imposed inversion point at the center of the molecule. An ORTEP view of **2** is shown in Figure 2. The Mn-Mn distance of 3.113 (2) Å is again nonbonding, and the terminal alkyl groups and phenolic groups are arranged so as to minimize steric interactions. The aryl rings are at an angle of 64.7° to the Mn_2O_2 plane, and presumably this is the optimum geometry to maximize the distance between the ortho *t*-Bu groups and the neophyl units. The Mn-C(7) distance is 2.104 (8) Å, which is shorter than that found in **1**, while the Mn-O distances are similar at 2.058 (5) and 2.073 (4) Å. The latter bond length is very similar to the Mn-O distances in $Mn_3(OCH\text{-}t\text{-}Bu_2)_6$[11] and $Li\{Mn(N(SiMe_3)_2)(OC\text{-}t\text{-}Bu_3)_2\}$.[12]

Both complexes are paramagnetic (**1**, $\mu_{eff} = 3.1\ \mu_B$ per Mn atom; **2**, $\mu_{eff} = 5.2\ \mu_B$ per Mn atom; room temperature, Evans method). The lower magnetic moment for **1** suggests some degree of cooperative magnetic behavior through the bridging phosphorus atoms. The ESR spectra at 125 K in frozen toluene solutions of both **1** and **2** consist of a single broad signal (**1**, $g = 1.98$; **2**, $g = 1.98$); no fine coupling to P is observed in the spectrum of **1**. All compounds gave satisfactory elemental analysis (C, H).

Mention should also be made of the absence of agostic[5] CH···Mn interactions in both **1** and **2**. Although H atoms were not located in the X-ray structures of either **1** or **2**, there are no close Mn-C distances that might indicate the presence of an agostic C-H···Mn interaction.[13] Also, IR spectra of both complexes do not contain any particularly low ν_{C-H} bands in the 2700-2800 cm^{-1} region indicative of agostic interactions.[5] In most other Mn alkyl complexes in which such interactions occur, they involve bridging rather than terminal alkyl units.[4,8,9] In **1** and **2** the phosphido and aryloxy ligands clearly prefer bridging positions, forcing the alkyl units to occupy terminal sites. These alkyl groups are then prevented from close interaction with the metal centers by the steric bulk of the bridging units. Further studies are in progress.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8517759), the Robert A. Welch Foundation (Grant No. F-816), and the Texas Advanced Technology Research Program for support. R.A.J. thanks the Alfred P. Sloan Foundation for a fellowship (1985-1989).

Supplementary Material Available: Tables of all bond lengths and angles, positional parameters, and thermal parameters and experimental details and crystal structure details for **1** and **2** (14 pages); tables of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(13) For **1** the closest nonbonded Mn-C distances (Å) are as follows: Mn-C(4), 3.20 (3); Mn-C(14), 3.62 (2); Mn-C(24), 3.69 (2). If hydrogen atoms are placed in idealized positions on these carbon atoms with C-H distances of 0.95 Å, then the closest Mn···H distance is 2.608 Å in Mn···H-C(4). For **2** the closest nonbonded Mn-C distances (Å) are as follows: Mn-C(22), 3.33 (1); Mn-C(24), 3.46 (1); Mn-C(62), 3.29 (9); Mn-C(64), 3.528 (9). If the hydrogen atoms are placed in idealized locations on these C atoms, the closest Mn···H distance is 2.360 Å in Mn···H-C(64).

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Sequential Synthesis of "FePt", "$FePt_2$", and "$FePt_3$" Complexes from the Reaction of $Fe(CO)_4(PR_2H)$ with $Pt(C_2H_4)_2(PCy_3)$. A Detailed Look at a Cluster Assembly Process

Sir:

While $Pt(C_2H_4)_n(PR_3)_{3-n}$ (n = 1-3) complexes are excellent precursors to a range of chemically interesting "Pt_x" and "M_yPt_x" cluster compounds,[1] very little is known with respect to the mechanisms by which these cluster compounds are assembled. Herein we report preliminary observations concerning the preferred reaction pathways in "FePt", "$FePt_2$", and "$FePt_3$" cluster synthesis from the reaction of $(OC)_4Fe(PR_2H)$ with $Pt(C_2H_4)_2(PCy_3)$—a system in which the serendipitous occurrence of appropriate relative rates and sequential isomerization processes provide considerable insight into and detail of a platinum cluster assembly process.

