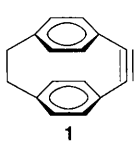
[2.2]Paracyclophane-1-yne: preparation and structural analysis of the bis(triphenylphosphane)platinum complex

Karsten Albrecht,[a] David C. R. Hockless,[b] Burkhard König,[c] Horst Neumann,[b] Martin A. Bennett*[b] and Armin de Meijere*[a]

[a] *Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 2, D-37077 Göttingen, Germany*
[b] *Research School of Chemistry, Australian National University Canberra, ACT 0200, Australia*
[c] *Institut für Organische Chemie der Technischen Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany*

The first platinum complex of [2.2]paracyclophane-1-yne with a formal triple bond in the two-carbon bridge is prepared and fully characterized by spectroscopic techniques as well as an X-ray crystal structure analysis; accordingly, it is best described as a platinacyclopropene.

[2.2]Paracyclophane, the smallest stable member in the [*m.n*]paracyclophane series,[1,2] is characterized by a strong interaction between its two π systems resulting from the proximity of the benzene rings, which are separated by only 2.96 Å (av.). Introduction of one or two double bonds into the bridges of the phane skeleton further increases the inherent strain.[3] The even more highly strained [2.2]paracyclophane-1-yne **1** cannot be isolated, but it has been implied by Psiorz and Hopf as a transient intermediate that undergoes rapid cyclotrimerisation.[4] The occurrence of similar intermediates has been suggested in the synthesis of various 1:2,9:10-dibenzo[2.2]paracyclophane-1,9-diene derivatives.[5]



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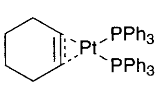

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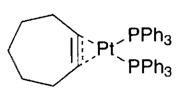
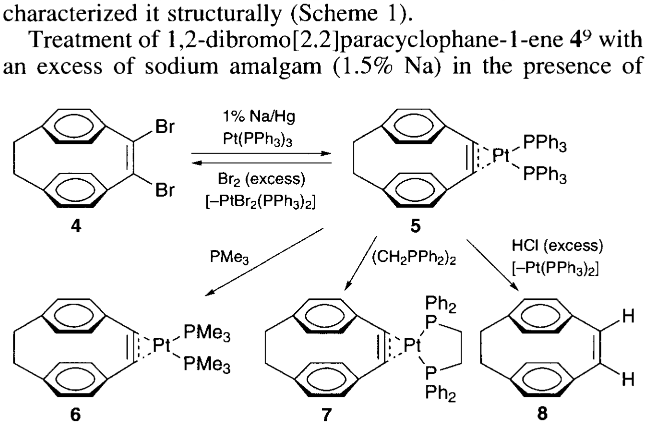


3

Highly strained cycloalkynes and dehydroarenes can be stabilized as complexes with transition-metal fragments such as $(\eta\text{-}C_5H_5)_2Zr(PMe_3)$, $Ni[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]$ and $Pt(PPh_3)_2$.[6] We have previously trapped the zirconocene complex of **1** in the form of its insertion product with but-2-yne and have isolated the $(\eta\text{-}C_5H_5)_2Zr(PMe_3)$ complex of **1**, but were unable to obtain crystals suitable for X-ray analysis.[7] By use of the method reported for the synthesis of the cyclohexyne and cycloheptyne complexes $[Pt(C_6H_8)(PPh_3)_2]$ **2** and $[Pt(C_7H_{10})(PPh_3)_2]$ **3**,[8] respectively, we have prepared the $Pt(PPh_3)_2$ complex **5** of [2.2]paracyclophane-1-yne and have characterized it structurally (Scheme 1).

Treatment of 1,2-dibromo[2.2]paracyclophane-1-ene **4**[9] with an excess of sodium amalgam (1.5% Na) in the presence of $[Pt(PPh_3)_3]$ or $[Pt(C_2H_4)(PPh_3)_2]$ gave **5** as a pale yellow solid in *ca.* 50% yield.†‡ The ^{31}P chemical shift (δ 26.9) and Pt–P coupling constant (3539 Hz) are similar to those of the $Pt(PPh_3)_2$ complexes of cyclohexyne and cycloheptyne.[6] The coordinated carbon atoms give rise to a five-line AA′X pattern (A = ^{31}P, X = ^{13}C) centred at δ 152.2 in the ^{13}C NMR spectrum, and are thus appreciably more shielded than the carbon atoms in **2** (δ 131.6) or **3** (δ 124.0). The IR spectrum of **5** contains no absorption in the 1700–1800 cm^{-1} region where the $\nu(C\equiv C)$ vibrations of **2** and **3** are observed, but it does show an intense band at 1590 cm^{-1} which overlaps with the expected weaker aromatic C=C absorption at 1585 cm^{-1} and is tentatively assigned to $\nu(C\equiv C)$. These observations imply that the description of the Pt–(C≡C) interaction in **5** as a metallacyclopropene is even more valid than in the case of **2** and **3**.



