4-Homoadamantyne: Generation, Chemical Trapping and Structure of its Pt(0) Complex

Koichi Komatsu,[*] [a] **Hiroshi Kamo,**[a] **Ryotaro Tsuji,**[a] **Hideki Masuda**[b] **and Ken'ichi Takeuchi**[a]

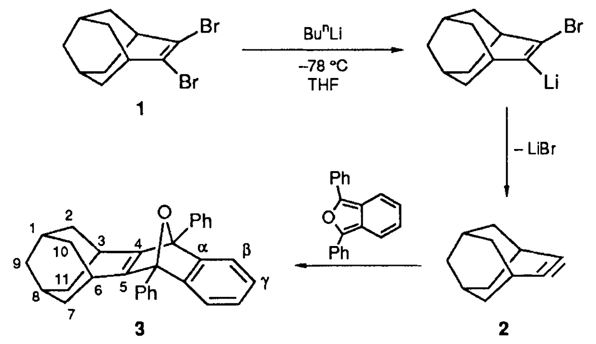
[a] *Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan*
[b] *Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

A highly strained polycyclic alkyne with a cage structure, 4-homoadamantyne **2**, has been generated and trapped with diphenylisobenzofuran and by complexation with Pt(0); X-ray crystallography of the Pt(0) complex **4** and molecular mechanics calculations for **2** indicate that the molecular strain in **2** and in **4** is nearly as large as that in cyclohexyne and in its Pt(0) complex.

The mono- or poly-cyclic alkynes serve as a model of strained acetylene, the strain can be controlled by size and rigidity of the cyclic carbon frameworks.[1] Whereas there are some recent reports describing the generation and reactions of highly strained bicycloalkynes,[2] studies on tricyclic alkynes are quite limited.[1] Here, we describe the facile generation of a new tricyclic acetylene, 4-homoadamantyne (tricyclo-[4.3.1.1^{3,8}]undec-4-yne) **2**, and its trapping using both organic and inorganic reagents.

The alkyne **2** formally contains a cycloheptyne unit in its structure. However, according to the results of molecular mechanics calculations (MM2), the values of the C–C≡C angle and the strain energy of **2** [140.8° and 63.7 kcal mol^{-1}, respectively (1 cal = 4.184 J)] are closer to those of cyclohexyne (140.4°, 58.2 kcal mol^{-1}) rather than to those of cycloheptyne (150.4°, 31.7 kcal mol^{-1}), owing to the intrinsic molecular rigidity of **2**. Thus, it seemed of interest to investigate the generation of **2** and also the structural characteristics of a stabilized form, *e.g.*, a metal complex.

When LiBu (1 equiv.) was added to 4,5-dibromo-4-homoadamantene **1** in tetrahydrofuran (THF) at −78 °C in the presence of diphenylisobenzofuran (DPIBF) (1 equiv.) and the solution slowly warmed to room temperature, adduct **3**† was formed in 34.2% yield; its structure was established by complete 2D NMR analyses (COSY and C/H COSY). Because the results of control experiments did not indicate any reactivity of DPIBF either toward **1** or toward LiBu under the same conditions, the adduct **3** must have arisen from [4 + 2] cycloaddition of DBIBF to the acetylene **2**, formed by lithiation of **1** followed by LiBr elimination, Scheme 1.



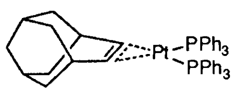
Scheme 1

In order to substantiate further the formation of the intermediate alkyne **2**, its complexation with Pt(0) was attempted.[3] In the presence of Pt(PPh$_3$)$_3$ ($\frac{1}{3}$ equiv.), reaction of **1** with Na–Hg (1%) (3.3 equiv.) was carried out in THF at room temperature for 1 h. The THF-soluble crude product was separated and recrystallized from benzene–ethanol (2 : 3) to give air-stable, colourless prisms, which were identified as the Pt(0) complex **4**‡§ [51.0% yield based on Pt(PPh$_3$)$_3$]. In the ^{1}H NMR spectrum, the 3-H signal exhibits a typical 1 : 4 : 1 satellite structure due to ^{195}Pt splitting ($^3J_{H,Pt}$ 47.6 Hz). In the ^{13}C NMR spectrum, the C-4 signal also shows a similar

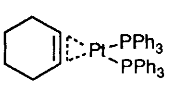
Table 1. Comparison of important bond parameters[a]

	Bond angle (°)			Bond length (Å)	
Compound	C–C≡C	C–Pt–C	P–Pt–P	C≡C	C–Pt
4	129.4	37.6	105.6	1.321	2.052
5[b]	127.3	37.1	109.5	1.297	2.039
6[b]	138.9	36.5	102.6	1.283	2.050

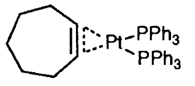
[a] Averaged value. [b] Ref. 5.