Oxidative addition of the P-H bond of $(OC)_4Fe(PR_2H)$[2], (**1**, R = Cy, Ph, *n*-Pr) to $Pt(C_2H_4)_2(PCy_3)$ in CD_2Cl_2 (ca. 20 °C) gives rise to a range of "FePt", "$FePt_2$", and "$FePt_3$" clusters depending on the initial Fe:Pt stoichiometry (Scheme I). Reaction of **1** with 1 molar equiv of $Pt(C_2H_4)_2(PCy_3)$ results in the rapid formation of $(OC)_4Fe(\mu\text{-}PR_2)PtH(PCy_3)$ (**2**), identified by ^1H and $^{31}P\{^1H\}$ NMR.[3] Complex **2**, which may be formulated as octahedral Fe (valency II) and square-planar Pt (valency II) linked by a phosphido bridge and a "bent" Fe-Pt bond, quickly rearranges (ca. 2-3 min, 20 °C) to the μ-hydrido complex **4**, presumably via the μ-carbonyl intermediate **3**[4] (not observed spectroscopically). Within 10-15 min the complex **4** equilibrates with the terminal (Fe-H) hydrido isomer **5**. (At equilibrium, 20 °C, in C_6D_6 the **2**:**4**:**5** ratio (μ-PPh_2) is ca. 1:3:6.) Particularly diagnostic of the terminal Fe-H structure in **5** is the rather small value of $^2J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ (ca. 15 Hz).[3,5] Complex **5** crystallizes from solution on addition of hexanes. When **5** is redissolved, the **5** ⇄ **4** ⇄ **2** equilibria are reestablished.

Reaction of **1** with 2 molar equiv of $Pt(C_2H_4)_2(PCy_3)$ in CD_2Cl_2 solution (an NMR study) gives rise to the same sequence of events documented above except that now the resonances due to **5** are of much lower intensity, suggestive of a "steady state concentration", and new signals assignable to the trinuclear "$FePt_2$" complex **6**, in which a CO bridges two platinums, are observed.[3] Complex **6** does *not* form prior to the formation of **5**. Isolated **5**, on redissolving in CD_2Cl_2, reacts rapidly with $Pt(C_2H_4)_2(PCy_3)$

