Compound **7** is also quantitatively obtained when the hydride **1** is reacted with the side-on and end-on bonded complex **5**. The formation of **7** could be explained by a 1:1 addition of **1** on phosphorus P_B of **5**. This is corroborated by the following experiment: reaction of the hydride **4** $[Et_4N][HW(CO)_5]$ with **5** leads to the formation of another anionic diphosphane complex, **8** (mp 116 °C dec; yield 62%). ^{31}P and ^{1}H NMR spectra clearly show that the phosphorus atom P_B is bonded to a proton and to $W(CO)_5$: $^{31}P\{^1H\}$ NMR (CD_3CN) $\delta(P_A)$ 74.85 (d), $\delta(P_B)$ −6.64 (d), $J_{P_AP_B} = 220$ Hz ($J_{^{31}P-^{183}W} = 208.5$ Hz); ^{31}P NMR (CD_3CN) $\delta(P_A)$ 74.85 (d), $\delta(P_B)$ −4.49, −8.42 (dd, $^1J_{PH} = 324.4$ Hz, $J_{P_AP_B} = 220$ Hz, $J_{^{31}P-^{183}W}$) = 208.5 Hz); ^1H NMR (CD_3CN; except $N(C_2H_5)_4$ resonances) δ 6.75 (dd, $^1J_{PH} = 324.4$ Hz, $^2J_{PH} = 7.92$ hZ, $J_{^1H-^{183}W} = 22.7$ Hz), 7.35 and 7.66 (m, Ph); IR ν(CO) (CH_2Cl_2) 2072 (w), 2040 (m), 2022 (m), 1940 (s), 1915 (sh) cm^{-1}.

These results summarized in Scheme I provide a new field of investigations for the synthesis of other unknown mono- or polymetallic complexes of phosphorus derivatives and demonstrated the potential utility of the $HFe(CO)_4$ anion. The extension of this work to other anionic hydridocarbonylmetalates and a variety of group 15 chlorides is in progress.

Acknowledgment. Thanks are due to Dr. Pierrot (Faculté des Sciences de Saint-Jérome, Marseille, France) for the X-ray crystallographic determination.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters (3 pages); a table of structure factors (8 pages). Ordering information is given on any current masthead page.

X-ray Crystal Structure of the Boron-Stabilized Carbanion $[Li(12\text{-crown-}4)_2][CH_2C_6H_2(3,5\text{-}Me_2)(4\text{-}B\{2,4,6\text{-}Me_3C_6H_2\}_2)]\cdot Et_2O$: Evidence for "Boron Ylide" Character

Ruth A. Bartlett and Philip P. Power*

Department of Chemistry, University of California
Davis, California 95616

Received April 23, 1986

Summary: The first X-ray crystal structure of a boron-stabilized carbanion is described; the title compound, made by treatment of $B(2,4,6\text{-}Me_3C_6H_2)_3$ with *n*-BuLi in THF, was crystallized as a crown ether salt. The major structural features of the carbanion suggest that stabilization is achieved by extensive delocalization rather than steric effects. A significantly shortened B–C bond, 1.522 (10) Å, was also observed, suggesting substantial "boron ylide" character.

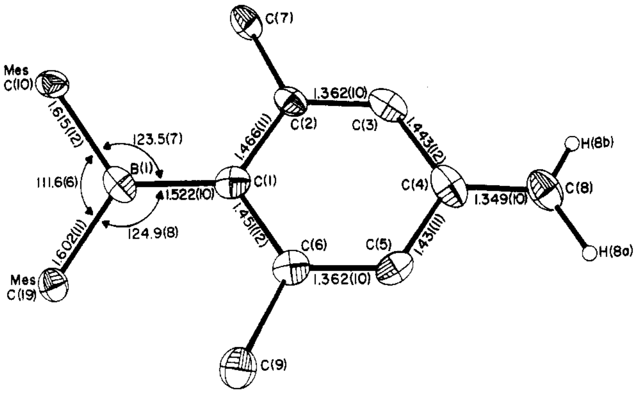


Figure 1. Important bond distances and angles for the anion of 1.

Recently we showed that 12-crown-4 could be used to crystallize the lithium salts of the free carbanions $[CPh_3]^-$ and $[CHPh_2]^-$.[1] At the same time we reported that we could isolate a yellow microcrystalline substance which probably contained the next member of the series $[CH_2Ph]^-$ as a free ion. Unfortunately we were unable to grow crystals of this material, suitable for X-ray crystallography, due to its high reactivity toward ether solvents. In our search for ways of reducing the powerful nucleophilic character of the benzyl carbanion $[CH_2Ph]^-$, we were drawn to the report[2] of Ramsey and Isabelle, who showed (NMR) that by treating $BMes_3$ (Mes = mesityl, $2,4,6\text{-}Me_3C_6H_2$) with *n*-BuLi, they could obtain the anion $[CH_2C_6H_2(3,5\text{-}Me_2)(4\text{-}B\{2,4,6\text{-}Me_3C_6H_2\}_2)]^-$ (**1**) in THF or Me_2SO solution. This anion arose by the deprotonation of one of the para methyl groups of $BMes_3$ and has a benzyl-like environment at the deprotonated carbon. As part of our interest in carbanion structures, we decided to investigate the structural effects of a boron-centered stabilizing group on a carbanion.