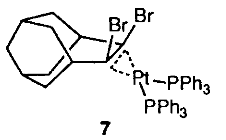
4



5



6



7

---

‡ We consider that **4** was formed by trapping of incipient **2** and not by reduction of the first formed alkene complex such as **7**, based on the results of a control experiment: when the reaction was conducted in the absence of Na–Hg, the rate of consumption of **1** was much slower and no formation of **7** or any other complexes derived therefrom was observed.

† *Physical and spectroscopic data:* **3** m.p. 185.5–187 °C (decomp.); IR (KBr disc) ν 965 cm^{-1} (C–O–C); UV–VIS (CHCl$_3$) λ_{max} 257, 262, 268 and 275 nm (ε 1 500, 1 560, 1 470 and 1 360 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 0.94 [d, 2H, 7,11-H (equatorial with respect to the cyclohexane ring)], 1.43 [dm, 2H 7,11-H(ax)], 1.69 (br s, 2H, 9-H), 1.74 (br s, 1H, 8-H), 1.86 [m, 2H, 2,10-H (eq)], 2.02 [d, 2H, 2,10-H(ax)], 2.21 (br s, 1H, 1-H), 2.62 (br s, 2H, 3,6-H), 7.04 (d, 2H, β-H), 7.37 (d, 2H, γ-H), 7.40 (t, 2H, *p*-H), 7.47 (t, 4H, *m*-H), 7.68 (d, 4H, *o*-H). ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ 28.6 (C-8), 29.1 (C-1), 30.1 (C-3,6), 31.7 (C-7,11), 33.6 (C-2,10), 36.4 (C-9), 93.4 (C–O), 120.3 (C-γ). 124.6 (C-β), 128.3 (C-*p*), 128.5 (C-*m*), 128.9 (C-*o*), 134.9 (C-*ipso*), 152.0 (C-α), 158.4 (C-4,5). Satisfactory microanalyses (C, H) were obtained.

§ *Physical and spectroscopic data:* **4** m.p. 164–176 °C (decomp.); IR (KBr disc) ν 1735 cm^{-1} (C≡C); UV–VIS (CH$_2$Cl$_2$) λ_{max} 260sh and 335sh nm (ε 22 900 and 3 470 dm^3 mol^{-1} cm^{-1}); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.80, 1.86 (br s ×2, 10H, CH$_2$), 2.16 (br s, 2H, 1,8-H), 2.71 [br t(1 : 4 : 1), 2H, 3,6-H], 7.10 (m, 18H, *m,p*-H), 7.34 (m, 12H, *o*-H); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ 29.8 [t(1 : 4 : 1)t, $^2J_{C,Pt}$ 18.6 Hz, $^3J_{C,P(trans)}$ = $^1J_{C,P(cis)}$ 9.3 Hz, C-3,6], 30.3 (C-1,8), 34.8 [t(1 : 4 : 1), $^3J_{C,Pt}$ 12.7 Hz, C-2,7,10,11], 38.5 (C-9), 127.4(t, $^3J_{C,P}$ = $^5J_{C,P}$ 9.8 Hz, C-*m*), 128.7 (C-*p*), 134.1 [t(1 : 4 : 1)t, $^3J_{C,Pt}$ 19.6 Hz, $^2J_{C,P}$ = $^4J_{C,P}$ 13.7 Hz, C-*o*], 137.3 [t(1 : 4 : 1)dd, $^2J_{C,Pt}$ 25.9 Hz, $^1J_{C,P}$ 23.1 Hz, $^3J_{C,P}$ 21.5 Hz, C-*ipso*], 139.8 [t(1 : 4 : 1)dd, $^1J_{C,Pt}$ 368.4 Hz, $^2J_{C,P(trans)}$ 84.0 Hz, $^2J_{C,P(cis)}$ 17.2 Hz, C-4,5). Satisfactory microanalyses (C, H, P) were obtained.

