The thiophene ligands of complexes **1**–**3** are labile. The dbt ligand of **1** is displaced by ca. 2 equiv of $CH_3CN$ in $CD_3NO_2$ solution at room temperature in about 1 week to give $[Fe(CH_3CN)(CO)_2(Cp)][BF_4]$ and free dbt. In contrast, the thiophene ligand of **2** is quantitatively displaced by $CD_3NO_2$ in ca. 3 h at room temperature.[27] The benzothiophene ligand of **3** is also displaced by $CH_3CN$ or $CD_3NO_2$. Decomposition of **3** to $[Fe(CO)_3(Cp)][BF_4]$ occurs during attempted slow recrystallization from dichloromethane/ethyl ether.

The $^{13}C$ NMR spectrum of benzothiophene complex **3** shows a singlet at room temperature for the two diasterotopic carbonyl ligands but two separate signals at 170 K ($\Delta G^* = 39$ kJ/mol at 190 K, the coalescence temperature in $CD_2Cl_2$) due to slowing of the stereochemical inversion at sulfur.[22,28] Free benzothiophene signals remained sharp and distinct from those of complex **3** at room temperature, ruling out an intermolecular mechanism for coalescence in **3**. To our knowledge, this is the first reported sulfur inversion barrier for a thiophene complex. For comparison, the $^{13}C$ NMR signals of the carbonyl ligands of $[Fe(PhSMe)(CO)_2(Cp)][PF_6]$ coalesce at 249 K with $\Delta G^* = 52$ kJ/mol.[22] In general, inversion barriers for $\pi$-conjugated sulfide ligands are about 10 kJ/mol lower than for saturated sulfide ligands, whereas cyclic sulfide ligands have inversion barriers slightly higher than acyclic ones.[28b]

Recent work by Angelici[8a,10a–c] suggests that $\pi$-bonded thiophene species are responsible for C–S bond cleavage and hydrogen/deuterium exchange on hydrodesulfurization catalysts. The isolation and characterization of **1** provides a structural model for the interaction of organic sulfur in coal with a metallic catalyst via sulfur only, which is a viable initial step in hydrodesulfurization.[17]

**Acknowledgment.** We thank the Consortium for Fossil Fuel Liquefaction Science, funded by the Pittsburgh Energy Technology Center, United States Department of Energy, for financial support, and Robert Angelici for helpful discussions and a preprint of ref 10c.

**Supplementary Material Available:** For the structure of **1**, tables of crystal data and details of the intensity collection and refinement, positional and thermal parameters, bond distances, bond angles, and least-squares planes (9 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(27) In our hands, the $^1H$ NMR spectrum of **2** in $(CD_3)_2CO$[13a] shows free thiophene and $[Fe\{(CD_3)_2CO\}(CO)_2(Cp)]^+$.

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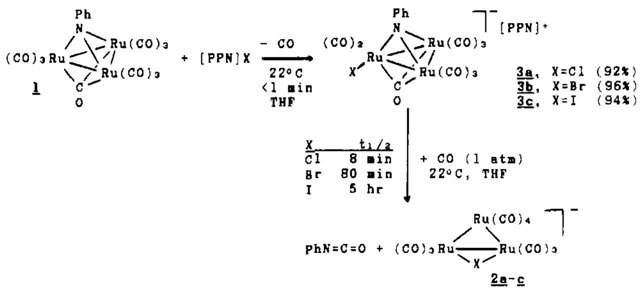
## Halide-Promoted Formation and Carbonylation of $\mu_3$-Nitrene Ligands on $Ru_3$ Clusters

*Sir:*

Bridging carbene ligands in polynuclear compounds often undergo facile carbonylation to form ketene ligands, $\mu\text{-}CR_2 + CO \rightarrow \mu\text{-}CR_2{=}C{=}O$.[1] However, the related carbonylation of bridging nitrene ligands to form isocyanates, $\mu\text{-}NR + CO \rightarrow \mu\text{-}RN{=}C{=}O$, has proven difficult to achieve,[2–5] even though such a reaction has been invoked as an important step in catalytic nitroaromatic carbonylation.[6] We earlier demonstrated that halides accelerate the methylene to ketene conversion,[1b] and herein we show that they also dramatically promote nitrene carbonylation to form isocyanates. Furthermore, halides have also been found to accelerate the *formation* of nitrene ligands from nitrosobenzene.

