohydride, Me<sub>2</sub>NCH<sub>2</sub>-

BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub><sup>-</sup>, is also a member of this class, where the "base" is Me<sub>2</sub>NCH<sub>2</sub>BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub><sup>-</sup>. From what is known about the hydrolytic stability of 1 and 2 vs. the lability of aminoborohydride and the four-membered ring CH<sub>2</sub>NMe<sub>2</sub>CH<sub>2</sub>BH<sub>2</sub>,<sup>3</sup> it may be deduced that hydrolytically stable members of the class would be derived from bases of steric requirements close to that of the *tert*-butyl group.

Structural identification is dependent on analyses and spectral data of the protonated and alkylated salts and the borane adduct. Analyses and infrared data are collected in Table I. Mass spectral data for the borane adduct (Tables II and III) confirm the formulations. Of particular importance is the assignment of the parent cluster (Table II) at *m/e* 160, 159, and 158 under high resolution to rational formulas arising from the proposed structure for 2. The observed 2:1 intensity ratio of the *m/e* 160 and 159 peaks conforms to that expected

Table III. Mass Spectral Data for Me<sub>3</sub>P·BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>·BH<sub>3</sub><sup>a</sup>

<i>m/e</i>	intens, %	assignt	dev, mmu	calcd intens <sup>b</sup>
160.1603	4.14	C <sub>6</sub> H <sub>21</sub> NP <sup>11</sup> B <sub>2</sub> (parent - 1)	0.5	4.14
159.1623	2.14	C <sub>6</sub> H <sub>21</sub> NP <sup>11</sup> B <sup>10</sup> B	-0.9	2.04
159.1676	0.12	C <sub>6</sub> H <sub>21</sub> NP <sup>10</sup> B <sub>2</sub>	0.5	0.25
158.1566	0.28	C <sub>6</sub> H <sub>20</sub> NP <sup>11</sup> B <sup>10</sup> B	1.0	
147.1355	1.90	C <sub>6</sub> H <sub>19</sub> NP <sup>11</sup> B	0.7	1.9
146.1386	0.19	C <sub>6</sub> H <sub>19</sub> NP <sup>10</sup> B	0.1	0.5
132.1124	4.7	C <sub>5</sub> H <sub>16</sub> NP <sup>11</sup> B	1.0	4.7
131.1155	0.4	C <sub>5</sub> H <sub>16</sub> NP <sup>10</sup> B	0.5	1.2
102.0793	24.6			
101.0747	10.3			
89.0700	5.3	C <sub>3</sub> H <sub>11</sub> <sup>11</sup> BP	0.9	5.3
88.0740	1.2	C <sub>3</sub> H <sub>11</sub> <sup>10</sup> BP	1.1	1.0
88.0740	1.2			
87.0546	1.1			
84.1172	27.0	C <sub>3</sub> H <sub>12</sub> N <sup>11</sup> B <sub>2</sub>	1.6	27.0
83.1185	17.1	C <sub>3</sub> H <sub>12</sub> N <sup>11</sup> B <sup>10</sup> B	-0.7	13.5
82.1247	1.2			
82.1131	1.5			
80.0860	4.2			
79.0896	1.6			
77.0527	11.2	C <sub>3</sub> H <sub>10</sub> P (Me <sub>3</sub> PH <sup>+</sup> )	0.7	
76.0459	82.3	C <sub>3</sub> H <sub>9</sub> P (Me <sub>3</sub> P)	1.7	
75.0381	19.0	C <sub>3</sub> H <sub>8</sub> P (Me <sub>2</sub> PCH <sub>2</sub> )	1.8	
73.0232	4.2			
72.0993	0.98	C <sub>3</sub> H <sub>11</sub> N <sup>11</sup> B	0.8	
71.0915	11.8	C <sub>3</sub> H <sub>10</sub> N <sup>11</sup> B (Me <sub>2</sub> NCH <sub>2</sub> BH <sub>2</sub> )	0.9	11.8
70.0971	3.5	C <sub>3</sub> H <sub>10</sub> N <sup>10</sup> B (Me <sub>2</sub> NCH <sub>2</sub> BH <sub>2</sub> )	2.8	3.0
70.0835	26.4	C <sub>3</sub> H <sub>9</sub> N <sup>11</sup> B	0.7	
69.0794	20.3			
68.0841	37.0	C <sub>2</sub> H <sub>8</sub> N <sup>11</sup> B <sub>2</sub>	-0.2	37
67.0882	16.1	C <sub>2</sub> H <sub>8</sub> N <sup>10</sup> B <sup>11</sup> B	0.3	18
66.0925	1.21			
66.0697	1.4			
62.0281	3.2			
61.0231	100	C <sub>2</sub> H <sub>7</sub> P ((CH <sub>2</sub> ) <sub>2</sub> PH <sub>2</sub> )	2.4	
60.0144	4.7	C <sub>2</sub> H <sub>6</sub> P	1.5	
59.0074	65.4	C <sub>2</sub> H <sub>5</sub> P	2.3	
58.0680	27.5	C <sub>3</sub> H <sub>8</sub> N	2.3	
56.9915	25.3	C <sub>2</sub> H <sub>6</sub> P	2.1	
56.0693	63.0	C <sub>2</sub> H <sub>7</sub> N <sup>11</sup> B	2.1	63
55.0728	15.1	C <sub>2</sub> H <sub>7</sub> N <sup>10</sup> B	2.0	13

