biochemical counterpart of the regiospecificity of Eschenmoser's biomimetic C-methylation of dipyrrocorphins[8] which is controlled by the presence (or absence) of a coordinating metal. The recent isolation[9] of a cobalt-free intermediate, precorrin 6x, in which six methylations, an oxidation, and ring contraction have already occurred, from genetically engineered *Pseudomonas denitrificans*, and its bioconversion to hydrogenobyrinic acid **5a** (Co^{++} = H) strongly suggest that, in this aerobic organism, the B_{12} pathway is different from that of *P. shermanii* in that cobalt insertion is postponed in *P. denitrificans*, whereas hydrogenobyrinic acid **5a** (Co^{++} = H) is *not* a precursor of cobyrinic acid in *P. shermanii*.[10]

Further implications of these new findings are under investigation.[11]

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(8) Leumann, C.; Hilpert, K.; Schreiber, J.; Eschenmoser, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1404.

(9) (a) Thibaut, D.; Debussche, L.; Blanche, F. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 8795. (b) Thibaut, D.; Blanche, F.; Debussche, L.; Leeper, F. J.; Battersby, A. R. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 8800.

(10) Müller, G.; Podschun, T. E. *Angew. Chem.* **1985**, *97*, 63.

(11) Supported by grants from the NIH (to A.I.S.) and DFG (to G.M.).

Simultaneous Conversion of Pd–PPh_3 and B–H to B–PPh_2 under Exceedingly Mild Conditions. Crystal and Molecular Structure of $PdPPh_3Cl\{7\text{-}SMe\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_{10}\}$

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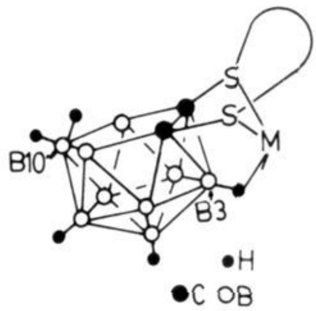

Figure 1. Schematic representation of the B(3)–H–M interaction in *exo*-dithiocarbaborane compounds.

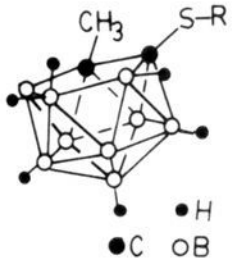

Figure 2. Molecular representation of the series of anions $\{7\text{-}SR\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}\}$. Only relevant hydrogen atoms have been indicated.

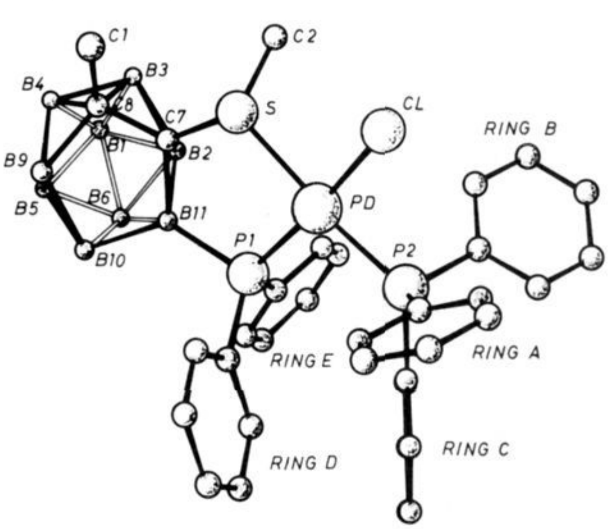

Figure 3. Molecular structure of **3** (hydrogens omitted). Selected intramolecular distances (Å) angles (deg) are as follows: Pd–S 2.355 (1); Pd–P1, 2.266 (1); Pd–P2, 2.309 (1); Pd–Cl, 2.342 (1); P1–B11, 1.922 (5); C7–B11, 1.609 (7); C7–S, 1.803 (5); C7–C8, 1.573 (6); C8–B9, 1.651 (8); B9–B10, 1.853 (9); B10–B11, 1.783 (7); S–Pd–P1, 90.2 (0); P2–Pd–P1, 100.2 (0); Cl–Pd–P2, 85.0 (0); Cl–Pd–S, 84.4.

We report an unexpected reaction that has implications for organoborane/organocarbaborane chemistry, the consequences of which are currently being tested in our program in asymmetric catalysis. Our research on the coordination chemistry of macrocyclic derivatives of *exo*-dithiocarbaborane compounds[1–6] has shown the singularity of their chemistry: great reactivity resemblance with diphosphines and, remarkably, the ability to form the unprecedented B(3)–H–M bond (Figure 1) which is modulated by the length of the exo-cluster macrocyclic chain.[7] This observation led us to the synthesis of $[N(CH_3)_4][RhCl\{7,8\text{-}\mu\text{-}S\text{-}(CH_2CH_2)S\text{-}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_9\}]$,[8] the first reported example of a B(3)–M interaction. All metal complex derivatives of these *exo*-dithiocarbaborane ligands contain the five-membered ring $\overline{S_a{-}M{-}S_b{-}C_c{-}C_c}$ as a common feature. The geometrical requirements of this ring together with the sulfur–carbaborane interaction have to be, in great part, responsible for this novel chemistry. To get further insight in the sulfur–carbaborane mutual influence, we have studied the reactivity of *exo*-monothiocarbaborane compounds. Even though there is only one sulfur atom on the molecule, the system evolves to the formation of a new five-membered $\overline{S_a{-}M{-}P{-}B{-}C_c}$ ring.