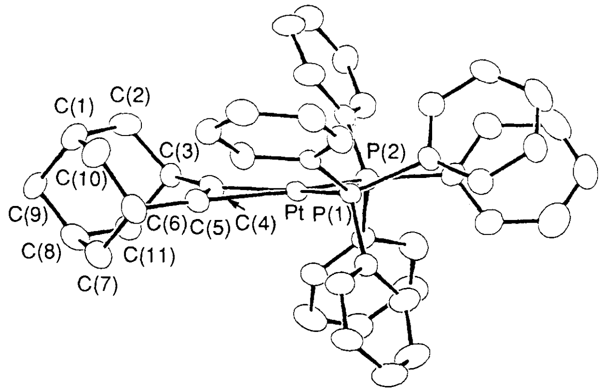


Fig. 1 An ORTEP drawing of one of the two molecules in the asymmetric unit of **4**. Selected bond lengths (Å) and angles (°) for this molecules are representative of all two independent molecules: Pt–P(1) 2.256(3), Pt–P(2) 2.260(4), Pt–C(4) 2.042(13), Pt–C(5) 2.068(14), C(4)–C(5) 1.314(20), P(1)–Pt–P(2) 108.8(1), C(4)–Pt–C(5) 37.3(5), C(3)–C(4)–C(5) 130.6(13), C(4)–C(5)–C(6) 129.1(13).

splitting ($^1J_{C,Pt}$ 368.4 Hz) as well as further splittings by *trans*- and *cis*-^{31}P ($^2J_{C,P}$ 84.0 and 17.2 Hz, respectively). The IR stretching for the unsaturated bond in **4** (1735 cm^{-1}) is rather closer to that reported for the cyclohexyne complex **5** (1721 cm^{-1})[4] than to that for the cycloheptyne complex **6** (1781 cm^{-1}).[4]

The X-ray crystal structure for **4**¶ is shown in Fig. 1. Some structural parameters (averaged values) are compared in Table 1 with those of **5** and **6**.[5] As expected from the results of MM2 calculations on the corresponding alkynes, the C–C$\equiv$C angle, which appears to be responsible for the molecular strain of **4**, is much closer to that of **5** than **6**. The C(4), C(5), Pt, P(1) and P(2) atoms form a near planar system typical of the tetra-coordinated Pt(0) complex. The dihedral angle between the planes Pt–C(4)–C(5) and Pt–P(1)–P(2) is 6.87° as the average for two independent molecules. The unsaturated bond in **4** appears to be slightly elongated compared with those in **5** and **6**.[5] This may be taken as a reflection of the electronic and steric effects of the homoadmantane σ-framework: the inductive electron release from the polycyclic σ-framework would increase the electron density of the bonding pπ orbital making the alkyne(π) → metal(dπ) σ-donation stronger, whereas a nearly coplanar arrangement of C(3)–C(4)–C(5)–C(6) enforced by the rigid tricyclic framework would securely fix the antibonding pπ orbitals to facilitate the metal (dπ) → alkyne (π*) π back donation. As a result, the metallacyclopropene character would be enhanced in **4** causing a slight elongation of the C$\equiv$C bond.

Received, 10th September 1990; Com. 0/04123H

References

1 A. Krebs and J. Wilke, in *Wittig Chemisty (Topics in Current Chemistry)*, ed. F. L. Boschke, Springer-Verlag, Berlin, 1983, vol. 109, p. 189; A. Greenberg and J. F. Liebman, *Strained Organic Molecules*, Academic Press, New York, 1978, p. 133; W. T. Borden, *Chem. Rev.*, 1989, **89**, 1095.
2 P. G. Gassman and I. Gennick, *J. Am. Chem. Soc.*, 1980, **102**, 6864; K. Shahlai and H. Hart, *J. Am. Chem. Soc.*, 1988, **110**, 7136; K. Komatsu, S. Aonuma, Y. Jinbu, R. Tsuji, C. Hirosawa and K. Takeuchi, *J. Org. Chem.*, in the press.
3 For a comprehensive review of alkyne–metal complexes, see M. A. Bennett and H. P. Schwemlein, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1296.
4 M. A. Bennett and T. Yoshida, *J. Am. Chem. Soc.*, 1978, **100**, 1750.
5 G. B. Robertson and P. O. Whimp, *J. Am. Chem. Soc.*, 1975, **97**, 1051.

¶ *Crystal data:* **4**: $C_{47}H_{44}P_2Pt$, M = 865.90, triclinic, space group $P\bar{1}$, a = 21.002(9), b = 15.117(5), c = 12.035(3) Å, α = 97.83(2), β = 94.81(3), γ = 97.27(3)°, U = 3735.0 Å^3, Z = 4, D_c = 1.540 g cm^{-3}, AFC-5R-(Rigaku) diffractometer, ω-scan, graphite monochromator, Mo-Kα radiation. The structure was solved by a combination of direct (MULTAN 78) and difference Fourier methods; non-hydrogen atoms were refined with anisotropic temperature factors, and hydrogen atoms with isotropic temperature factors; the positions of the H atoms were calculated: R = 0.061, R_w = 0.081 for 10 273 unique reflections with $|F_o| \geq 3\sigma(|F_o|)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.