The First Crystallographically Characterized Transition Metal Buckybowl Compound: $C_{30}H_{12}$ Carbon−Carbon Bond Activation by $Pt(PPh_3)_2$

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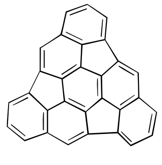
Semibuckminsterfullerene ($C_{30}H_{12}$, **1**) represents half of the buckminsterfullerene (C_{60}) molecule with the rim carbons capped by hydrogen atoms.[1−3] Unlike C_{60}, however, $C_{30}H_{12}$ has a readily accessible internal surface and π-system for the potential coordination of transition metal complexes. We have been studying the metal coordination chemistry of curved polyaromatic hydrocarbons such as corannulene ($C_{20}H_{10}$) and other buckybowls and report here the first structural characterization of the unusual product from the reaction of $Pt(CH_2{=}CH_2)(PPh_3)_2$ and **1**.



1

$C_{30}H_{12}$ and $Pt(CH_2{=}CH_2)(PPh_3)_2$ were reacted together at room temperature in toluene under inert atmosphere conditions for 15 h and then refluxed for 1 h. $Pt(\eta^2\text{-}\sigma\text{-}C_{30}H_{12})(PPh_3)_2$, **2**, was isolated in low yield (~5−10%) via column chromatography and recrystallized by slow evaporation of a benzene/cyclohexane solution.[4] A single-crystal X-ray structural determination revealed that the $Pt(PPh_3)_2$ unit has indeed coordinated to the buckybowl (Figure 1).[5,6] But instead of binding to one of the localized C=C double bonds on either the inner or outer surface the Pt(0) center has oxidatively added to and broken one of the rim C−C bonds to form an η^2-σ-bonded Pt(II)-buckybowl compound.

The structure of **2** is shown in Figure 1 along with selected bond distances and angles in Table 1. As one might qualitatively expect, the Pt center is folded 42° outward (from the mean plane defined by atoms C1−C5) to the less sterically hindered exo-face of the $C_{30}H_{12}$ ligand (Figure 1b). The breaking of the C1−C5 σ-bond in **1** will naturally splay the resulting sp^2 hybrid orbitals to the position of the Pt center shown in Figure 1. The 9,10-dihydroplatina-anthracene system, $Pt(PR_3)_2(\sigma\text{-}\eta^2\text{-}C_6H_4CH_2C_6H_4)$, **3**, prepared from the dilithioorganic precursor and not from a C−C bond breaking reaction, is the most analogous model compound that has been structurally characterized.[7]

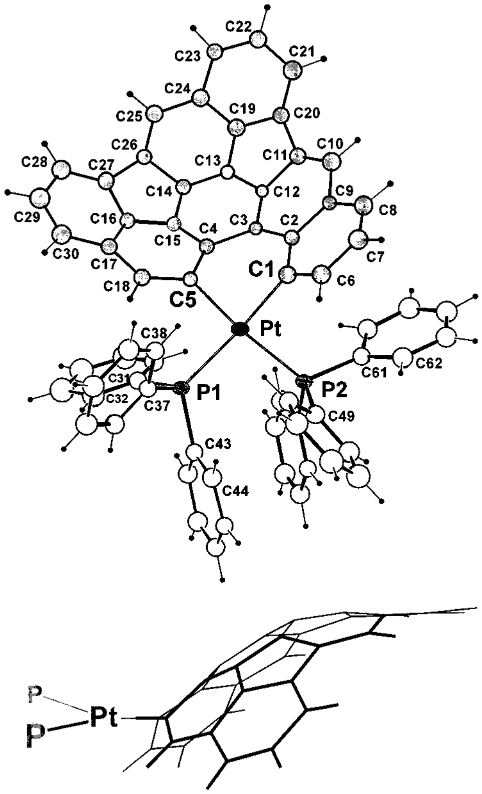
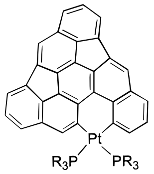


Figure 1. (top) ORTEP plot of **2**. (bottom) Stick figure representation of **2** with the phenyl rings on the PPh_3 ligands omitted for clarity.



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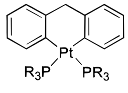

3

The bond distances and angles about the metal centers in **2** and **3** are quite similar, except for the C1−Pt−C5 angle, which is opened up 6° in **2** (87.9(5)° vs 81.3(4)° for **3**) and the larger C1−C5 separation (2.84 Å in **2** vs 2.67 Å in **3**). This reflects the considerably greater ring strain present in the curved structure of precursor **1**. The other structural differences present are also related to the larger and more sterically demanding structure of **2** relative to 9,10-dihydroplatina-anthracene. There is a distinct 16° rotation of the PPh_3−Pt−PPh_3 plane relative to the C−Pt−C plane caused by steric hindrance between the PPh_3 and the $C_{30}H_{12}$ ligands. The higher flexibility of the 9,10-dihydroplatina-anthracene moiety also leads to greater folding of the anthracene environment about the Pt away from square planar (average C_6 dihedral angle of 37.5°) relative to **2** (23.5°).

