Formal Insertion of Acetylide into a C–H Bond To Give a Bis(diphenylphosphino)propenyl Ligand

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Received August 16, 1988

Bridging ligands are commonly used to prevent fragmentation of binuclear or cluster complexes and have aided the systematic development of chemistry and catalysis involving such compounds. The most commonly used binucleating ligand is bis(diphenylphosphino)methane, dppm, which is relatively inert under mild conditions.[2,3] However, under basic conditions, the deprotonated form $(Ph_2P)_2CH^-$ may be formed and further derivatized by reaction with electrophiles, while ortho-metalation of a phenyl substituent or cleavage of Ph–P or P–CH$_2$ bonds or both may occur on thermolysis of metal complexes of dppm.[4] This article reports a new reaction, which occurs at room temperature, to give a formal insertion of acetylide into a CH bond of dppm. The reaction was discovered in an attempt to extend the modeling, using coordinatively unsaturated cluster complexes, of reactions of acetylene on a platinum(111) surface to the binding of a possible acetylide species on platinum.[5]

The new chemistry is summarized in Scheme I. Reaction of $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, **1**,[6] $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCH})(CO)(\mu\text{-dppm})_3]^{2+}$, **2**,[5] or $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCH})Cl(\mu\text{-dppm})_3]^+$, **3**,[5] with excess NaCCH in CH$_2$Cl$_2$-xylene gave the new complex $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCH})(\mu\text{-dppm})_2\{\mu_2\text{-}\eta^3\text{-}(Ph_2P)_2CHCH=CH\}]^+$, **4**, as the PF$_6^-$ salt. The reaction with **1** requires proton abstraction from solvent to give the μ_3-HCCH group and proceeds in lower yield (46%) compared to the reaction with **3** (yield 82%) which does not require this step.

The structure of the cation **4** was determined crystallographically[7] and is shown in Figure 1. The overall structure is similar to that found for **3**, with some differences in the binding of the HCCH ligand. Thus the Pt(3)–C(5) distance [2.11 (2) Å] is somewhat longer than the analogous distance in **3** [1.99 (3) Å], reflecting the higher trans influence of the vinylic carbon than of the chloride ligand. The most surprising feature was the formation of the $\mu_2\text{-}\eta^3$-3,3-bis(diphenylphosphino)propen-1-yl ligand, defined in Figure 1 by atoms P(3), P(4), C(2), C(7), and C(6). The distances C(6)–C(7) and C(2)–C(7) are 1.30 (3) and 1.57 (3) Å, typical of carbon–carbon double and single bonds,

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(7) Crystallographic measurements were made with Mo Kα X-rays and an Enraf-Nonius CAD4F diffractometer. Red transparent prisms were grown from dichloromethane and pentane by slow diffusion. A suitable crystal was chosen and sealed in a capillary as it decomposed rapidly in air by loss of solvent. Crystal data for $[Pt_3(\mu_3\text{-}\eta^2\text{-HCCH})\{\mu_2\text{-}\eta^3\text{-}(Ph_2P)_2CHCH=CH\}(\mu\text{-dppm})_2][PF_6]\cdot2CH_2Cl_2$: $C_{81}H_{73}Cl_4F_6P_7Pt_3$, MW = 2104.4, triclinic, $P\bar{1}$, a = 14.167 (3) Å, b = 14.466 (3) Å, c = 20.120 (6) Å, α = 85.49 (2)°, β = 88.24 (2)°, γ = 86.00 (2)°, U = 4099 (2) Å^3, Z = 2, D_c = 1.705 g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 54.80 cm^{-1}, T = 296 K. The structure was solved by using 6349 independent reflections, with absorption corrected intensities, $2° \leq \theta$(Mo Kα) $\leq 22°$ and $I \geq 3\sigma(I)$. Full-matrix least-squares refinement of 366 parameters (phenyl rings as rigid hexagons of 6/mmm symmetry and C–C = 1.38 Å) gave R = 0.045, R_w = 0.064. All calculations were performed on a GOULD 32/27 computer with the GX suite of programs.[8] Complex neutral atom scattering factors were taken from ref 9. Atomic coordinates, anisotropic displacement parameters, bond lengths and angles, and structure factors have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1988.
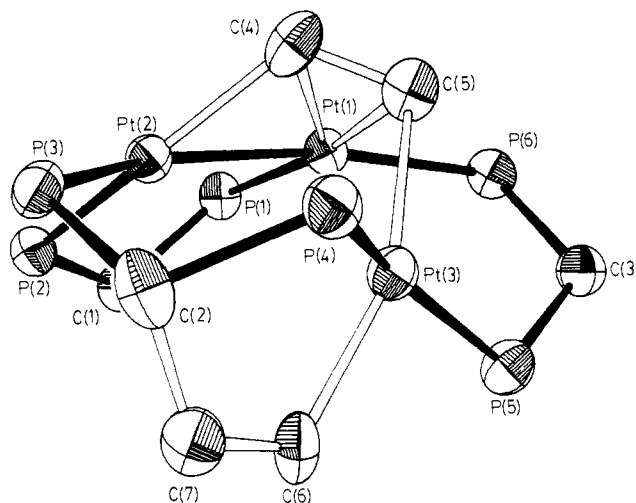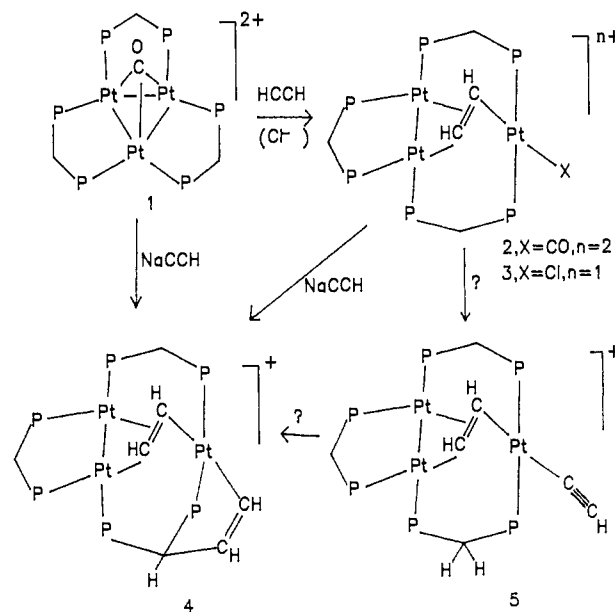