**Scheme I**



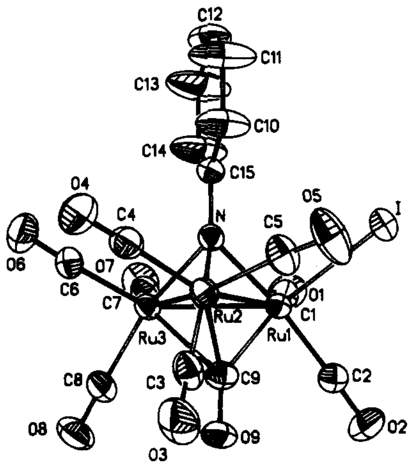


**Figure 1.** ORTEP drawing of the cluster anion in [Na(18-crown-6]-$[Ru_3(\mu_3\text{-}NPh)(CO)_9(I)]$ (**3c**): Ru(1)–Ru(2), 2.770 (1) Å; Ru(1)–Ru(3), 2.740 (1) Å; Ru(2)–Ru(3), 2.711 (1) Å; Ru(1)–I, 2.762 (1) Å; Ru(1)–N, 2.056 (5) Å; Ru(2)–N, 2.077 (5) Å; Ru(3)–N, 2.052 (6) Å; Ru(1)–C(9), 2.053 (7) Å; Ru(2)–C(9), 2.168 (6) Å; Ru(3)–C(9), 2.329 (7) Å; Na···I, 3.680 (5) Å; Na···O(6), 2.871 (7) Å; Ru(1)–Ru(2)–Ru(3), 60.0 (0)°; Ru(2)–Ru(3)–Ru(1), 61.1 (0)°; Ru(3)–Ru(1)–Ru(2), 58.9 (0)°; Ru(1)–C(9)–O(9), 139.1 (5)°; Ru(2)–C(9)–O(9), 132.8 (5)°; Ru(3)–C(9)–O(9), 126.8 (6)°.

The resistance of nitrene clusters to carbonylation is particularly well illustrated by the high yield recovery of $M_3(\mu_3\text{-}NPh)_2(CO)_9$ (M = Fe, Ru) following attempted carbonylation at 120 atm, 150

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(1) (a) Bassner, S. L.; Geoffroy, G. L. *Adv. Organomet. Chem.*, in press. (b) Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541. (c) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783. (d) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679. (e) Roper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, *219*, C5. (f) Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508.

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(3) Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. *Organometallics* **1984**, *6*, 1311.

(4) The $M_3(\mu_3\text{-}NPh)_2(CO)_9$ clusters were recovered in 69% (M = Ru) and 89% (M = Fe) yields, respectively.

(5) Basu, A.; Bhaduri, S.; Khwaja, H. *J. Organomet. Chem.* **1987**, *319*, C28.

(6) (a) Bhaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; Jones, P. G.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1984**, 1765. (b) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; Monica, G. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1286. (c) Alper, H.; Hashem, K. E. *J. Am. Chem. Soc.* **1981**, *103*, 6514. (d) Des Abbayes, H.; Alper, H. *J. Am. Chem. Soc.* **1977**, *99*, 98. (e) L'Eplattenier, F.; Matthys, P.; Calderazzo, F. *Inorg. Chem.* **1970**, *9*, 342. (f) Alper, H.; Paik, H. N. *Nouv. J. Chem.* **1978**, *2*, 245.

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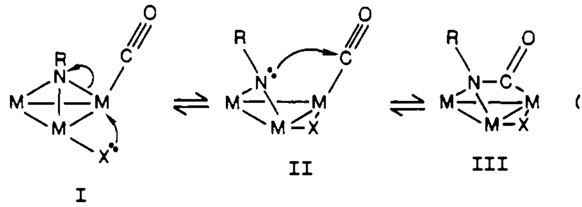
°C for 22 h in THF solution.[2,4] The mono(nitrene) cluster $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ (**1**) is a bit more reactive and has been reported to slowly (6.5 h) carbonylate to give PhN=C=O and $Ru(CO)_5$ under 170 atm of CO at 120 °C,[3] although we observed no reaction when lower CO pressures (4 atm, 120 °C, 22 h) were used. A recent report showed that these carbonylations are markedly solvent dependent and that both **1** and $Ru_3(\mu\text{-}NPh)_2(CO)_9$ form PhN=C=O and $Ru_3(CO)_{12}$ when heated at 140 °C under 20 atm of CO in $CH_3CN$ solutions.[5]