<sup>a</sup> Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE. Electron ionization, 70 eV; direct inlet; room temperature to 50 °C. <sup>b</sup> Calculation for boron-isotope distribution, normalized to highest observed peak in any grouping.

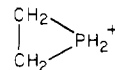
for a B<sub>2</sub> compound. The *m/e* 77, 76, 75 and 61, 60, 59 clusters are attributable to trimethylphosphine in the fragmentation.

Table IV. Proton NMR Data<sup>a</sup>

species	resonances, <sup>b</sup> ppm	assignt	intens		solvent
			calcd	obsd	
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub>	1.26 d <sup>c</sup>	Me <sub>3</sub> P	3	3	neat
	2.08	Me <sub>2</sub> N	2	2	
	2.54	impurity			
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> ·BH <sub>3</sub>	1.32 d <sup>c</sup>	Me <sub>3</sub> P	9	9	CH <sub>2</sub> Cl <sub>2</sub>
	2.46 with sh	Me <sub>2</sub> N and CH <sub>2</sub>	8	8.1	
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> H <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	1.33 d <sup>c</sup>	Me <sub>3</sub> P	9	9	CD <sub>3</sub> CN
	2.77	Me <sub>2</sub> N	8	8	
	2.45 sh	CH <sub>2</sub>			
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	1.28 d <sup>c</sup>	Me <sub>3</sub> P	1.5	1.56	CD <sub>3</sub> CN
	2.62	Me <sub>2</sub> N	1	1	
	2.75	Me <sub>3</sub> N	1.5	1.44	
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> BH <sub>2</sub> - Me <sub>2</sub> NCH <sub>2</sub> BH <sub>2</sub> NMe <sub>3</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	1.30 d <sup>c</sup>	Me <sub>3</sub> P	1	1	CD <sub>3</sub> CN
	2.52	Me <sub>2</sub> N	2.78	2.24	
	2.66 with sh	Me <sub>2</sub> NCH <sub>2</sub>			
Me <sub>3</sub> P·BH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> BH <sub>2</sub> - Me <sub>2</sub> NCH <sub>2</sub> BH <sub>2</sub> PMe <sub>3</sub> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	1.30 d <sup>c</sup>	Me <sub>3</sub> P	1	1	CD <sub>3</sub> CN
	2.63 with sh	Me <sub>2</sub> NCH <sub>2</sub>	0.89	0.89	

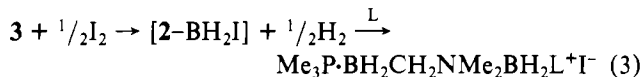
<sup>a</sup> Run at 60 MHz on a Hitachi-PE R24B. <sup>b</sup> Downfield from internal tetramethylsilane. <sup>c</sup> *J*<sub>PCH</sub> = 11 Hz.

The *m/e* 61 peak is the most intense fragment of the spectrum and is assignable to Me<sub>2</sub>P<sup>+</sup>, probably a cyclic ion such as<sup>4</sup>



The presence of Me<sub>2</sub>NCH<sub>2</sub>BH<sub>2</sub> in the fragmentation is not clearly established. The *m/e* 70, 69 pair observed for this fragment in the spectrum of (Me<sub>2</sub>NCH<sub>2</sub>BH<sub>2</sub>)<sub>2</sub><sup>5</sup> is not readily identifiable in the high-resolution data. A peak at *m/e* 70.0835, of 26%, is rationalized by a correct formula for the monomer, but a *m/e* 69.0864 peak for the <sup>10</sup>B isotope fragment is not discernible unless it is obscured by the *m/e* 69.0794 peak for which a fragmentation formula cannot be written.

A series of borane salts were established from <sup>1</sup>H NMR measurements (Table IV) of products isolated from the monoidination of the borane adduct of **2** followed by base displacement (eq 3). Comparison of the NMR data with those



L = Me<sub>3</sub>N, Me<sub>3</sub>P·BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, Me<sub>3</sub>N·BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>

of known salts of Me<sub>3</sub>N·BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> shows the expected greater shielding of the CH<sub>2</sub>NMe<sub>2</sub> methyl protons cations derived from **2**. These salts represent interesting alternating sequences of phosphorus and nitrogen centers in cations closely related to quaternary ammonium salts. For example, Me<sub>3</sub>P·BH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>BH<sub>2</sub>NMe<sub>2</sub>CH<sub>2</sub>BH<sub>2</sub>PMe<sub>3</sub><sup>+</sup>, is a tris(borane) with two each BP and BN dative bonds in a single-chain heptapolar 11-membered backbone. The single positive charge is spread mostly over ten methyl groups.