Figure 1. The structure of **4**, with phenyl rings omitted for clarity; the atoms are represented by thermal ellipsoids of 50% probability. Selected bond lengths are as follows: Pt(1)–Pt(2) 2.655 (2), Pt(1)–C(4) 2.20 (2), Pt(1)–C(5) 2.24 (2), Pt(2)–C(4) 2.04 (2), Pt(3)–C(5) 2.11 (2), and Pt(3)–C(6) 2.11 (2) Å.

Scheme I

respectively. The new ligand bridges the nonbonded metal atoms Pt(2) and Pt(3) through the phosphorus donors P(3) and P(4), and it also chelates the Pt(3) center by forming the Pt(3)–P(4) and Pt(3)–C(6) bonds. There is a severe tetrahedral distortion from square-planar coordination geometry around the Pt(3) atom [C(5)–Pt(3)–C(6) = 158.2 (7)°, P(4)–Pt(3)–P(5) = 151.7 (2)°]. The ^{1}H, ^{31}P{^{1}H}, and ^{195}Pt{^{1}H} NMR data,[10] including the 2D ^{1}H–^{1}H correlated spectrum needed to assign proton signals, are fully consistent with structure **4** and prove that there is no fluxionality of the acetylene ligand.

(8) Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51.

(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, Great Britain, 1974; Vol. IV, pp 99, 149.

(10) NMR data (ref Me$_4$Si (^{1}H), H$_3$PO$_4$ (^{31}P), K$_2$PtCl$_4$ (^{195}Pt)), multiplicities due to ^{195}Pt couplings not reported, *J* values in Hz. **4**: δ (^{31}P, acetone) −11.2 [*m*, ${}^3J$(P^{1}P^3) = 9.0, ${}^2J$(P^{1}P^2) = 43, P^1], −6.6 [*m*, ${}^2J$(P^{2}P^3) = 24, P^2], 53.8 [*m*, ${}^3J$(P^{3}P^6) = 97, ${}^2J$(P^{3}P^4) = 128, P^3], 48.5 [*m*, ${}^2J$(P^{4}P^5) = 477, P^4], 6.6 [*m*, ${}^2J$(P^{5}P^6) = 64, P^5], 2.5 [*m*, P^6]; δ (^{195}Pt, acetone) −3521 [dd, ${}^1J$(Pt^{1}P^6) = 3390, ${}^1J$(Pt^{1}P^1) = 3890, ${}^1J$(Pt^{1}Pt^2) = 2375, Pt^1], −2852 [dddd, *J*(Pt^{2}P^5) = 125, ${}^2J$(Pt^{2}P^6) = 624, ${}^1J$(Pt^{2}P^2) = 2288, ${}^1J$(Pt^{2}P^3) = 3757, Pt^2], −2618 [dd, ${}^1J$(Pt^{3}P^4) = 3471, ${}^1J$(Pt^{3}P^5) = 3692, *J*(Pt^{2}Pt^3) = 790, Pt^3]; δ (^{1}H, acetone) 13.0 [s, 1 H, C${}^4H$], 8.0 [C${}^5H$], 6.05 [C${}^6H$], 3.91 [m, 2 H, C${}^7H$, C${}^2H$], other methylene protons at δ 4.13, δ 4.58, δ 5.00 ppm.