We find that addition of 1 equiv of halide to THF solutions of **1** dramatically promotes the carbonylation such that it proceeds rapidly and under far milder conditions (22 °C, 1 atm CO) than those noted above. The products of this reaction are PhN=C=O and the known halide-bridged clusters **2a–c**, Scheme I.[7–9] Infrared spectral changes showed that the halide promotion proceeds via the near instantaneous formation of the substituted cluster anions **3a–c**, and these in turn react with CO to give the observed products. The half-life data given in Scheme I show that chloride is clearly the superior promoter. The cluster anions **3a–c** can be isolated in high yield from the direct reaction of **1** with halides *in the absence of CO*,[10] and complex **3c**, as its $[Na(18\text{-crown-}6)]^+$ salt, was structurally characterized (Figure 1).[11] Similar structures are indicated for **3b** and **3c** on the basis of IR data. The iodide is terminally bonded to one Ru trans to the $\mu_3$-CO ligand. The only notable structural consequence of the halide substitution is a movement of the $\mu_3$-CO ligand closer to Ru(1) and away from Ru(2), but there is little change in Ru–Ru and Ru–N distances as compared to **1**.[12]

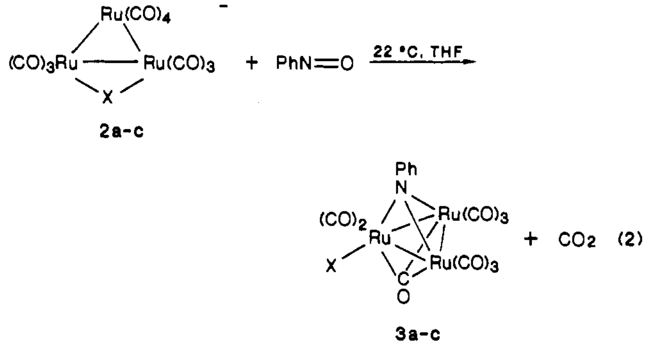
Although the reasons for the observed halide promotion are unknown, we suggest that halides facilitate the reaction by labilizing a Ru–N bond to form a *di*bridging nitrene that then undergoes nucleophilic attack on a coordinated CO (eq 1). This



I II III

may occur as a consequence of the increased cluster electron density caused by the presence of the halide, or as indicated in eq 1, it may be induced by the halide assuming a bridging position as it displaces a PhN→Ru bond. Note that there is no change in cluster electron count in the I → II → III conversion, and these three species may actually be in equilibrium. In support of this suggestion we note that $H_2Os_3(\mu\text{-}RNCO)(CO)_8(PMe_2Ph)$ (R = *t*-BuCH=N) has an isocyanate ligand bonded exactly as depicted in III, and furthermore this latter species was suggested to derive by *reversible* attack of a transient $\mu_2$-nitrene on a coordinated CO as in the II to III conversion.[13] Further support for the mechanistic suggestion of eq 1 comes from our observation that the $CN^-$ analogue of **3** does not readily carbonylate, which can be attributed to the fact that $CN^-$ is not a good bridging ligand and thus does not displace a PhN→Ru bond.

Halides also significantly *promote the formation* of nitrene ligands from nitrosobenzene. The unpromoted reaction between $Ru_3(CO)_{12}$ and PhNO proceeds slowly at 57 °C to give **1** in modest yield (46%, 2 h, THF).[14] However, in the presence of 1 equiv of halide, the reaction occurs *within minutes at 22 °C* to give the nitrene clusters **3a–c** in >95% yield. Halides are known to react with $Ru_3(CO)_{12}$ to rapidly form clusters **2a–c**,[8] and we find that these species in turn react with PhN=O to form **3a–c**, (eq 2).[15] Note that chloride is again the superior promoter.