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(3) Spectroscopic data for representative examples of "$FePt_x(\mu\text{-}PPh_2)$" complexes (Scheme I). **2**: ^1H NMR (hydrido region) $\delta(H)$ −5.3 ($J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 1770 Hz, $J_{^{31}\mathrm{P}-^{1}\mathrm{H}}$ = 24, 2 Hz); $^{31}P\{^1H\}$ NMR (relative to 85% H_3PO_4) $\delta(P_\mu)$ 96 ($J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 2140 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 311 Hz), $\delta(PCy_3)$ 41 ($J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 2920 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 311 Hz). **4**: IR (ν(CO) region, cm^{-1}) 2036 (m) (PtCO), 1976 (s), 1908 (m), 1895 (m); ^1H NMR (hydrido region) $\delta(H)$ −10.3 ($J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 525 Hz, $J_{^{31}\mathrm{P}-^{1}\mathrm{H}}$ = 35, 12 Hz); $^{31}P\{^1H\}$ NMR $\delta(P_\mu)$ 178 ($J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 1584 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 166 Hz), $\delta(PCy_3)$ 41 ($J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 2520 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 166 Hz). **5**: IR (ν(CO), cm^{-1}) 2037 (vs) (PtCO), 2000 (s), 1958 (m), 1940 (m); ^1H NMR (hydrido region) $\delta(H)$ −11.2 ($J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 16 Hz, $J_{^{31}\mathrm{P}-^{1}\mathrm{H}}$ = 59, 10 Hz); $^{31}P\{^1H\}$ NMR $\delta(P_\mu)$ 164 ($J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 2819 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 12 Hz), $\delta(PCy_3)$ 46 ($J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 3290 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 12 Hz). **6**: IR (ν(CO), cm^{-1}) 2014 (m), 1948 (s, br), 1753 (μ-CO); ^1H NMR (hydrido region) $\delta(H)$ −7.1 ($^1J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 580, $^2J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 75 Hz, $J_{^{31}\mathrm{P}-^{1}\mathrm{H}}$ = 10, 0, 0 Hz); $^{31}P\{^1H\}$ NMR $\delta(P_\mu)$ 282 ($^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 2032 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 131 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 18, 8 Hz), $\delta(PCy_3)$ (cis μ-PPh_2)) 71 ($^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 5480 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 320 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 18 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 18 Hz), $\delta(PCy_3$ (cis μ-H)) 53 ($^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 4360 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 230 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 8 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 18 Hz). **8**: IR (ν(CO), cm^{-1}) 2019 (m), 1950 (s), 1926 (s), 1755 (μ-CO); ^1H (hydrido region, −64 °C) $\delta(H)$ −7.3 ($^1J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 720 Hz, $^2J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 70 Hz, $J_{^{31}\mathrm{P}-^{1}\mathrm{H}}$ = 87, 20, 10 Hz); $^{31}P\{^1H\}$ NMR $\delta(P_\mu)$ 327 ($J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 2217, 1815 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 0, 0 Hz), $\delta(PCy_3$ (cis μ-H)) 42 $^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 3780 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 0 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 0 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 59 Hz), $\delta(PCy_3$ (cis μ-CO)) 55 ($^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 4032 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 70 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 0 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 59 Hz). **11**: IR (ν(CO), cm^{-1}, CH_2Cl_2) 1981 (s), 1931 (m), 1827 (m), 1780 (s); NMR $\delta(H)$ −18.4 ($J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 350 Hz, $^2J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ ≈ 50 Hz (br resonances, $\Delta\delta_{1/2}$ ≈ 50 Hz), $\delta(P_\mu)$ 470 ($^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 1726, 1134 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}_\mu}$ = 80 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}_\mu}$ = 297, 7, 0 Hz), $\delta(PCy_3$ (1) (cis to μ-PPh_2)) 57 ($^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 3948 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 268, 0 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 39, 7 Hz), $\delta(PCy_3$ (2) (cis to μ-PPh_2)) 74 ($^1J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 4904 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 340, 0 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 39, 0, 0 Hz), $\delta(PCy_3$ (3)) 23 ($^uJ_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 2885 Hz, $^2J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}$ = 0, 0 Hz, $J_{^{31}\mathrm{P}-^{31}\mathrm{P}}$ = 297, 0, 0 Hz). Anal. Calcd (found) for **11** (μ-PPh_2) ($C_{70}H_{110}FeO_4P_4Pt_3$): C, 47.19 (46.91); H, 6.18 (6.04).

