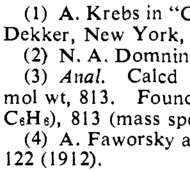
Stabilization of Small-Ring Acetylenes by Complex Formation with Platinum

Sir:

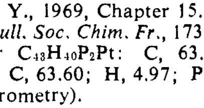
The smallest cyclic acetylene which has been isolated is cyclooctyne, although there is indirect evidence for the existence of cycloheptyne and cyclohexyne as short-lived intermediates.[1] We report the capture of these reactive species by platinum(0), together with an X-ray structural analysis of the cycloheptyne complex. The structure of the cyclohexyne analog will be described subsequently.

1,2-Dibromocycloheptene[2] reacts at room temperature with sodium amalgam in THF in the presence of $Pt(PPh_3)_3$ to give colorless diamagnetic crystals (63% yield) of formula $C_7H_{10}Pt(PPh_3)_2$ (**1**):[3] mp 163–166°; ir (KBr disk) 1770 cm^{-1} [$\nu(C{\equiv}C)$]; nmr ($CDCl_3$) δ 2.24 (broad, 4, $C\mathit{H}_2C{\equiv}CC\mathit{H}_2$), 1.69 (broad, 6, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$). A similar reaction using 1,2-dibromocyclohexene[4] gives colorless crystals (59% yield) of $C_6H_8Pt(PPh_3)_2$ (**2**):[5] mp 157–159°; ir (KBr disk) 1721 cm^{-1} [$\nu(C{\equiv}C)$]; nmr ($CDCl_3$) δ 2.54 (broad, 4, $C\mathit{H}_2C{\equiv}CC\mathit{H}_2$), 1.76 (broad, 4, $CH_2C\mathit{H}_2C\mathit{H}_2CH_2$). The mass spectra of **1** and **2** show the molecular ions $[C_{n+2}H_{2n}Pt(PPh_3)_2]^+$ (**1**, $n = 5$; **2**, $n = 4$) and the fragment ion $[Pt(PPh_3)_2]^+$. The complexes are apparently similar to the cyclooctyne complex $C_8H_{12}Pt(PPh_3)_2$ which was made from $Pt(PPh_3)_4$ and the acetylene.[6,7]

Treatment of **1** with CF_3CO_2H in benzene at room temperature gives the σ-cycloheptenyl complex σ-C_7H_{11}-$Pt(OCOCF_3)(PPh_3)_2$ (**3**): mp 178–180°; ir (KBr disk) 1600 cm^{-1} [$\nu(C{=}C)$ as shoulder on $\nu(C{=}O)$]; nmr ($CDCl_3$) δ 5.02 (t, 1, $J_{H-H} = 6$ Hz, $J_{Pt-H} = 67$ Hz, $C{=}C\mathit{H}$), δ 1.8–0.3 (broad multiplets, 10, $C\mathit{H}_2$). The σ-cyclohexenyl complex σ-$C_6H_9Pt(OCOCF_3)(PPh_3)_2$ (**4**) is similarly obtained from **2**: mp 190–192° dec; ir (KBr disk) 1610 cm^{-1} [$\nu(C{=}C)$]; nmr ($CDCl_3$) δ 4.92 (broad t, 1, $C{=}C\mathit{H}$), 1.36 (4), 0.76 (2), 0.46 (2) (broad multiplets, $C\mathit{H}_2$). The protonations 1 → 3 and 2 → 4 can only give rise to a cis arrangement about the double bond, in agreement with previous work on acyclic acetylene complexes.[8]



1, 2



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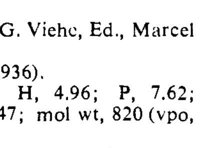

5, 6

1, 3, 5, $n = 5$; **2, 4, 6**, $n = 4$

Reaction of **1** with $Ph_2PCH_2CH_2PPh_2$ leaves the cycloheptyne intact and displaces the triphenylphosphine groups to give $C_7H_{10}Pt(diphos)$ (**5**): mp 172–174° dec; ir (KBr disk) 1761 cm^{-1} [$\nu(C{\equiv}C)$]; nmr ($CDCl_3$) δ 3.02 (m, 4, $C\mathit{H}_2C{\equiv}CC\mathit{H}_2$), 1.97 (m, 6, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$). The complex (cyclohexyne)Pt(diphos) (**6**), mp 163–166° dec, can be prepared similarly. Coordinated cyclohexyne cannot be displaced from **2** by $HC{\equiv}CCO_2CH_3$, $PhC{\equiv}CPh$, or $CH_3O_2CC{\equiv}CCO_2CH_3$, but reaction with tetracyanoethylene (TCNE) gives $(TCNE)Pt(PPh_3)_2$.[9] These qualitative observations suggest that cycloalkyne–platinum(0) complexes are even more stable than the corresponding acyclic alkyne complexes.[10,11]

Crystals of **1** are monoclinic, space group $P2_1/c$, $a = 8.95$, $b = 33.52$, $c = 13.10$ Å, $\beta = 114.24°$, $Z = 4$. The 4936 unique reflections with $F_o^2/\sigma(F_o^2) \geqslant 3.0$ were collected on a Picker FACS-I automatic diffractometer using crystal-monochromated Cu Kα radiation. Allowing for anisotropic thermal motion of the platinum and phosphorus atoms, block-diagonal least-squares analysis of all atomic positional and carbon isotropic thermal parameters converged to a conventional R of 0.053. Data have yet to be corrected for absorption and extinction effects. Esd's of the bond distances at the present stage of refinement are: Pt–P, 0.002; Pt–C, 0.01; P–C, 0.01; C–C, 0.017 Å.