Scheme 1

This conclusion is supported by the results of a single-crystal X-ray analysis of **5** (Fig. 1).§ The structure is typical of a trigonal-planar platinum(0)–alkyne complex, the Pt–P and Pt–C distances being equal within experimental error to those in **2** and **3**.[15] The C(1)–C(2) distance [1.35(2) Å] is close to the standard C=C bond length and is significantly greater than the corresponding separations in **2** and **3** [1.297(8), 1.283(5) Å, respectively].[15] As in [2.2]paracyclophane[16] and [2.2]paracyclophane-1,9-diene,[17] the phane-benzene rings of **4** adopt tub

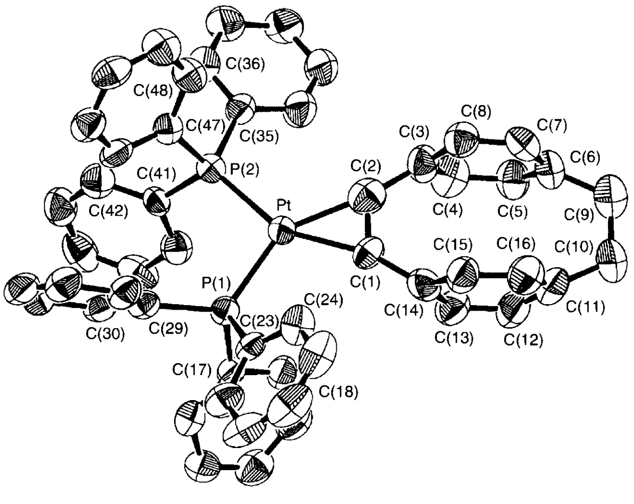
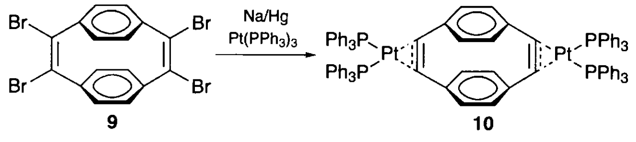


Fig. 1 Molecular structure of **4** with 50% ellipsoids; hydrogen atoms have been omitted. Important bond lengths (Å) and angles (°): Pt–P(1) 2.286(3), Pt–P(2) 2.274(3), Pt–C(1) 2.02(1), Pt–C(2) 2.04(1), C(1)–C(2) 1.35(2), C(2)–C(3) 1.50(2), C(1)–C(14) 1.44(2), C(6)–C(9) 1.49(2), C(10)–C(11) 1.49(2), C(9)–C(10) 1.51(2), phane aromatic C–C 1.36–1.42, P(1)–Pt–P(2) 101.58(2), P(2)–Pt–C(1) 151.8(3), P(2)–Pt–C(2) 113.3(4), C(1)–Pt–C(2) 38.8(5), C(1)–C(2)–C(3) 121(1), C(2)–C(1)–C(14) 122(1), C(9)–C(10)–C(11) 115(1), C(2)–C(3)–C(8) 121(1), C(2)–C(3)–C(4) 119(1), C(4)–C(3)–C(8) 116(1), C(5)–C(6)–C(9) 120(1), C(7)–C(6)–C(9) 122(1), C(5)–C(6)–C(7) 117(1).



Scheme 2

conformations, the bridgehead atoms lying between 0.13(2) and 0.18(2) Å outside the plane of the four unsubstituted carbon atoms. The presence of different bridging groups causes a slight tilting (2.92°) of the phane-benzene rings. The separations between the corresponding substituted carbon atoms C(6)···C(11) and C(3)···C(14) of the phane rings are 2.79 and 2.90 Å, respectively, and the mean distance between the four corresponding unsubstituted carbon atoms is 3.16 Å.

The triphenylphosphane ligands of **5**, like those of **3**,[18] are replaced reversibly by trimethylphosphane to give initially the $Pt(PPh_3)(PMe_3)$ complex of **1** and finally the $Pt(PMe_3)_2$ complex **6** of [2.2]paracyclophane-1-yne, which were readily identified by ^1H and ^{31}P NMR spectroscopy. The platinum–alkyne bond is cleaved by an excess of bromine to give initially a 2-bromovinylplatinum(II) complex and, after 12 h, a mixture of 1,2-dibromo[2.2]paracyclophane-1-ene **4** and *cis*-$[PtBr_2(PPh_3)_2]$.

Treatment of 1,2,9,10-tetrabromo[2.2]paracyclophanediene **9** with sodium amalgam and $[Pt(PPh_3)_3]$ gave, after work-up, a solid whose ^1H and ^{31}P NMR spectroscopic data are consistent with its formulation as the dinuclear bis(triphenylphosphane)platinum complex of [2.2]paracyclophane-1,9-diyne **10** (Scheme 2),¶ but owing to its poor solubility in common organic solvents we have been unable so far to obtain X-ray quality crystals.