The anion **1** was crystallized as its $[Li(12\text{-crown-}4)_2]^+$ salt by the addition of 2 equiv of 12-crown-4[3] to a solution of a lithium salt of **1**. The resultant red crystals were isolated in 35% yield. Important bond distances and angles of **1** arising from the X-ray data are illustrated in Figure 1. Crystal data at 140 K: $C_{47}H_{74}O_9BLi$, *M*, 800.86, monoclinic, space group $P2_1/n$, $a = 15.187$ (7) Å, $b = 11.791$ (4) Å, $c = 26.031$ (11) Å, $\beta = 105.12$ (3)°, $U = 4500$ (3) Å^3, $D_{calcd} = 1.18$ g cm^{-3} for $Z = 4$, $\lambda = 0.71069$ Å, $\mu = 0.76$ cm^{-1}, 2580 data with $I > 4\sigma(I)$, $R = 0.069\%$. The structure confirms the removal of one of the para methyl protons by *n*-BuLi. The compound is clearly a boron-stabilized carbanion, and **1** is the first X-ray structural proof of this type of stabilization. The growing interest in this class of compound originated with the work of Rathke and Kow[4] although boron-stabilized carbanions had been proposed as intermediates much earlier.[5] The spectroscopically characterized boron-stabilized carbanions for the most part involve deprotonation of an α-carbon atom, for example, in *B*-methyl-9-boradicyclononane,[4] $4\text{-}Et_2B$-fluorene,[6] or the versatile reagent Mes_2BMe developed by Wilson, Pelter, and co-workers.[7,8] The latter have shown that anions produced by the deprotonation of organoboranes undergo many of the same reactions as ylides; hence their designation as Boron–Wittig reagents.

The most interesting aspect of **1** concerns the core B-

---

(1) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174.

(2) Ramsey, B. G.; Isabelle, L. M. *J. Org. Chem.* **1981**, *46*, 179.

(3) 12-Crown-4 has been used by us to coordinate Li^+ in several other systems: Hope, H.; Olmstead, M. M.; Power, P. P.; Xu, *J. Am. Chem. Soc.* **1983**, *106*, 819. Power, P. P.; Xu, X. *J. Chem. Soc., Chem. Commun.* **1984**, 358. Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, 4337. Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 4235.

(4) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854; **1973**, *95*, 2715.

(5) Zweifel, G.; Arzoumanian, H. *Tetrahedron Lett.* **1966**, 2535. Matteson, D. S. *Synthesis* **1975**, 147. Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834.

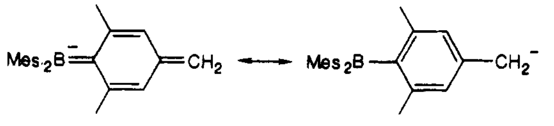
(6) Paetzold, P.; Boeke, B. *Chem. Ber.* **1976**, *109*, 1011.

(7) Wilson, J. W. *J. Organomet. Chem.* **1980**, *186*, 297. Brown, N. M. D.; Davidson, F.; Wilson, J. W. *J. Organomet. Chem.* **1980**, *185*, 277.

(8) Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 621. Pelter, A.; Briaden, G.; Roesser, R. *Tetrahedron Lett.* **1985**, *26*, 5097 (part 8 of a series, see references therein).

0276-7333/86/2305-1916$01.50/0 © 1986 American Chemical Society

(1)C(1)C(10)C(19) in which the B(1)–C(1) length 1.522 (10) Å averages 0.087 Å (5.4%) shorter than either B(1)–C(10), 1.615 (12) Å, or B(1)–C(19), 1.602 (11) Å. In the C(1) ring, C(2)–C(3) and C(3)–C(6) are both 1.362 (10) Å and are significantly shorter than the other ring C–C distances and the C–C lengths in the remaining mesityl rings. The exocyclic, para C(4)–C(8) bond 1.349 (10) Å is also much shorter than the corresponding distance in the ether solvated benzyllithium complex $[(Li(Et_2O)CH_2C_6H_5)_\infty]$, 1.432 (1) Å.[9] These distances suggest a significant contribution to the structure of 1 by canonical form **1a**. Since the carbanion center in **1b** has little or no protection from the 3,5 Me groups, it appears that the stability of 1 is due mainly to delocalization rather than steric effects.