The geometry at the platinum atom is essentially planar, the overall stereochemistry of the molecule being shown in Figure 1. Figure 2 shows the more important bond distances and angles, together with the distances of the cycloheptyne carbon atoms from the plane [C(1), C(2), C(3), C(7)].

The Pt–P distances (av 2.268 (2) Å, equal within experimental error), the distances Pt–C(1) and Pt–C(2) (2.04 (1) and 2.07 (1) Å, respectively), the angle P(1)–Pt–P(2) (102.5°), and the angle C(1)–Pt–C(2) (36.7°) are very similar to the corresponding values found for the diphenylacetylene complex $(PhC{\equiv}CPh)Pt(PPh_3)_2$.[12] The dihedral angle between the planes [Pt, P(1), P(2)] and [Pt, C(1), C(2)] is 8.3°; *cf.* 14° in $(PhC{\equiv}CPh)Pt(PPh_3)_2$,[12] 12° in $(C_2H_4)Ni(PPh_3)_2$,[13] and 6° in $(CS_2)Pt(PPh_3)_2$.[14]

It has been suggested[15] that a deformation of 25° of the C≡C–C angle would be the principal means by which the inherent strain of the free cycloheptyne would be relieved. This nonlinearity causes the in-plane acetylenic π orbitals to acquire substantial s character, thus reducing the π-bond order relative to a linear C–C≡C–C arrangement and increasing the localization of electrons at the acetylenic carbon atoms. This factor may be responsible for the stability of **1** relative to the analogous linear alkyne–platinum(0) complexes since the angle deformation at C(1) and C(2) (41°) is very similar to that observed in $(PhC{\equiv}CPh)Pt(PPh_3)_2$ (39°).[12] It is probable that coordination of the cycloheptyne also reduces the π-bond order of the alkyne link-

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(1) A. Krebs in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 15.

(2) N. A. Domnin, *Bull. Soc. Chim. Fr.*, 1735 (1936).

(3) *Anal.* Calcd for $C_{43}H_{40}P_2Pt$: C, 63.45; H, 4.96; P, 7.62; mol wt, 813. Found: C, 63.60; H, 4.97; P, 7.47; mol wt, 820 (vpo, C_6H_6), 813 (mass spectrometry).

(4) A. Faworsky and W. Bushowsky, *Justus Liebigs Ann. Chem.*, **390**, 122 (1912).

(5) *Anal.* Calcd for $C_{42}H_{38}P_2Pt$: C, 63.07; H, 4.79; P, 7.75; mol wt, 799. Found: C, 63.29; H, 4.96; P, 7.81; mol wt, 729 (vpo, C_6H_6), 799 (mass spectrometry).

(6) T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *Chem. Commun.*, 821 (1968).

(7) G. Wittig and S. Fischer, unpublished results, 1968, cited in ref 1, p 1038.

(8) B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Commun.*, 1330 (1970).

(9) W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(10) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc., London*, 208 (1957).

(11) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(12) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, **7**, P9 (1967).

(13) C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Chem. Commun.*, 426 (1967).

(14) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 1767 (1970).

(15) Reference 1, p 1006.

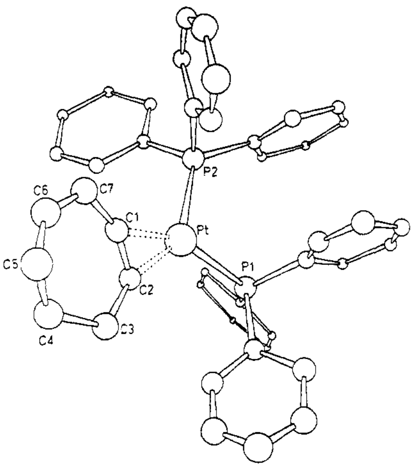

Figure 1. The overall stereochemistry of (cycloheptyne)Pt$(PPh_3)_2$.

