J. Am. Chem. Soc. **1995,** *117,* 1163−1164

A Remarkably Stable Transition-Metal−Benzyne Complex: Synthesis and Structure of $Cp(PMe_3)(\eta^2\text{-}C_6H_4)Ta(Et_2C_2B_4H_4)$[1]

Karl L. Houseknecht, Kenneth E. Stockman, Michal Sabat, M. G. Finn,* and Russell N. Grimes*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received September 15, 1994

Mononuclear η^2-benzyne complexes of transition metals are typically highly reactive species, and to our knowledge all known and characterized examples are air-sensitive.[2] Since it is well established that $R_2C_2B_4H_4^{2-}$ *nido*-carborane ligands can stabilize organometallic assemblies that are otherwise unstable or nonexistent[3] [e.g., (η^6-arene)iron(III) and (η^6-arene)ruthenium(III) complexes[4]], it occurred to us that this property might be exploited to construct robust benzyne-metallacarborane clusters. Such species could subsequently be tailored via controlled substitution[5] on the carborane ligand to achieve a desired level of reactivity toward organic substrates. Here we report the synthesis and structural characterization of an air- and moisture-stable benzyne−tantalacarborane whose low reactivity is apparently unprecedented for an η^2-benzyne−transition-metal complex.

As shown in Scheme 1, the $Et_2C_2B_4H_5^-$ anion (obtained by deprotonation of the neutral carborane with NaH in THF) reacted with $CpTaCl_4$ to generate the dichlorotantalum(V) complex **1**, which was subsequently converted to the diphenyl species **2** via treatment with phenylmagnesium bromide.[6] Thermolysis of **2** in the presence of an excess of trimethylphosphine afforded the title complex **3**, which was purified via recrystallization from methanol and characterized from its ^1H, ^{11}B, ^{31}P, and ^{13}C NMR spectra, mass spectrum, elemental analysis, and an X-ray crystal structure determination.[7,8] The 300 MHz proton NMR spectrum of **3** exhibits two sets of ethyl resonances, one of which is shifted upfield owing to a ring current generated by the benzyne ligand. Other features of the NMR spectra[7] are consistent with the geometry indicated in Scheme 1.

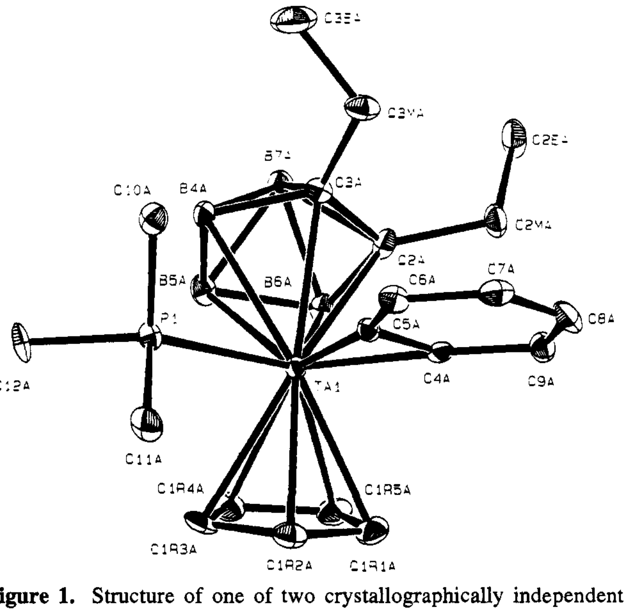
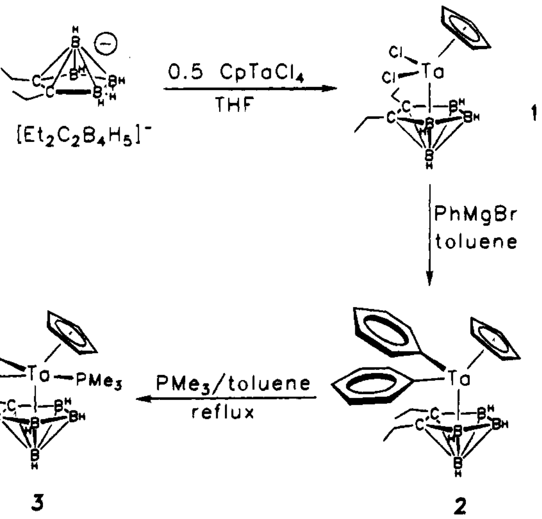


Figure 1. Structure of one of two crystallographically independent molecules of **3** drawn with 30% thermal ellipsoids (hydrogen atoms omitted).