2a-c

3a-c

| X | $t_{1/2}$ |
|---|---|
| Cl | <1 min |
| Br | <1 min |
| I | 15 min |

Halides have been demonstrated to be effective promoters for ligand-substitution reactions of $Ru_3(CO)_{12}$, and although the mechanism has not been firmly established, clusters **2a–c** may be intermediates in this process.[8a] Since the nitrosobenzene to nitrene conversion likely proceeds via deoxygenation of a *coordinated* PhN=O ligand, we suggest that the halide promotion of the PhN=O reaction is simply a consequence of the halide promotion of PhN=O for CO substitution. Note that the relative halide-promoting ability of the ligand substitution reaction[8a] is exactly the same as that observed for reaction 2: $Cl^- > Br^- > I^-$. Our observation that PhN=O reacts within seconds with $Ru_3(CO)_{11}(CH_3CN)$[16] at 22 °C to form $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ supports the proposal that halides promote the reaction by accelerating the opening of a coordination site for PhN=O to bind.[2c]

Cenini et al. have previously shown that halides are effective promoters for the $Ru_3(CO)_{12}$-catalyzed carbonylation of $PhNO_2$ in the presence of ROH to form alkyl *N*-phenylcarbamates and aniline (160–170 °C, 82 atm, 7 h, $Cl^-/Ru_3 = 7/1$).[6b] These workers observed that chloride was a much superior promoter than iodide, both for percent conversion and selectivity to the desired carbamate. Our findings are consistent with their observations since chloride is a substantially better promoter than iodide for both the PhNO to $\mu_3$-NPh conversion and the nitrene carbonylation. We thus suggest that the stoichiometric reactions observed in our study model the individual reaction steps that occur during the halide promoted catalysis.

**Acknowledgment.** We thank the Office of Basic Energy Sciences, Department of Energy, for support of this research, Johnson Matthey for a loan of Ru salts, and Wayne Gladfelter for stimulating discussions.

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(7) $PPN^+ = (PPh_3)_2N^+$.

(8) (a) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647. (b) Reference 8a only reports IR data for **2a**. Our spectra for **2b,c** are identical with that of **2a** and furthermore upon protonation they give the $Ru_3(CO)_{10}(H)(X)$ clusters previously characterized in ref 8c. (c) Kampe, C. E.; Boag, N. M.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390. (d) Although clusters **2a,b** are the initial products of this reaction, they each rapidly add CO to form $[PPN][Ru_3(CO)_{11}(X)]$ (**4a,b**). These latter clusters have not been previously reported, although their formation has been established (Gladfelter, W. L., private communication; see also ref 8a). IR for **4a**: $\nu_{CO}$ (THF) = 2099 (w), 2060 (w), 2026 (vs), 2010 (s), 1991 (sh), 1970 (sh), 1961 (m), 1828 (m), 1773 (w) $cm^{-1}$. IR for **4b**: $\nu_{CO}$ (THF) = 2097 (w), 2058 (m), 2026 (vs), 2010 (m), 1991 (m), 1975 (w), 1962 (m), 1828 (m) $cm^{-1}$.

(9) Phenyl isocyanate was identified by its characteristic IR band at 2260 $cm^{-1}$ and by its conversion to PhNHC{O}OMe upon addition of MeOH.

(10) IR (THF) for **3a**: $\nu_{CO}$ = 2070 (m), 2039 (vs), 2016 (s), 1991 (s), 1703 (w) $cm^{-1}$. IR (THF) for **3b**: $\nu_{CO}$ = 2027 (m), 2041 (vs), 2018 (s), 1989 (s), 1941 (sh), 1707 (w) $cm^{-1}$. IR (THF) for **3c**: $\nu_{CO}$ = 2070 (m), 2039 (vs), 2014 (s), 1991 (s), 1970 (m, sh), 1948 (m, sh), 1907 (w) $cm^{-1}$. Anal. Calcd for $C_{51}H_{35}O_9N_2P_2IRu_3$: C, 46.68; H, 2.67. Found: C, 46.14; H, 2.70.

(11) Crystallographic data for $[Na(18\text{-crown-}6)][Ru_3(\mu_3\text{-}NPh)(CO)_9I]$: $P\bar{1}$, $a = 10.369$ (3) Å, $b = 13.335$ (3) Å, $c = 13.738$ (3) Å, $\alpha = 79.54$ (2)°, $\beta = 77.03$ (2)°, $\gamma = 86.76$ (2)°, $V = 1820.1$ (6) Å$^3$, $Z = 2$, and $R_F = 4.55\%$, $R_{wF} = 5.20\%$ for 5663 reflections with $F_o \geqslant 4\sigma(F_o)$.

(12) Bhaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2339.

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(15) $CO_2$ was collected and identified by high-resolution mass spectrometry.