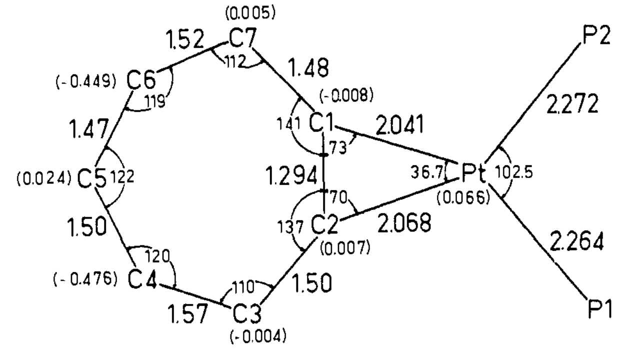

Figure 2. Important bond lengths (ångströms) and bond angles (degrees) for (cycloheptyne)Pt$(PPh_3)_2$. Deviations from the least-squares plane through C(1), C(2), C(3), and C(7) are shown in parentheses.

age. Although the aliphatic C–C distances in the cycloheptyne ring are normal, significant deviations from the tetrahedral angle occur at C(4), C(5), and C(6), presumably in an attempt to relieve ring strain. Atoms C(1), C(2), C(3), and C(7) are coplanar within experimental error and C(5) is only 0.024 Å above this plane. The cycloheptyne ring can, therefore, be described as having a distorted chair conformation.

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Addition of Diborane(6) to Boron Hydride Anions. New Syntheses of Hexaborane(12) and Pentaborane(11)

Sir:

In recent years, the conjugate bases of B_5H_9, B_6H_{10}, and B_4H_{10} ($B_5H_8^-$,[1–4] $B_6H_9^-$,[3,4] and $B_4H_9^-$ [5–7]) have been prepared and characterized. The Lewis basicity of these species makes them potentially valuable synthetic reagents, as has been demonstrated for $B_5H_8^-$.[2,8–10] At this time we wish to report a sequence of reactions in which the BH_3 group adds to these bases in a way which apparently expands the polyhedral framework. Thus, we have observed that diborane(6) reacts in a 0.5 *M* ratio with $B_4H_9^-$, $B_5H_8^-$, and $B_6H_9^-$ to produce $B_5H_{12}^-$, $B_6H_{11}^-$, and $B_7H_{12}^-$, respectively. From the first two anions we have obtained B_5H_{11} and B_6H_{12}, respectively, in good yields (60–70%) by treatment with anhydrous liquid hydrogen chloride. These syntheses of B_5H_{11} and B_6H_{12} are summarized by the following equations.

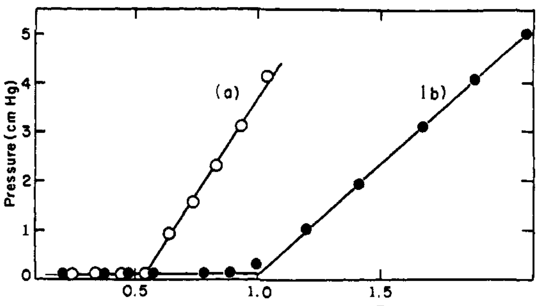

Figure 1. Tensiometric titrations of $B_5H_8^-$ with B_2H_6 at −78° in $(C_2H_5)_2O$: (a) completed in one day, (b) sufficient time allowed for complete reaction of each increment (see text).

$$MB_5H_8 + {}^1/_2B_2H_6 \xrightarrow[(CH_3)_2O]{-78^\circ} MB_6H_{11} \qquad (1a)$$

$$MB_6H_{11} + HCl(l) \xrightarrow{-110^\circ} B_6H_{12} + MCl \qquad (1b)$$

$$KB_4H_9 + {}^1/_2B_2H_6 \xrightarrow[(C_2H_5)_2O]{-35^\circ} KB_5H_{12} \qquad (2a)$$

$$KB_5H_{12} + HCl(l) \xrightarrow{-110^\circ} B_5H_{11} + H_2 + KCl \qquad (2b)$$

Treatment of $B_7H_{12}^-$ with HCl yields B_6H_{10} as the major product; minor components are still under study. In view of the commercial availability of B_5H_9,[11] the reactions outlined above (1a, 1b) make B_6H_{12} conveniently available in the laboratory for the first time. Furthermore, the reactions outlined for the preparation of B_5H_{11} provide an attractive alternative to currently employed procedures.[12]

Tensiometric titrations of LiB_5H_8 or KB_5H_8 at −78° in diethyl ether (Figure 1) with B_2H_6 clearly reveal a

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[1] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 3375 (1967).
[2] R. A. Geanangel and S. G. Shore, *ibid.*, **89**, 6771 (1967).
[3] H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *ibid.*, **91**, 2131 (1969).
[4] H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).
[5] A. C. Bond and M. L. Pinsky, *J. Amer. Chem. Soc.*, **92**, 7585 (1970).
[6] H. D. Johnson, II, and S. G. Shore, *ibid.*, **92**, 7586 (1970).
[7] G. Kodama, J. E. Dunning, and R. W. Parry, Abstracts, 25th Annual Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 17–18, 1970, paper no. 98; G. Kodama, J. E. Dunning, and R. W. Parry, *J. Amer. Chem. Soc.*, submitted for publication.
[8] D. F. Gaines and T. V. Iorns, *ibid.*, **90**, 6617 (1968).
[9] A. B. Burg and H. Heinen, *Inorg. Chem.*, **7**, 1021 (1968).
[10] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **92**, 4571 (1970).
[11] Callery Chemical Co., Callery, Pa.
[12] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **55**, 4009 (1933); R. T. Holtzman, Ed., "Production of Boranes and Related Research," Academic Press, New York, N. Y., 1967, pp 68–70.