Scheme 1



The crystallographically determined structure of **3** contains two independent enantiomeric molecules in the asymmetric unit, one of which is presented in Figure 1. All atoms, including hydrogens, were located. The presence of an η^2-C_6H_4 ligand on tantalum is clearly established, with the Ta atom virtually coplanar with the benzyne ring. The TaC_2B_4 cluster is normal with no significant distortions, although the Ta to cage carbon distances are slightly shorter than the Ta−boron connections (⟨2.412(3)⟩ vs ⟨2.473(3)⟩ Å). The cyclopentadienyl−Ta−carborane array is bent (dihedral angle between the Cp and C_2B_3 planes, 49°) to accommodate the benzyne and phosphine ligands, as in analogous $Cp_2M(L)$(benzyne) complexes. The metal−benzyne moiety in **3** has a mean M−C bond distance of 2.187(3) Å for the two molecules, and the mean length of the

---

(1) Organotransition-Metal Metallacarboranes. 36. Part 35: Stephan, M.; Hauss, J.; Zenneck, U.; Siebert, W.; Grimes, R. N. *Inorg. Chem.* **1994**, *33*, 4211.

(2) (a) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696 and references therein. See also: (b) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (c) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697. (d) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992. (e) Buchwald, S. L.; Watson, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (f) Cockroft, J. K.; Gibson, V. C.; Howard, J. A. K.; Poole, A. D.; Siemeling, U.; Wilson, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1668. (g) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404.

(3) (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (b) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081.

(4) Merkert, J. M.; Geiger, W. E.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1991**, *10*, 3545.

(5) (a) Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171. (b) Piepgrass, K. W.; Grimes, R. N. *Organometallics* **1992**, *11*, 2397. (c) Piepgrass, K. W.; Stockman, K. E.; Sabat, M.; Grimes, R. N. *Organometallics* **1992**, *11*, 2404.

(6) (a) A preliminary report on the synthesis and characterization of early transition metal small metallacarborane complexes has been presented; see: Stockman, K. E.; Finn, M. G.; Sabat, M.; Grimes, R. N. *Abstracts of Papers*, Fourth Boron U.S.A. Workshop, Syracuse, NY, July 1994; Abstract 9. (b) Stockman, K. E.; Houseknecht, K. L.; Curtis, M. A.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. Manuscript in preparation.

(7) Experimental details on the synthesis of precursor complexes **1** and **2** are provided as supplementary material. A solution of $Cp(Et_2C_2B_4H_4)Ta(C_6H_5)_2$ (**2**) (0.704 g, 1.33 mmol) and 13.3 mmol of PMe_3 in 20 mL of toluene was refluxed under argon for 2 h. The solvent was removed in vacuo and the residue extracted with warm methanol. Concentration and cooling of the solution followed by filtration afforded **3** as an analytically pure white powder (0.329 g, 47%). ^1H NMR (300 MHz, $CDCl_3$): δ 0.65 (t, 3H), 0.86 (dq, 1H), 1.01 (dq, 1H), 1.35 (t, 3H), 1.89 (d, J = 8.4 Hz, 9H), 2.13 (dq, 1H), 2.52 (dq, 1H), 5.21 (d, J = 1.5 Hz, 5H), 7.16 (m, 2H), 7.59 (d, 1H), 7.71 (t, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.9, 16.3, 21.3 (d, J = 31.8 Hz), 21.7, 25.3, 100.3, 110.9, 113.6, 129.3, 129.6, 130.6, 132.4, 141.8 (d, J = 36.6 Hz), 168.6 (d, J = 10.6 Hz). ^{11}B NMR (115.8 MHz, CH_2Cl_2): δ 0.70 (1B), 10.96 (1B), 12.99 (2B). ^{31}P NMR (121.4 MHz, $CDCl_3$, referenced to external 85% H_3PO_4 and D_2O standard): δ −6.19. Mass spectrum: *m/z* 527 corresponding to parent ion envelope, base peak *m/z* 525; the intensity pattern is consistent with the calculated spectrum based on natural isotope abundances. Anal. Calcd for $TaPC_{20}B_4H_{32}$: C, 45.53; H, 6.11. Found: C, 45.13; H, 6.12.

0002-7863/95/1517-1163$09.00/0

C−C edge coordinated to the metal is 1.344(6) Å. These structural parameters fall within the normal range for such complexes,[9] with the C(4A)−C(5A) and Ta−C(4A)/C(5A) distances supporting a large C−C bond order and strong Ta−C_6H_4 binding. The remaining benzyne C−C lengths in **3** are all close to 1.40 Å with no apparent long−short pattern, consistent with an electron-delocalized aromatic ring. This can be compared with the structure of Cp*$TaMe_2(\eta^2\text{-}C_6H_4)$ in which the C−C distances do alternate,[2c] varying by ca. 0.04 Å.