The structural features of the $C_{30}H_{12}$ ligand in **2** are surprisingly similar to that predicted from *ab inito* calculations for **1**, particularly with respect to the C−C bond distances, which, at first glance, appear to be somewhat randomly distributed as short and longer distances.[6] The main difference, of course, is that

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(1) Rabideau, P. W.; Abdourazak, A. H.; Folsom, H.; Marcinow, Z.; Sygula, A.; Sygula, R. *J. Am. Chem. Soc.* **1994**, *116*, 7891−2.

(2) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res* **1996**, *29*, 235−42.

(3) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406−408.

(4) Spectroscopic data: ^1H NMR (250 MHz, $CDCl_3$) 4.2 (td, 1H, J_{X-H} = 7 Hz, J_{Pt-H} = 110 Hz, X coupling could be to a P or H), 5.7 Hz (d, 1H, J_{X-H} = 7 Hz, X coupling could be to a P or H), 6.6 (t, 1H, J_{X-H} = 7 Hz, X coupling could be to a P and/or H), 6.9−7.3 (m, PPh_3 phenyl H), 7.5−7.8 (m); $^{31}P\{^1H\}$ NMR (250 MHz, $CDCl_3$, H_3PO_4 ref) 26.1 (pseudo-singlet, J_{Pt-P} = 3876 Hz, the Pt satellites show a doublet−doublet ^{31}P pattern, indicating that the primary ^{31}P peak at 26.1 is not a first-order singlet, consistent with the formal lack of symmetry and presence of magnetic inequivalence between the two PPh_3 groups in **2**).

(5) Crystal Data: monclinic $P2_1/n$, Z = 4, a = 14.646(6) Å, b = 16.392(3) Å, c = 28.02(1) Å, b = 95.78(3)°, V = 6691(1) Å.[3] Data collected at 150K. Refinement on F^2 converged at R = 7.4%, R_w = 6.2%, with GOF(F^2) = 1.383. There were three benzene and one cyclohexane solvent molecules present in the unit cell. One of the benzenes is disordered with a likely partial substitution of cyclohexane at that site.

(6) Supporting Information. See masthead for instructions.

(7) Alcock, N. W.; Bryars, K. H.; Pringle, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 1433−1439.

S0002-7863(97)03454-9 CCC: $15.00

Table 1. Selected Bond Distances (Å) and Angles (deg) for **2**[a]

Pt−P1	2.348(4)	Pt−P2	2.323(4)
Pt−C1	2.04(2)	Pt−C5	2.05(1)
C1−C2	1.37(2)	C1−C6	1.44(2)
C2−C3	1.45(2)	C2−C9	1.45(2)
C3−C4	1.49(2)	C3−C12	1.41(2)
C4−C5	1.47(2)	C4−C15	1.37(2)
C5−C18	1.39(2)	C6−C7	1.41(2)
C7−C8	1.36(2)	C8−C9	1.42(2)
C9−C10	1.48(2)	C10−C11	1.33(2)
C11−C12	1.44(2)	C11−C20	1.50(2)
C12−C13	1.39(2)	C13−C14	1.36(2)
C13−C19	1.35(2)	C14−C15	1.41(2)
C14−C26	1.45(2)	C15−C16	1.37(2)
C16−C17	1.43(2)	C16−C27	1.43(2)
C17−C18	1.42(2)	C17−C30	1.43(2)
C19−C20	1.41(2)	C19−C24	1.41(2)
C20−C21	1.37(2)	C21−C22	1.43(2)
C22−C23	1.34(2)	C23−C24	1.42(2)
C24−C25	1.44(2)	C25−C26	1.37(2)
C26−C27	1.51(2)	C27−C28	1.38(2)
C28−C29	1.42(2)	C29−C30	1.38(2)
P1−Pt−P2	96.0(1)	C1−Pt−C5	87.9(5)
P1−Pt−C5	89.9(4)	P2−Pt−C1	88.0(4)
P2−Pt−C5	164.8(4)	P1−Pt−C1	171.9(4)
Pt−C1−C2	125(1)	Pt−C1−C6	120(1)
Pt−C5−C4	113.7(9)	Pt−C5−C18	130(1)
C2−C1−C6	115(1)	C3−C2−C9	114(1)
C4−C3−C12	115(1)	C4−C5−C18	114(1)
C10−C11−C20	133(1)	C12−C11−C20	106(1)
C11−C12−C13	106(1)	C12−C13−C19	111(1)
C15−C14−C26	111(1)	C4−C15−C16	125(1)
C14−C15−C16	106(1)	C15−C16−C27	112(1)
C17−C16−C27	125(1)	C16−C17−C18	115(1)
C16−C17−C30	113(1)	C18−C17−C30	130(1)
C5−C18−C17	126(1)	C13−C19−C20	109(1)
C20−C19−C24	127(1)	C11−C20−C19	105(1)
C11−C20−C21	136(1)	C19−C24−C23	112(1)
C23−C24−C25	127(1)	C14−C26−C25	115(1)
C14−C26−C27	103(1)	C25−C26−C27	138(1)
C16−C27−C26	105(1)	C26−C27−C28	135(1)
C28−C29−C30	125(1)		