The reaction of $[NMe_4]\{7\text{-}SMe\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}\}$ (**1**) (Figure 2) with $Pd(PPh_3)_2Cl_2$ (**2**) in degassed ethanol resulted in the formation of a yellow solid (**3**). Absorptions (ppm) at −4.5, −6.3, −8.9, −12.9, −14.1, −20.15, −23.1, −27.2, and −33.8, all of intensity 1, are observed in the ^{11}B NMR {H} spectrum. The absorption at −8.9 was split in two equal absorptions in the ^{11}B NMR and ^{11}B NMR {H} spectra (J = 200 Hz), suggesting B–P bond formation. It was previously known that thermolysis of the *closo*-3,3-(triarylphosphine)$_2$-3,1,2-$NiC_2B_9H_{11}$ series in benzene solution leads to the formation of the corresponding *closo*-3,8-(triarylphosphine)$_2$-3-H-3,1,2-$NiC_2B_9H_{11}$.[9] Similar ligand-interchange

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(1) Teixidor, F.; Rudolph, R. W. *J. Organomet. Chem.* **1983**, *241*, 301.

(2) Viñas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Organometallics* **1984**, *3*, 503.

(3) Viñas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 4369.

(4) Teixidor, F.; Romerosa, A. M.; Escriche, Ll.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sanchez, E. *Inorg. Chim. Acta* **1990**, *176*, 71.

(5) Teixidor, F.; Romerosa, A. M.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sánchez, E. *J. Chem. Soc., Dalton Trans.* **1990**, 525.

(6) Teixidor, F.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *Inorg. Chem.* **1990**, *29*, 149.

(7) Teixidor, F.; Casabó, J.; Viñas, C.; Sánchez, E.; Escriche, Ll.; Kivekäs, R. *Inorg. Chem.* **1991**, *30*, 3053.

(8) Teixidor, F.; Romerosa, A.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1991**, 192.

0002-7863/91/1513-9895$02.50/0

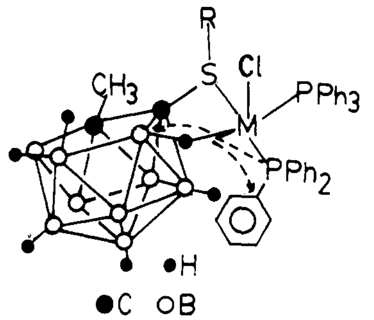

Figure 4. Proposed intermediate in the synthesis of 3. The dashed lines indicate possible pathways for the P–C cleavage by the activated hydrogen atom and subsequent B–P formation.

reactions are also found in (phosphine)rhodacarborane,[10] (phosphine)ruthenacarborane,[11] and (phosphine)platinacarborane.[12] In these examples a metal-bonded PPh_3 unit migrates and forms a $B-P(PPh_3)$ bond with the formally B(10) in the free ligand. Since the ^{11}B NMR spectrum of 3 presents a doublet of doublets at −27.2 ppm attributable to a $B(10)-H_2$ fragment, it may be concluded that B(10) remains unaltered. The absorption at −23 ppm (attributed to B(4) or B(2)) is observed at a considerably higher field than in the free ligand (at least 5 ppm), thus suggesting that either B(4) or B(2) is experiencing a strong effect, probably an "antipodal effect",[13] which is equivalent to considering that the antipodal boron atom (i.e., B(11) if B(4) is taken) has been significantly altered, e.g., by formation of a B–P bond. This favors a P disposition on B(11) or B(9) which is also in agreement with the ^{11}B NMR absorption (B–P) at −8.9 ppm. The subsequent X-ray analysis of 3[14] clearly establishes the position of the B–P moiety at the B(11) position, but surprisingly, the phosphine is a PPh_2 fragment and not the PPh_3 unit (Figure 3). The Pd is square planar surrounded by $P(PPh_3)$, $P(PPh_2\text{-carbaborane})$, S, and Cl, so that the compound has the formula $PdPPh_3Cl\{7\text{-}SMe\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9\}$ (3) which includes the new ligand $\{7\text{-}SMe\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9\}$. Similarly to the *exo*-dithiocarbaborane metal complexes, a five-membered ring is also formed, $\overline{S_a\text{–}M\text{–}P\text{–}B\text{–}C_c}$, which now includes one sulfur and one phosphorus instead of two sulfur atoms. While examples of this kind of bond cleavage and P–B bond formation have already been published, never previously had they been observed in the same compound and under such exceedingly mild conditions. Examples of relatively mild phase-transfer-catalyzed P–C bond cleavage in platinum[15] and iridium[16] have recently been reported, but in all these cases, basic conditions were required. The ligand modification (B–P formation and P–C cleavage) is not restricted to the particular case presented here, but to every R (Figure 2) tested so far (R = CH_3, CH_2CH_3, $(CH_2)_3$, $CH_2CH_2C(CH_3)_3$, CH_2Ph). We believe that the system evolves from an initial agostic B(11)–H···M (Figure 4) interaction which enhances the strong hydrido character of the hydrogen. This in turn produces the P–C bond cleavage favored by the formation of the five-membered ring to form a phosphido group[17–23] which couples with the carbaborane cage.