In contrast to previously reported benzyne complexes,[2a,10] e.g., $Cp_2Zr(PMe_3)(\eta^2\text{-}C_6H_4)$,[2e] **3** gave no coupling reactions (room temperature in C_6D_6 under argon for ≥24 h) with equimolar amounts of unsaturated substrates including acetone, benzophenone, benzaldehyde, acetonitrile, bis(trimethylsilyl)acetylene, or 3-hexyne, owing to nonlability of the PMe_3 ligand. Indeed, no exchange was observed between **3** and a 10-fold excess of $PMe_3\text{-}d_9$ in $CDCl_3$. Similarly, the compound is unreactive toward methanol and may be recrystallized from that solvent. These findings demonstrate the remarkable stabilizing power of the *nido*-$R_2C_2B_4H_4^{2-}$ ligands in organometallic systems, a property that can be at least partially attributed to electron delocalization in the metallacarborane cluster framework and the associated stabilization of high formal metal oxidation states.

Thermolysis of the diphenyl precursor complex **2** in the presence of excess methanol (reflux in 3:10 v/v MeOH/toluene for 40 h) induced clean conversion to the phenyl methoxy derivative $Cp(OMe)(\eta^1\text{-}C_6H_5)Ta(Et_2C_2B_4H_4)$,[11] presumably via a nonstabilized Ta−benzyne intermediate. Treatment of **2** with MeOD afforded the analogous $\eta^1\text{-}C_6H_4D$ complex, as shown by proton NMR. However, metallacyclic products generated by thermal decomposition of **2** in the presence of an excess of unsaturated substrates have thus far proven elusive. Clear evidence of reactivity has been observed for **3** in one instance: treatment with CF_3COOH in air results in protonation of the benzyne ring, as clearly shown by deuterium labeling experiments with CF_3COOD.[12] Further investigation of this reaction is in progress.

The intrinsic stability of **3**, taken together with the fact that it is nevertheless reactive under some circumstances, implies that its chemistry can be "tuned" by suitable modification, e.g., by varying substituents on the carborane ligand;[5] hence a family of **3**-based reagents tailored to have a range of reactivities can be envisioned. Studies of the properties of this complex and related species are continuing.

Acknowledgment. This work was supported by the National Science Foundation, Grant No. CHE 9322490 to R.N.G.

Supplementary Material Available: Details on synthesis and characterization of **1** and **2**, NMR data on treatment of **3** with CF_3-COOD, and tables of crystal structure data, thermal parameters, atom coordinates, bond distances and angles, and mean planes for **3** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for information.

JA943043M

---

(8) Crystal data: $M = 527.63$; triclinic, space group $P\bar{1}$; $a = 15.529(3)$ Å, $b = 15.782(2)$ Å, $c = 8.990(1)$ Å, $\alpha = 90.11(1)°$, $\beta = 96.38(4)°$, $\gamma = 99.56(1)°$, $V = 2158.6(6)$ Å^3, $Z = 4$, $d_{calcd} = 1.62$ g cm^{-3}; crystal size 0.42 × 0.24 × 0.25 mm; μ(Mo Kα) = 51.06 cm^{-1}. The structure was solved by direct methods in TEXSAN 5.0. Full-matrix least-squares refinement yielded $R(F) = 0.025$ and $R_w(F) = 0.031$ for 5438 absorption-corrected reflections with $I > 3\sigma$ measured up to $2\theta = 50°$ on a Rigaku AFC6S diffractometer at −120 °C (Mo Kα radiation, $\lambda = 0.710\,69$ Å. All hydrogen atoms were found from difference Fourier maps and included in calculations without further refinement.

(9) Corresponding values in related structures: Cp*$TaMe_2(\eta^2\text{-}C_6H_4)$,[2c] 2.075(2) and 1.364(5) Å; $Cp_2Zr(PMe_3)(\eta^2\text{-}C_6H_4)$,[2e] 2.248(4) Å and 1.364(8) Å; (2,6-i$Pr_2C_6H_3N)Cp(PMe_3)Nb(\eta^2\text{-}C_6H_4)$,[2f] 2.164(5) and 1.342(11) Å; $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$,[2g] 2.092(2) and 1.355(3) Å; $(Cy_2PCH_2CH_2PCy_2)$-$Ni(\eta^2\text{-}C_6H_4)$ (Cy = cyclohexyl),[2d] 1.869(3) and 1.332(6) Å.

(10) The $CpMMe_2$(benzyne) (M = Ta, Nb) complexes reported by Schrock et al.[2b] are atypical for this class, in that their reaction with ethylene to give benzometallocyclopentadiene complexes is relatively slow. In contrast, a proposed tantalum−benzyne complex reaction intermediate is so reactive that it could not be isolated or directly observed; see: Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffmann, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471.

(11) ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, 3H), 1.19 (t, 3H), 2.35 (dq, 2H), 2.51 (dq, 2H), 4.15 (s, 3H), 6.10 (s, 5H), 6.98 (t, 1H), 7.02 (d, 2H), 7.15 (t, 2H). Mass spectrum: parent ion envelope at *m/z* 483.

(12) The proton NMR signal of the *o*-C_6H_4 protons is reduced by $^1/_2$ when **3** is treated with CF_3COOD, as depicted in the supplementary material.