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**Supplementary Material Available:** Tables of atomic positional parameters and isotropic thermal parameters, bond lengths, bond angles, anisotropic temperature factors, and calculated hydrogen atom positions and isotropic thermal parameters (6 pages); a listing of observed and calculated structure factors for **3c** (42 pages). Ordering information is given on any current masthead page.

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## Lewis Acidity of Germanium(II) in a $\eta^5$-*closo*-Germacarborane: Synthesis and Structure of 1-(2,2′-Bipyridine)-2,3-bis(trimethylsilyl)-2,3-dicarba-1-germa-*closo*-heptaborane(6)

*Sir:*

Of all the group 14 metallacarboranes, the *closo*-stannacarboranes have been widely explored in terms of their reactivity and bonding.[1-4] This has partly been the result of more structural data being available for these compounds.[2] It has been established that the apical tin atom in the stannacarborane is in its +2 oxidation state and has an unshared pair of electrons.[1c,2b] Despite the presence of this lone pair, there seems to be no tendency to form donor–acceptor complexes with Lewis acids, such as $BF_3$. On the contrary, the tin atom acts as a Lewis acid site and forms red complexes with tetrahydrofuran, 2,2′-bipyridine, and 2,2′-bipyrimidine.[2,3] Our more recent synthetic and structural studies on the donor–acceptor complexes of the *closo*-stannacarboranes have raised several fundamental questions regarding the bonding of tin to the $C_2B_3$ face of carboranes.[3] To date, the specific factors influencing the orientation of the base bound to the apical tin and the slippage of this metal in the complex toward the three borons of the $C_2B_3$ pentagonal face have not been explained theoretically.

During the course of our investigation in this area, we sought to examine the reactivity of the analogous *closo*-1-Ge-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$ (I)[4] toward Lewis bases. In addition, we also intended to investigate further whether the same factors that determine slippage of the heteroatom and orientation of the base in the *closo*-stannacarboranes could be operative in the donor–acceptor complex with *closo*-germacarborane I, if this complex could be made at all. When a benzene solution of I and 2,2′-bipyridine at 0 °C was stirred in vacuo, a red solution formed immediately indicating that a complexation has occurred between the reactants. This reaction produced in high yield a previously unknown germacarborane complex, which was isolated as an air-sensitive, bright red, crystalline and sublimable solid.[5] The structure of the new germacarborane complex, II, could not be determined from its IR, NMR, and mass spectra[6] as these data are almost identical with those of its precursor I[4] and 2,2′-bipyridine. Furthermore, the structures of both *closo*-$Ge^{II}(RR'C_2B_9H_9)$ and *closo*-$Ge^{II}(RR'C_2B_4H_4)$ (R, R′ = $Me_3Si$, Me, or H) systems[1,4,7] have not been reported. Therefore, an X-ray analysis of the red, crystalline solid was undertaken that unambiguously confirmed the solid to be the novel germacarborane complex, 1-$Ge(C_{10}H_8N_2)$-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$ (II) as rep-

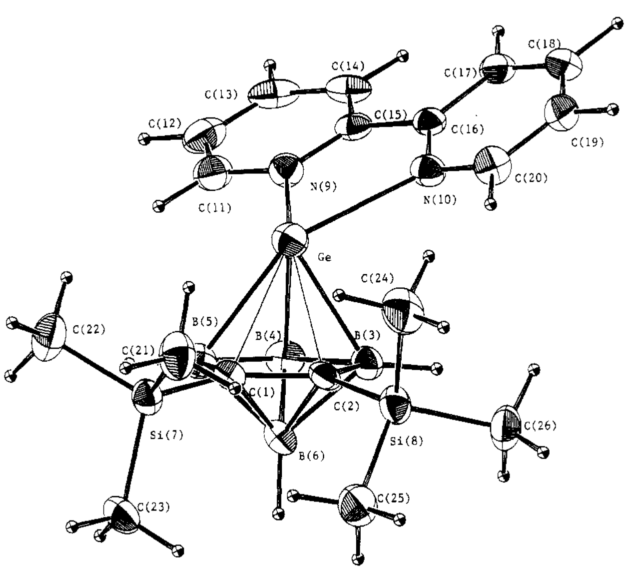

**Figure 1.** ORTEP view of II showing the atom numbering scheme and thermal ellipsoids at the 30% probability level. Pertinent bonding parameters: Ge–N(9), 2.321 (4) Å; Ge–N(10), 2.474 (4) Å; Ge–B(3), 2.255 (7) Å; Ge–B(4), 2.208 (7) Å; Ge–B(5), 2.371 (7) Å; Ge–C(1), 2.579 (5) Å; Ge–C(2), 2.510 (5) Å.