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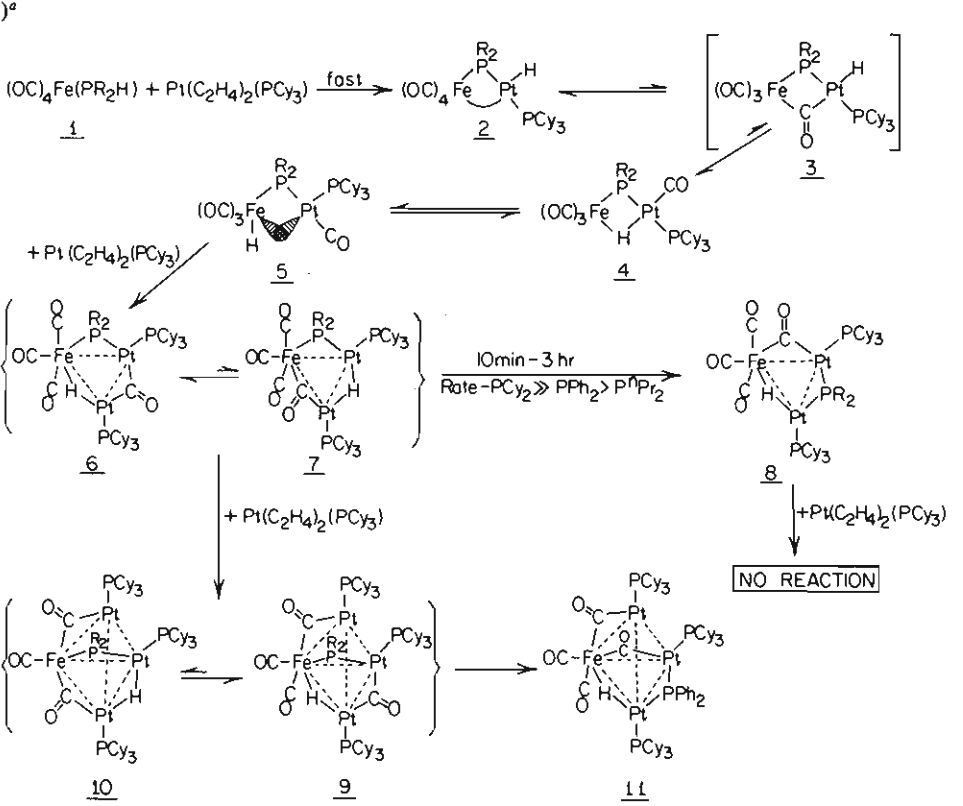
0020-1669/88/1327-4526$01.50/0

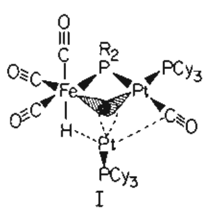
Scheme I. Sequential Reaction Pathways Observed in the Formation of "FePt$_x$" Complexes (x = 1–3) from the Reaction of $(OC)_4Fe(PR_2H)$ with $Pt(C_2H_4)_2(PCy_3)$[a]



[a] The "FePt$_2$" complex **8** is fluxional at room temperature with respect to μ-H ⇄ μ-CO site interchange (may be frozen out at -64 °C). The "FePt$_3$" complex **9** exhibits rapid, reversible migration of μ-H and μ-CO ligands such that the two "Pt(PCy$_3$) units" not bonded to μ-PR$_2$ are equivalent on the NMR time scale at 20 °C. The P^{t}Bu$_2$Ph analogue of **10** has been structurally characterized by single-crystal X-ray diffraction.[6] Typical structural data for these FePt$_x$ compounds are given in ref 3.

to give **6**. On standing, **6** equilibrates with a second minor (~10%) "FePt$_2$" complex, **7** (presumably an intramolecular μ-H ⇄ μ-CO interchange), and both **6** and **7** then transform into the "FePt$_2$" complex **8**, in which the μ-phosphido group has migrated from an "FePt" position to a "PtPt" position.[3] Complex **8** is the thermodynamically preferred "FePt$_2$" product and can be crystallized from the reaction. On redissolving, **8** does *not* equilibrate with **6** and **7**.

A critical step in the formation of **6** as the initial product of "Pt(PCy$_3$) addition" is the rearrangement of **4** to **5**, which results in an exposed and *sterically accessible*, "bent" Fe–Pt bond. Reaction of **5** with $Pt(C_2H_4)_2(PCy_3)$ probably occurs via an associative, sequential substitution of C_2H_4 and formation of an intermediate such as I, which clearly would lead to **6** (as opposed to **7** or **8**) being formed as the initial product. To date we have obtained no evidence for formation of "FePt$_2$" species from the direct reaction of $Pt(C_2H_4)_2(PCy_3)$ with **2** or **4**. Presumably the Fe–Pt bond in **2** is not sufficiently accessible for reaction to occur. The rate of formation of **8** from **6** and/or **7** is sensitive to the nature of the μ-PR$_2$ ligand being in the order μ-PCy$_2$ ≫ μ-PPh$_2$ > μ-P^{n}Pr$_2$. This order suggests that Fe–PR$_2$ bond dissociation is rate-determining in the intramolecular **6**/**7** to **8** rearrangement.



