

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

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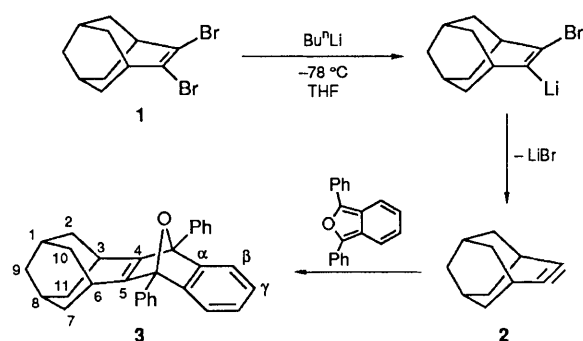
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A highly strained polycyclic alkyne with a cage structure, 4-homoadamantyne **2**, has been generated and trapped with diphenylisobenzofuran and by complexation with Pt(0); X-ray crystallography of the Pt(0) complex **4** and molecular mechanics calculations 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

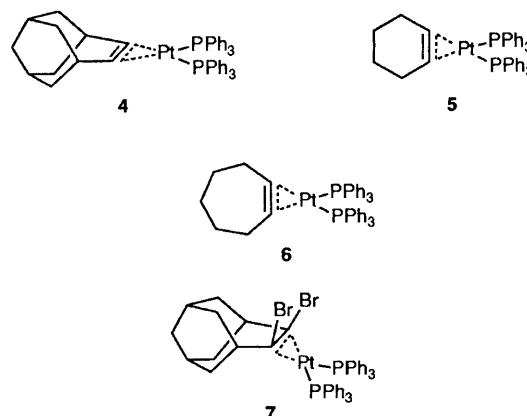
[†] Physical and spectroscopic data: **3** m.p. 185.5–187 °C (decomp.); IR (KBr disc) ν 965 cm^{−1} (C–O–C); UV–VIS (CHCl₃) λ_{max} 257, 262, 268 and 275 nm (ϵ 1 500, 1 560, 1 470 and 1 360 dm³ mol^{−1} cm^{−1}); ¹H NMR (CDCl₃, 270 MHz) δ 0.94 [d, 2H, 7,11-H (equatorial with respect to the cyclohexane 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). ¹³C NMR (CDCl₃, 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.

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(PPh₃)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(PPh₃)₃]. In the ¹H NMR spectrum, the 3-H signal exhibits a typical 1 : 4 : 1 satellite structure due to ¹⁹⁵Pt splitting (³J_{H,Pt} 47.6 Hz). In the ¹³C NMR spectrum, the C-4 signal also shows a similar

Table 1. Comparison of important bond parameters^a

Compound	Bond angle (°)			Bond length (Å)	
	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.



§ 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: **4** m.p. 164–176 °C (decomp.); IR (KBr disc) ν 1735 cm^{−1} (C≡C); UV–VIS (CH₂Cl₂) λ_{max} 260sh and 335sh nm (ϵ 22 900 and 3 470 dm³ mol^{−1} cm^{−1}); ¹H NMR (CDCl₃, 270 MHz) δ 1.80, 1.86 (br s \times 2, 10H, CH₂), 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); ¹³C NMR (CDCl₃, 67.8 MHz) δ 29.8 [t (1 : 4 : 1) t, ²J_{C,Pt} 18.6 Hz, ³J_{C,Pt(trans)} = ¹J_{C,Pt(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,Pt} = ⁵J_{C,Pt} 9.8 Hz, C- m), 128.7 (C- p), 134.1 [t (1 : 4 : 1) t, ³J_{C,Pt} 19.6 Hz, ²J_{C,Pt} = ⁴J_{C,Pt} 13.7 Hz, C- o], 137.3 [t (1 : 4 : 1) dd, ²J_{C,Pt} 25.9 Hz, ¹J_{C,Pt} 23.1 Hz, ³J_{C,Pt} 21.5 Hz, C- $ipso$], 139.8 [t (1 : 4 : 1) dd, ¹J_{C,Pt} 368.4 Hz, ²J_{C,Pt(trans)} 84.0 Hz, ²J_{C,Pt(cis)} 17.2 Hz, C-4,5]. Satisfactory microanalyses (C, H, P) were obtained.

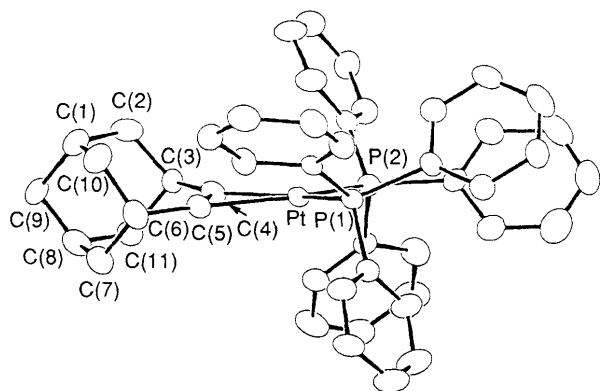


Fig. 1 An ORTEP drawing of one of the two molecules in the asymmetric unit of **4**. Selected bond lengths (Å) and angles (°) for this molecule are representative of all two independent molecules: Pt–P(1) 2.256(3), Pt–P(2) 2.260(4), Pt–C(4) 2.042(13), Pt–C(5) 2.068(14), C(4)–C(5) 1.314(20), P(1)–Pt–P(2) 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 ($^1J_{\text{C,Pt}}$ 368.4 Hz) as well as further splittings by *trans*- and *cis*- ^{31}P ($^2J_{\text{C,P}}$ 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

† Crystal data: **4**: $\text{C}_{47}\text{H}_{44}\text{P}_2\text{Pt}$, $M = 865.90$, triclinic, space group $P\bar{1}$, $a = 21.002(9)$, $b = 15.117(5)$, $c = 12.035(3)$ Å, $\alpha = 97.83(2)$, $\beta = 94.81(3)$, $\gamma = 97.27(3)^\circ$, $U = 3735.0$ Å³, $Z = 4$, $D_c = 1.540$ g cm^{-3} , AFC-5R-(Rigaku) diffractometer, ω -scan, graphite monochromator, Mo-K α 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.

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 π orbital making the alkyne(π) \rightarrow metal($d\pi$) 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 π orbitals to facilitate the metal ($d\pi$) \rightarrow alkyne (π^*) π back donation. As a result, the metallacyclopentene character would be enhanced in **4** causing a slight elongation of the C \equiv C bond.

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