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(5) A benzene (10 mL) solution of $Ge^{II}(Me_3Si)_2C_2B_4H_4$ (I) (0.62 g, 2.13 mmol) was added to a benzene (10 mL) solution of freshly sublimed anhydrous 2,2′-bipyridine, $C_{10}H_8N_2$ (0.33 g, 2.13 mmol) in vacuo, and the resulting red solution was constantly stirred for 4 h at 0 °C. After removal of $C_6H_6$ at 0 °C via vacuum distillation for 4 h, the reaction flask was attached to a detachable high-vacuum U-trap, and the flask was heated gently to 50 °C to sublime the unreacted 2,2′-bipyridine (0.11 g; 0.71 mmol) out of the flask into the U-trap. With identical sublimation procedures and times as described for stannacarborane–2,2′-bipyridine complexes,[2b-d] at the sublimation temperature of 90 °C, compound II (0.46 g, 1.03 mmol; 73% yield based on $C_{10}H_8N_2$ consumed) was collected in one of the detachable U-traps held at 0 °C as a bright red crystalline solid. This solid (m.p. 88 °C) is highly soluble in both polar and nonpolar organic solvents.

(6) IR ($CDCl_3$ vs $CDCl_3$; $cm^{-1}$): 3050 (m, s), 2920 (s, br), 2860 (w) [$\nu$(C–H)]; 2580 (s) [$\nu$(B–H);] 1880 (m, br), 1620 (m, s), 1555 (s), 1450 (m), 1415 (w, br), 1250 (w, br), 1145 (m, s), 1085 (m, s), 1065 (w), 1035 (m, br), 990 (m), 960 (w), 930 (w), 820 (vs, br), 750 (vs, br), 670 (m), 650 (w), 610 (m), 390 (m). FT NMR Data: $^1H$ NMR ($C_6D_6$, relative to external $Me_4Si$) $\delta$ 8.63 [d, 2 H, bpy ring, $J(^1H–^1H)$ = 4.3 Hz], 8.56 [d, 2 H, bpy ring, $J(^1H–^1H)$ = 4.9 Hz], 7.27 [t, 2 H, bpy ring, $J(^1H–^1H)$ = 7.2 Hz], 6.76 [t, 2 H, bpy ring, $J(^1H–^1H)$ = 6.2 Hz], 3.92 [q (br), 3 H, basal $H_t$, $^1J(^1H–^{11}B)$ = 137 Hz], 1.64 [q (br), 1 H, apical $H_t$, $^1J(^1H–^{11}B)$ = 164 Hz], 0.38 [s, 18 H, $(CH_3)_3Si$]; $^{11}B$ NMR ($C_6D_6$, relative to external $BF_3{\cdot}OEt_2$) $\delta$ 23.14 [d, 3 B, basal BH, $^1J(^{11}B–^1H)$ = 137 Hz], –5.30 [d, 1 B, apical BH, $^1J(^{11}B–^1H)$ = 164 Hz]; $^{13}C$ NMR ($C_6D_6$, relative to external $Me_4Si$) $\delta$ 156.02 [s, 2,2′-C, bpy ring], 148.86 [d, bpy ring, $^1J(^{13}C–^1H)$ = 178 Hz], 136.20 [d, bpy ring, $^1J(^{13}C–^1H)$ = 162 Hz], 123.27 [d, bpy ring, $^1J(^{13}C–^1H)$ = 164 Hz], 120.77 [d, bpy ring, $^1J(^{13}C–^1H)$ = 167 Hz], 132.88 [s (br), cage carbon], 1.35 [q, $(CH_3)_3Si$, $^1J(^{13}C–^1H)$ = 119 Hz]; $^{29}Si$ NMR ($C_6D_6$, relative to external $Me_4Si$) $\delta$–1.30 [m, $Si(CH_3)_3$, $^2J(^{29}Si–^1H)$ = 6.4 Hz]; Mass Spectrum: The electron-impact (EI) mass spectrum of II does not exhibit the parent ion. However, both the bipyridine ion fragment with 100% relative intensity and the germacarborane precursor ion (I) were present in the EI mass spectrum.

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