I

The kinetically formed "FePt$_2$" species **6** and/or **7** (R = Ph, *n*-Pr) have sufficient lifetimes to react further with $Pt(C_2H_4)_2(PCy_3)$ to give the "FePt$_3$" tetranuclear clusters **9** and **10**. (The structure of the P^{t}Bu$_2$Ph analogue of **10**, obtained from the reaction of $(OC)_4Fe(P^nPr_2H)$ with excess $Pt(C_2H_4)_2(P^tBu_2Ph)$, has been determined by single-crystal X-ray diffraction.[6]) On standing, **9**/**10** rearrange to give a second tetranuclear species, **11** (containing a "Pt(μ-PR$_2$)Pt" group), as the final product. The structure of **11** is based primarily on elemental analysis, ^1H and $^{31}P\{^1H\}$ NMR, and IR data,[3] which clearly indicate the presence of three "Pt(PCy$_3$)" units, a "Fe(μ-H)Pt" group, a "Pt(μ-PR$_2$)Pt" unit, and two bridging carbonyl ligands.[7] Surprisingly, the trimer **8**, which stereochemically may be perceived as an obvious precursor for the formation of **11**, does *not* react with $Pt(C_2H_4)_2(PCy_3)$. In view of the stereochemical requirements observed above for the addition of a second "Pt(PCy$_3$) fragment" to dinuclear "FePt" complexes to form an "FePt$_2$" species, one may hypothesize that formation of an "FePt$_3$" complex requires an analogous reorganization of the "FePt$_2$" complexes to give an intermediate containing an exposed and sterically accessible metal–metal bond. One such *possibility* which provides a rationale for the observed results involves an intramolecular meridional to facial reorganization of the "(OC)$_3$Fe" unit and the formation of a "puckered" species such as I or II (formed from **7**). (The valence bond representation II, which contains an octahedral Fe and two planar Pt units, involves a bent two-electron–three-center FePt$_2$ bond and a two-electron–three-center FeHPt bond with the remaining metal–ligand bonds being two-electron–two-center bonds. The intermediate II is structurally similar to intermediate I, which could be derived from the *mer–fac* reorganization of **6** or from the reaction of **5** with $Pt(C_2H_4)_2(PCy_3)$.) Addition of a "Pt(PCy$_3$) unit" to the exposed metal–metal bond of II, followed by a *fac–mer* reorganization at Fe, leads to **9** as the initially formed "FePt$_3$" species. In contrast the analogous puckered "FePt$_2$" species III, obtained by a *mer* to *fac* reorganization of the "(OC)$_3$Fe" moiety of **8**, would be considerably less reactive toward the addition of another "Pt(PCy$_3$) unit" owing to steric hindrance by the μ-PR$_2$

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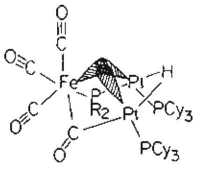
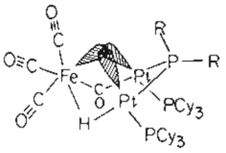
(6) Powell, J.; Gregg, M. R.; Sawyer, J. F. Unpublished result.

(7) Crystals of **11** suitable for X-ray diffraction studies have yet to be obtained. It may be that the actual structure of **11** is a very *closely related* isomeric form of **11** as drawn.



II



III

group, which in III is on the same side of the $FePt_2$ ring as the "$FePt_2$ bond" (in contrast to the case for II). The strength of the hypothesis that the addition of further "$Pt(PCy_3)$" units requires the prior reorganization of "FePt" and "$FePt_2$" systems to conformations containing an exposed, sterically accessible $FePt_x$ bond is its ability to account for the observed reaction sequences shown in Scheme I. The above correlations are the first definitive mechanistic results with respect to delineating a platinum cluster assembly process.

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Articles

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Further Synthetic Studies of $B_9H_{11}NH$. The Crystal Structure of $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,2\text{-}CoNHB_9H_9$

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Received June 3, 1988

The synthesis of $B_9H_{11}NH$ has been improved. The first closo metallaazaborane, $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,2\text{-}CoNHB_9H_9$ (space group $P2_1/n$, a = 15.035 (28) Å, b = 12.042 (25) Å, c = 14.017 (27) Å, β = 110.54 (2)°, Z = 8), has been prepared and characterized, including a single-crystal X-ray structure determination. Two-dimensional ^{11}B–^{11}B NMR and ^{14}N NMR studies of certain azaborane derivatives have been completed.