Supplementary Material Available: Tables of bond angles, positional parameters for non-hydrogen atoms, anisotropic thermal coefficients for non-hydrogen atoms, and bond lengths for 3 (10 pages); listing of observed and calculated structure factors for 3 (38 pages). Ordering information is given on any current masthead page.

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(9) King, R. E., III; Miller, S. B.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3548.

(10) Baker, R. T.; Delaney, M. S.; King, R. E., III; Knobler, C. B.; Long, J. A.; Marder, T. B.; Paxson, T. E.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2965.

(11) Jung, C. W.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 3024.

(12) Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J.; Wolsey, W. C. *J. Chem. Soc., Chem. Commun.* **1980**, 627.

(13) Teixidor, F.; Viñas, C.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 3339.

(14) Crystal data: space group $P\bar{1}$; $Z = 2$; $a = 10.181$ (3) Å, $b = 13.312$ (4) Å, $c = 14.433$ (3) Å; $\alpha = 95.07$ (2)°, $\beta = 92.24$ (2)°, $\gamma = 107.30$ (2)°; $V = 1855.9$ (9) Å^3. Data collection parameters: maximum 2θ range 54°, Mo Kα radiation, $\lambda = 0.710\,69$ Å. The structure was solved by the MULTAN program and refined by the SHELX-86 program to $R = 0.0587$ for 8060 absorption-corrected reflections having $F_o^2 > 3.0\sigma(F_o^2)$. A full report of the structure determination will be given later.

(15) Lin, I. J. B.; Lai, J. S.; Liu, C. W. *Organometallics* **1990**, *9*, 530.

(16) Grushin, V. V.; Vymenits, A. B.; Yanovsky, A. I.; Struchkov, Y. T.; Vol'pin, M. E. *Organometallics* **1991**, *10*, 48.

(17) For a selection of recent references to phosphido bridge reactivity, see: (a) Rosenberg, S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1184. (b) Nucciarone, D.; Maclaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 106.

(18) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47.

(19) (a) Yu, Y. F.; Chan, C. N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *J. Am. Chem. Soc.* **1984**, *106*, 3704. (b) Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5934.

(20) Werner, H.; Zolk, R. *Chem. Ber.* **1987**, *120*, 1003.

(21) Horton, A. D.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1985**, 247.

(22) Yu, Y. F.; Cha, C. N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *J. Am. Chem. Soc.* **1984**, *106*, 3104.

(23) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 814.

Theoretical Calculations on Nb and Ta Trihydride Complexes. Relations with the Problem of Quantum Mechanical Exchange Coupling

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The anomalous NMR properties of some transition metal trihydrides, namely $(C_5Me_5)RuH_3PR_3$ (**1**),[1] $[(C_5H_5)IrH_3PR_3]^2$ (**2**), and $(C_5H_3R'R'')_2NbH_3$ ($R' = R'' = H$ (**3a**); $R' = SiMe_3$, $R'' = H$ (**3b**); $R' = R'' = SiMe_3$ (**3c**))[3] have recently attracted considerable interest. Thus these compounds which adopt a similar geometry implying a coplanar configuration for the hydrides show NMR spectra characterized by AB_2 type patterns for the hydrides but with large temperature-dependent J_{A-B} coupling constants. The largest observed value is so far 1565 Hz in an iridium complex, well outside the normal range of H–H coupling constants.[2] The physical phenomenon has been clearly identified by two groups[4,5] as due to quantum mechanical exchange of hydrides. However, the chemical origin of these couplings remains unclear. One striking problem was the presence of the anomalous couplings in niobium derivatives of type **3** whereas they were not found in the related isoelectronic and isostructural tantalum compounds $[(C_5H_3R'R'')_2TaH_3$: $R' = R'' = H$ (**4a**); $R' = SiMe_3$, $R'' = H$ (**4b**); $R' = R'' = SiMe_3$ (**4c**)]. The variation of the NMR spectra

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(1) (a) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C. R. Hebd. Acad. Sci. Ser. 2* **1987**, *305*, 1523. (b) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.

(2) (a) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303. (b) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909.

(3) Antinolo, A.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jalon, F.; Morris, R. H.; Otero, A.; Schweitzer, C. T. *J. Chem. Soc., Chem. Commun.* **1988**, 1210.

(4) Jones, D.; Labinger, J. A.; Weitekamp, J. *J. Am. Chem. Soc.* **1989**, *111*, 3087.

(5) (a) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. *J. Am. Chem. Soc.* **1989**, *111*, 3088. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Neshyba, S. P.; Duchamp, J. C.; Szczyrba, J. *J. Am. Chem. Soc.* **1990**, *112*, 920.

0002-7863/91/1513-9896$02.50/0