1a **1b**

The B(1)–C(1) bond length 1.522 (10) Å also merits further comment. It is significantly shorter than those seen in trialkyl- or triarylboranes.[10] A number of recent publications have referred to boron carbon multiple bonds as part of various cyclic systems.[11,12] The only X-ray structural determination involves the 1,3-dihydro-1,3-diborete $Me_2N\overline{B\text{–}C(t\text{-}Bu)\text{–}B(NMe_2)\text{–}C}(t\text{-}Bu)$. This also features shortened B–C bond lengths of 1.501 (5) and 1.503 (5) Å.[13] These are consistent with calculations which consider the four-membered $-\overline{BCBC}-$ ring as an aromatic 2π-electron system isoelectronic with the [cyclobutadiene]$^{2+}$ cation.[14] It appears then that the B(1)–C(1) moiety in 1 is the first structurally characterized example of an exocyclic B–C multiple bond. Further evidence for the formulation of B(1)–C(1) as multiple bond may be seen in (i) the angles at B(1) which involve a much smaller C(10)B(1)C(19) angle, 111.6 (6)°, than the other two which have values of 123.5 (7)° and 124.9 (8)° and (ii) the low dihedral angle of 25.8° between the near planar core B(1)C(1)C(10)C(19) and the C(1) ring. This is much smaller than the typical dihedral of ca. 50° seen in $BMes_3$[15] and $BMeMes_2$[16] or the other dihedral angles in 1 of 56.3° for C(1) ring and 52.9° for the C(19) mesityl ring.

Acknowledgment. We thank the National Science Foundation (CHE-8116355) and the A. P. Sloan Foundation for financial support.

Registry No. $[Li(12\text{-crown-}4)_2][CH_2C_6H_2(3,5\text{-}Me_2)(4\text{-}B\{2,4,6\text{-}Me_3C_6H_2\}_2)]\cdot Et_2O$, 103712-53-4.

Supplementary Material Available: Summary of data collection and refinement and tables of atom coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (9 pages); a listing of structure factors (16 pages). Ordering information is given on any current masthead page.

---

[9] Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117.

[10] Odom, J. D. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982, Vol. 1, p 238.

[11] van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kern-van Hoof, A.; van der Kerk, G. M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 48. Bock, H.; Roth, B.; Maier, C. B. *Chem. Ber.* **1984**, *117*, 172. Broxterman, Q. B.; Hogeveen, H. *Tetrahedron Lett.* **1983**, 639. Courtneige, J. L.; Davies, A. G.; Lusztyke, E.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 155.

[12] Wehrmann, R.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 369. Wehrmann, R.; Pues, C.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 372. Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 877.

[13] Hildebrand, M.; Pritzkow, H.; Zennech, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 371.

[14] Cremer, D.; Gauss, J.; Schleyer, P. v. R.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 370. Schleyer, P. v. R.; Budzelaar, P. H. M.; Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 374.

[15] Blount, J. F.; Finocchario, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.

[16] Bartlett, R. A.; Power, P. P., unpublished results.

Photoactivation of Methyl Acetate by Chromium Atoms

W. E. Billups,* John P. Bell, Robert H. Hauge, Ellen S. Kline, A. Wesley Moorehead, and John L. Margrave

Department of Chemistry, Rice University
Houston, Texas 77251

Fred B. McCormick*

3M Central Research Laboratories
St. Paul, Minnesota 55144

Received November 19, 1985

Summary: Photolysis of the cocondensate of methyl acetate and chromium vapor yields a complex that decomposes to acetaldehyde and formaldehyde.

The advent of metal vapor synthesis during the past decade provides an important new method for the preparation of certain organometallic species that are difficult to synthesize by more traditional routes.[1] Metal atoms are in a state of "ultimate coordinative unsaturation" and are highly reactive. However, in any metal vapor reaction there is always a major competing reaction—metal atom recombination to form metal clusters and particles. If the desired metal atom/substrate reaction has a significant activation barrier, then clustering may become the dominant reaction at the low temperatures required by the technique unless the substrate has a significant ability to adduct with the metal atoms. Even then, there has been no convenient method of imparting the addition energy into the system needed to make the reaction proceed.

Photolysis has often been used in matrix isolation spectroscopy as a way of introducing additional energy into the systems studied.[2-5] Photoexcitation of macroscale metal vapor reactions promises to be a similiarly useful method of producing new chemistry. We report here the results of a study on the photoactivation of methyl acetate by chromium atoms using a metal vapor reactor.[6]

---

[1] The following books and review articles give an overview of metal vapor chemistry. (a) Timms, P. L. In *Cryochemistry*; Moskovits, M., Ozin, G. A., Eds.; Wiley: New York, 1976; pp 61–134. (b) McGlinchey, M. J.; Skell, P. S. *Ibid.*; pp 135–194. (c) Blackborow, J. R.; Young, D. *Metal Vapor Synthesis in Organometallic Chemistry*; Springer-Verlag: Berlin, 1979. (d) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980. (e) Timms, P. L. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 121. (f) Timms, P. L.; Turney, T. W. *Adv. Organomet. Chem.* **1977**, *15*, 53. (g) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393. (h) Shriver, D. F. *Inorg. Synth.* **1979**, *19*, 59.

[2] Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393.

[3] Ozin, G. A.; McIntosh, D. F.; Mictchell, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 1574.

[4] Ozin, G. A.; McCaffrey, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 7351.

[5] Ozin, G. A., McCaffrey, J. G. *Inorg. Chem.* **1983**, *22*, 1397.

[6] Howard and Miles have used a similar device in their ESR studies.[7,8] Ours is a true preparative device, while theirs is a microscale matrix isolation device.

0276-7333/86/2305-1917$01.50/0