Introduction

Since the discovery of nitrogen-containing boranes in 1967,[1] the development of the chemistry of azaboranes has been slow. While several azaboranes have been synthesized by various methods,[1-3] the most useful synthetic procedure at present is reaction of decaborane(14) with sodium nitrite.[3-6] Recently, we described our initial studies in this area, which included the synthesis of the first closo azaborane, B_9H_9NH.[6] We report here some NMR studies of these azaboranes, as well as the synthesis and structure of the first closo metallaazaborane.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.8 MHz with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3{\cdot}OEt_2$ (positive values downfield). Proton (^1H) NMR spectra were obtained on the same instrument and were referenced by using the proton solvent impurities. Nitrogen (^{14}N) NMR spectra were obtained at 26.1 MHz on the same instrument and were externally referenced to neat nitromethane (δ = 0 ppm; positive values downfield). Two-dimensional NMR spectra (^{11}B–^{11}B) were obtained on the same instrument. Broad-band ^1H decoupling (3W) was continuously used. High-resolution mass spectra data were recorded on a Kratos MS-80 instrument. Infrared data were obtained by using KBr disks with a Perkin-Elmer 283 spectrometer. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories.

Materials. All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran (THF), benzene, and pentane were distilled from sodium benzophenone ketyl. Acetonitrile and methylene chloride were dried over calcium hydride and distilled before use. Anhydrous cobalt chloride was prepared from the hexahydrate according to the method of King.[7] All other commercially available reagents were used as received. Decaborane(14) was sublimed before use.

$B_9H_{11}NH$. After $NaNO_2$ (3.70 g, 54.7 mmol) was heated in a three-neck, 500-mL round-bottom flask under vacuum for 2 h at 100 °C to remove any water present, 100 mL of THF was added and the mixture cooled by using a room-temperature water bath. A solution of $B_{10}H_{14}$ (5.05 g, 41.3 mmol) in 100 mL of THF was added dropwise over 6 h, stirred for an additional 3 h, and then filtered to remove unreacted $NaNO_2$ (0.84 g; identity confirmed by infrared spectroscopy). Analysis of the homogeneous filtrate by ^{11}B NMR spectroscopy indicated the presence of $B_9H_{12}NH^-$ and $B_{10}H_{15}^-$ in a ratio of 80:20. The THF was removed under vacuum and the resulting yellow powder dissolved in 300 mL of CH_3CN (gas evolution was observed). Iodine (6.3 g, 24.8 mmol) was dissolved in 250 mL of CH_3CN and added dropwise to the above solution over 4 h. A jacketed tube was attached to the flask and filled with an ice/water mix, and CH_3CN was removed under vacuum at 60 °C, giving a yellow powder. The ice/water mix was replaced by a dry ice/acetone slush bath, and pure $B_9H_{11}NH$ (2.91 g, 57% based on $B_{10}H_{14}$) sublimed over several hours. The ^{11}B NMR spectrum of this product was identical with that previously reported.[6] The high-resolution mass spectrum of this compound contained a parent ion peak at m/e 125.1807 (calcd for $^{11}B_9{}^1H_{12}{}^{14}N$ m/e 125.1806).

$(C_5H_5)Co(B_9H_9NH)$. Into an "H-reactor" was placed 2.0 g of NaH (approximately 42 mmol) as an oil dispersion. An H-reactor consists of two flasks joined by a glass frit, forming a vessel in the shape of an H. The frit is in the bridge of the "H", and both sides of the H-reactor have two ground-glass joints for introduction of reagents and an inert atmosphere. Under an atmosphere of nitrogen, the NaH was washed with several portions of pentane to remove the oil and then 30 mL of THF was added. Freshly cracked cyclopentadiene (1.0 g, 15.1 mmol) and $B_9H_{11}NH$ (1.0 g, 8.1 mmol) were added to the THF slurry, and the mixture was stirred for 1 h. Gas evolution was observed. The reaction mixture was filtered through the glass frit of the H-reactor and the resulting

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