[a] Only angles for the buckybowl portion of the structure that deviate more than ±4° from 120° are listed. Values in parentheses are esd's.

the curvature of the bowl is less in **2** due to the breaking of one of the rim five-membered-ring C−C bonds. The calculated average quaternary carbon atom pyramidalization angle (POAV1) for **1** is 4.8° versus 2.9° for the X-ray structure on **2**.[6,8−11]

Homogeneous C−C σ-bond breaking reactions are quite difficult and usually only occur with strained rings such as cyclopropane,[12] biphenylene,[13−15] or when a C−C σ-bond is held in close proximity to a metal center combined with the generated aromaticity of the product.[16] In the case of saturated hydrocarbons such as cyclopropane, C−H bond activation is believed to be the first step, followed by C−C bond cleavage.[12] In the case of unsaturated π-systems, coordination of the metal center to the π-system followed by oxidative addition of the C−C bond to the metal center represents an alternate mechanistic possibility. Jones and co-workers have carefully studied the C−C bond breaking reactions in biphenylene and find that $Cp^*Rh(CH_2{=}CH_2)_2$ accomplishes this by initial C−H bond activation followed by C−C bond cleavage (and subsequent reformation of the C−H bond).[14] They have tried the same reaction with biphenylene and $M(PEt_3)_3$ (M = Pd, Pt) and also see C−C bond cleavage reactions, but in this case they believe that C−C bond breaking is probably preceded by simple η^2-π-arene coordination.[15] To our knowledge, this is the first example of metal induced C−C bond cleavage in a nonheterocyclic five-membered ring. This is probably related to the fact that **1** possesses very unusual, highly strained five-membered rings. We believe that the cleavage is proceeding via simple π-coordination of $Pt(PPh_3)_2$ to one of the rim C=C bonds adjacent to the five-membered-ring site in **1**, followed by C−C oxidative addition.

That **1** should possess strained C−C bonds along the rim of the molecule is not surprising. The synthesis of **1** requires high-temperature pyrolysis to provide enough thermal energy for the more "open" precursor species to close the rim bonds to form the curved buckybowl.[1] The site of C−C bond cleavage is also where one would predict the maximum release of steric strain, i.e., the five-membered, formally nonaromatic ring sites, which are the source of curvature in **1**. These also are the longest and most strained C−C bonds in the structure (1.51 Å from the X-ray structure on **2**, 1.53 Å from ab initio calculations on **1**). The 3-fold symmetry in **1**, of course, means that C−C bond breaking can occur at any of the three equivalent rim five-membered-ring exo C−C bonds.

The coordination of transition metal centers to these unusual curved polyaromatic hydrocarbon ligands is a new area of organometallic chemistry and several researchers are actively working on preparing new complexes and studying their reaction chemistry. Of course, the coordination of metals to C_{60} has also garnered considerable interest, although the coordination is generally limited to η^2-π-coordination.[17] Rubin and co-workers were the first to demonstrate the Co initiated C−C bond cleavage in a derivatized version of C_{60}.[18] Considerably less common is the use of fullerene subunits as ligands for transition metal centers. O'Connor, Siegel, and co-workers recently published a paper on the coordination of Cp*Ru to corannulene, the smallest curved polyaromatic hydrocarbon ligand, in an η^6-coordination mode.[19] Although they did not have an X-ray structure, it is likely that the Ru is coordinated to an exo-face of one of the rim C_6 corannulene rings. Balch and co-workers[20] have reported an X-ray structure on the more highly curved polyaromatic $C_{36}H_{12}$, first prepared by Scott and co-workers, and are working on preparing transition metal compounds of this ligand.[21] It is clear that interest in these novel ligands will continue to grow as improved syntheses are reported for these and other curved polyaromatic hydrocarbon compounds.

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Supporting Information Available: X-ray experimental details with positional parameters and full bond distances and angles; comparison of X-ray bond lengths for **2** with ab initio calculated bond lengths for **1**; calculated pyramidalization values for **2** (11 pages). See any current masthead page for ordering and Internet access instructions.

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(8) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137−142.

(9) Haddon, R. C. *Acc. Chem. Res* **1988**, *21*, 243−249.

(10) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385−3389.

(11) Haddon, R. C. *Science* **1993**, *261*, 1545−1550.

(12) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346−7355.

(13) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647−3648.

(14) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016−2023.

(15) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* Submitted for publication.

(16) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260−1261.

(17) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res* **1992**, *25*, 134−142.

(18) Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1997**, *118*, 3775−3776.

(19) Seiders, T. J.; Baldridge, K. K.; O'Conner, J. M.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 4781−4782.

(20) Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5766−5767.

(21) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744.