The experiments described above are further demonstrations of the concept of stabilizing short-lived reaction intermediates by coordination to a transition metal.

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Footnotes

† *Experimental*: all operations were carried out with use of dry, degassed solvents under purified argon. To a freshly prepared amalgam of mercury (16 g) and sodium (240 mg, 10.4 mmol, 1.5%) was added $[Pt(PPh_3)_3]$ (170 mg, 0.17 mmol) or $[Pt(C_2H_4)(PPh_3)_2]$ (127 mg, 0.17 mmol) in thf (5 ml). A solution of 1,2-dibromo[2.2]paracyclophane-1-ene (180 mg, 0.5 mmol) in thf (8 ml) was added dropwise from a syringe and the mixture was stirred at room temp. for 4 h. During this period the colour changed from yellow to grey and NaBr precipitated. The suspension was separated from the semi-solid amalgam and evaporated to dryness. The residue was treated with diethyl ether (3 × 10 ml) and the solution was filtered through Celite. It was again evaporated to dryness and the residual solid was taken up in a mixture of thf, C_6D_6 and ether. After several days at 0 °C the solution had deposited pale yellow crystals of **4** (74 mg, 46%) whose C, H analyses were satisfactory.

‡ *Physical data* for **5**: ^1H NMR (C_6D_6, 300 MHz) δ 2.94 (s, 4 H, CH_2), 6.55 (br s, 8 H, phane), 6.85–7.00 (m, 18 H, Ph), 7.69–7.78 (m, 12 H, Ph); ^{13}C NMR (C_6D_6, 75 MHz, APT): δ 35.35 (+, s, $C^{9,10}$), 125.88 (−, t, $^3J_{P-C}$ 6.0 Hz, $C^{4,8,13,15}$), 127.95 (−, d, $^3J_{P-C}$ 5 Hz, $C^{3',5'}$), 129.38 (−, s, $C^{4'}$), 131.62 (−, s, $C^{5,7,12,16}$), 134.50 (−, m, $C^{2',6'}$), 136.30 (+, m, $C^{1'}$), 138.69 (+, s, $C^{6,11}$), 143.55 (+, t, $^2J_{Pt-C}$ 10 Hz, $C^{3,14}$), 152.21 (+, 5-line AA′X, $J_{AX} + J_{A'X}$ 80.7 Hz, separation between outer lines 100.7 Hz, $C^{1,2}$); $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) δ 26.9 (t, $^1J_{PtP}$ 3539 Hz); MS(FAB): *m*/*z* (%) 924.2 (100) $[M^+]$, 719.1 (68) $[Pt(PPh_3)_2^+]$; IR (KBr): $\tilde{\nu}$/cm^{-1} 3050m, 3000w, 2910w, 2850w, 1590vs, 1480vs, 1095/1090s, 805m, 745vs, 715vs, 695vs, 540vs, 520/510vs, 500s.

§ **5**: $C_{52}H_{42}P_2Pt\cdot0.5C_6H_6$, M = 368.46, monoclinic, space group $P2_1/n$, a = 12.344(3), b = 26.498(2), c = 12.840(5) Å, β = 92.78(3)°, U = 4195(2) Å^3, Z = 4, D_c = 1.52 g cm^{-3}, dimensions 0.21 × 0.20 × 0.18 mm^3, μ(Cu-Kα) = 70.22 cm^{-1}. A unique diffractometer data set ($2\theta_{max}$ 110°; ω–2θ scan mode; monochromated Cu-Kα radiation, λ = 1.5418 Å) was measured at 213 K. Of the 5173 reflections measured, 4797 were independent; of these 4082 with $I > 3\sigma(I)$ were considered 'observed' and used in full-matrix least-squares refinement with Lorentz/polarisation, analytical absorption (min., max. transmission factors 0.217, 0.442) and 5.4% linear decay correction after solution of the structure by heavy-atom Patterson methods.[10] All non-hydrogen atoms were refined anisotropically. Difference map residues were modelled most satisfactorily as a benzene molecule of crystallization, refined with full occupancy as an idealized hexagon over a centre of symmetry. Hydrogen atoms were included in calculated positions and held fixed with common thermal vibration parameters for each of the two independent molecules. Refinement on F of a total of 524 individual parameters converged with residuals R = 0.052 and R_w = 0.059. Scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_C[12] and the values for f' and f'' were those of ref. 13. The structure was refined by use of the XTAL 3.2 program system.[14] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ *Physical data* for **10**; ^1H NMR (C_6D_6, 300 MHz) δ 6.52 (s), 6.85–7.08 (m), 7.41–7.81 (m); $^{31}P\{^1H\}$ NMR (C_6D_6, 121 MHz) δ 26.63 (t, $^1J_{PtP}$ 3550 Hz).

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