All preparations of **2** were contaminated with small amounts of (Me<sub>2</sub>NCH<sub>2</sub>BH<sub>2</sub>)<sub>2</sub> that could not be removed by trap-to-trap condensation. Because this impurity is not reactive with diborane or toward protonation, no great difficulty was encountered in using the crude product for chemical studies. Efforts to purify **2** by extraction from the protonated salt in strongly basic solution gave only 20% recovery, apparently because of poor solubility of **2** in hexane. Nevertheless, a product was obtained with but a trace of a 2.55-ppm <sup>1</sup>H NMR peak assignable to a trace impurity of [Me<sub>2</sub>NCH<sub>2</sub>BH<sub>2</sub>]<sub>2</sub>. Reaction of 150 mg of **2** and 0.2 mL of cetyl bromide in 1 mL of anhydrous dimethylformamide at 50 °C in a sealed ampule for 6 h gave 260 mg, 50%, of bromide salt, mp 112 °C. Metathesis with NH<sub>4</sub>PF<sub>6</sub> produced an oil that only slowly crystallized. Recrystallization from ethanol was effected by slow evaporation to incipient needle-crystal formation followed

by repeated small additions of water to give needles, mp 69–70 °C. Difficulties encountered were typical of the unsymmetrical low melting salts of 2.

Borane cations were prepared by adding dropwise  $1/2$  molar equiv of iodine in chloroform solution to a chloroform solution of 3. An equimolar amount of ligand (trimethylamine, 2, or 3) was added, and the mixture was allowed to stand for 12 h. Solvent was removed under vacuum and the residual oil taken up in water and metathesized with an aqueous solution of ammonium hexafluorophosphate. The  $\text{PF}_6^-$  salts precipitated as oils that were crystallized by cooling and scratching the vessel walls with stirring rod. Recrystallization from

water/ethanol (ca. 3:1) gave soft crystals.

**Registry No.** 1, 14175-47-4; 2, 76233-06-2; 3, 76250-75-4;  $\text{Me}_3\text{P}\cdot\text{BH}_2\text{CH}_2\text{NMe}_2\text{H}^+\text{PF}_6^-$ , 76233-07-3;  $\text{Me}_3\text{P}\cdot\text{BH}_2\text{CH}_2\text{NMe}_2\text{C}_{16}\text{H}_{33}^+\text{PF}_6^-$ , 76233-10-8;  $\text{Me}_3\text{P}\cdot\text{BH}_2\text{CH}_2\text{NMe}_2\cdot\text{BH}_2\text{NMe}_3^+\text{PF}_6^-$ , 76233-11-9;  $[\text{Me}_3\text{P}\cdot\text{BH}_2\text{CH}_2\text{NMe}_2]_2\text{BH}_2^+\text{PF}_6^-$ , 76233-14-2;  $\text{Me}_3\text{P}\cdot\text{BH}_2\text{CH}_2\text{NMe}_2\cdot\text{BH}_2\text{NMe}_2\text{CH}_2\cdot\text{BH}_2\text{NMe}_3^+\text{PF}_6^-$ , 76233-15-3;  $\text{Me}_3\text{P}\cdot\text{BH}_2\text{CH}_2\text{NMe}_3^+\text{PF}_6^-$ , 76233-16-4;  $\text{Me}_3\text{P}$ , 594-09-2;  $\text{B}_2\text{H}_6$ , 19287-45-7;  $\text{Me}_3\text{N}$ , 75-50-3; 2 (bromide salt), 76233-17-5.

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## Correspondence

### Comparisons of Experimental Activation Parameters for the $\text{Co}(\text{terpy})_2^{2+}$ - $\text{Co}(\text{bpy})_3^{3+}$ Redox Reaction with the Marcus Theory and the $\text{Fe}(\text{phen})_3^{2+,3+}$ System

Sir:

The Marcus theory<sup>1</sup> is most useful for examining the activation free energy and its components for adiabatic outer-sphere redox reactions through

$$k_{12} = Z \exp(-\Delta G^*_{12}/RT) \quad (1)$$

where

$$\Delta G^*_{12} = \omega_{12} + \lambda_{12}/4 + \Delta G^\circ_{12}/2 + (\Delta G^\circ_{12})^2/4\lambda_{12}$$

with  $k_{12}$ , the cross-reaction rate constant,  $Z$ , the collision frequency in solution ( $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ ), and  $\omega_{12}$ , the work term, and all others have their usual meaning. Due to the reasonably good agreement between the measured redox rate constant and the rate constant calculated from the Marcus theory for the  $\text{Co}(\text{terpy})_2^{2+}$ - $\text{Co}(\text{bpy})_3^{3+}$  system in water,<sup>2</sup> the comparison is extended here to include activation parameters. The Marcus theory predicts a simple relationship between the activation free energy of a cross reaction ( $\Delta G^*_{12}$ ) and the activation free energies of the self-exchange redox reactions of the reactants ( $\Delta G^*_{11}$ ,  $\Delta G^*_{22}$ ):

$$\Delta G^*_{12} = (\Delta G^*_{11} + \Delta G^*_{22})/2 + \Delta G^\circ_{12}(1 + \alpha)/2 \quad (2)$$

and

$$\alpha = \Delta G^\circ_{12}/4(\Delta G^*_{11} + \Delta G^*_{22})$$

Marcus and Sutin<sup>3</sup> showed that the activation parameters  $\Delta H^*_{12}$  and  $\Delta S^*_{12}$  for an electron-transfer reaction can be obtained by differentiating eq 2 with respect to temperature which yields

$$\Delta H^*_{12} = [(\Delta H^*_{11} + \Delta H^*_{22})/2](1 - 4\alpha^2) + (\Delta H^\circ_{12}/2)(1 + 2\alpha) \quad (3)$$

and

$$\Delta S^*_{12} = [(\Delta S^*_{11} + \Delta S^*_{22})/2](1 - 4\alpha^2) + (\Delta S^\circ_{12}/2)(1 + 2\alpha) \quad (4)$$

and that the relationships between the Marcus parameters and

the corresponding experimental terms are

$$\Delta G^* = \Delta G^\circ + RT \ln(hZ/\kappa T)$$

$$\Delta H^* = \Delta H^\circ + RT/2 \quad (5)$$

$$\Delta S^* = \Delta S^\circ - R \ln(hZ/\kappa T) + R/2$$

An activation free energy ( $\Delta G^*$ ) of 14.2 kcal/mol is obtained from eq 2 and 5 which is in good agreement with the experimental value of 13.6 kcal/mol.<sup>2</sup> The activation enthalpy and entropy of the cross reaction could not be compared due to the lack of data on the  $\text{Co}(\text{terpy})_2^{2+,3+}$  self-exchange. Consequently, eq 3 and 4 were used to estimate these parameters for this self-exchange redox system. With the activation parameters from the  $\text{Co}(\text{terpy})_2^{2+}$ - $\text{Co}(\text{bpy})_3^{3+}$  system<sup>2</sup> and the  $\text{Co}(\text{bpy})_3^{2+,3+}$  self-exchange,<sup>4</sup>  $\Delta H^\circ$  and  $\Delta S^\circ$  for the  $\text{Co}(\text{terpy})_2^{2+,3+}$  self-exchange are 9.4 kcal/mol and -12 eu, respectively. These values appear to be good estimates since their use in the  $\text{Co}(\text{terpy})_2^{2+}$ - $\text{Co}(\text{phen})_3^{3+}$  system<sup>2</sup> gave excellent agreement between the observed and calculated activation parameters obtained from eq 3 and 4.

The components of the activation free energy can be estimated from eq 1 which shows that the reorganization parameter  $\lambda_{12}$  can be determined if  $\omega_{12}$  and  $\Delta G^\circ_{12}$  are known or can be calculated. The experimental value for  $\Delta G^\circ_{12}$  is -0.69 kcal/mol<sup>2</sup> and the work term was estimated under the same experimental conditions from the expression<sup>5</sup>

$$\omega_{12} = (Z_1 Z_2 / D\bar{r}) \exp[-(8\pi e^2 N^2 \mu / 10^3 DRT)^{1/2} D\bar{r}] \quad (6)$$

with all terms having their usual meaning. Eq 6 yields a value of 0.62 kcal/mol for  $\omega_{12}$  from which  $\lambda_{12}/4$  is calculated to be 11.2 kcal/mol with use of eq 1. This result is in good agreement with the mean value of the reorganization parameters of the self-exchange redox reactions of the reactants which is 11.7 kcal/mol obtained from

$$\lambda_{12} = (\lambda_{11} + \lambda_{22})/2 \quad (7)$$

Both  $\lambda_{11}$  and  $\lambda_{22}$  were estimated from their respective  $\Delta G^*$  values where  $\Delta G^\circ$  is zero and the work terms were assumed to be similar to that of the cross reaction. Finally, Marcus considers the reorganization parameter to be composed of an inner-sphere ( $\lambda_i$ ) and outer-sphere  $\lambda_o$  component where

$$\lambda = \lambda_i + \lambda_o \quad (8)$$

and

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