It is possible that the reaction proceeds through an acetylide intermediate **5**, which then undergoes rearrangement to give **4**. The detailed mechanism is unknown, but, given the basic medium with excess NaCCH present, a multistep process involving deprotonation of a μ-dppm ligand is considered likely. Reaction of **2**-d_2, prepared from DCCD, with NaCCH led to scrambling of the deuterium label amongst the positions at C(4), C(5), C(6), and C(7). Therefore it is not possible to distinguish between mechanisms in which coupling of dppm with acetylide occurs or in which the carbanion center of a deprotonated dppm ligand attacks coordinated acetylene; the latter is favored by organometallic precedents and by proximity of the functional groups. The formation of **4** appears to be a unique functionalization of a μ-dppm ligand[2-4] and suggests that a more extensive chemistry, involving coupling of μ-dppm ligands and unsaturated reagents under basic conditions, is probable.

Supplementary Material Available: Tables of X-ray crystallographic data, fractional atomic coordinates and isotropic displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles (9 pages); table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

2-Seco[1.1.1.1]pagodyl Cation. Strong Stabilization of a Trivalent Carbocation by C–C σ-Bond Hyperconjugation[1]

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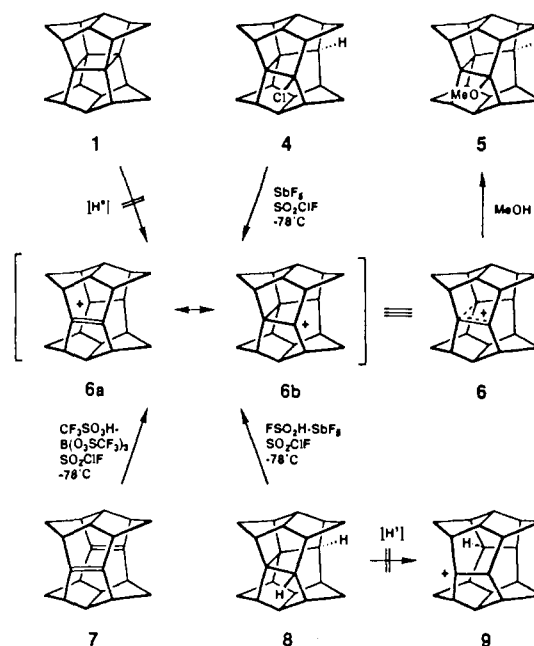
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During the course of our investigations[2,3] on the superacid-catalyzed isomerization of highly symmetrical undecacyclic $C_{20}H_{20}$ hydrocarbon [1.1.1.1]pagodane **1**[4] to its structurally closely related isomer, pentagonal dodecahedrane **2**,[5] we serendipitously discovered the formation of remarkably stable "pagodane dication" **3**. This novel 2π-electron homoaromatic system can be represented by several resonance structures (e.g., **3a**, **3b**), but D_{2h} equilibrium structure **3** is stabilized relative to any single localized structure like **3a** due to strong interaction of the two empty p-lobes with a periplanar strained C–C σ-bond.[2] In this context, we became

(1) Considered as Stable Carbocations, Part 274, at the University of Southern California. For part 273, see ref 2b.

(2) Prakash, G. K. S.; Krishnamurthy, V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. (a) *J. Am. Chem. Soc.* **1986**, *108*, 836-838. (b) *J. Am. Chem. Soc.* **1988**, *110*, 7764-7772.

(3) This transformation has been achieved by catalytic, thermodynamically controlled isomerization: Fessner, W.-D.; Murty, B. A. R. C.; Wörth, J.; Hunkler, D.; Fritz, H.; Prinzbach, H.; Roth, W. D.; Schleyer, P. v. R.; McEwen, A. B.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 452-453.

(4) Fessner, W.-D.; Sedelmeier, G.; Spurr, P. R.; Rihs, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1987**, *109*, 4626-4642.

(5) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446-5450.

Scheme I

interested in the bonding situation of the related 2-secopagodyl monocation **6** which is formally derived from pagodane **1** by protonation of the four-membered ring.
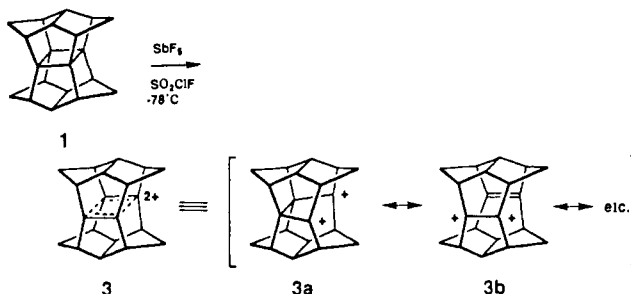
All our attempts to protonate pagodane **1** to generate cation **6** with superacids,[6a] including the newly developed only mildly oxidizing superacid system $CF_3SO_3H:B(O_3SCF_3)_3$,[6b] were unsuccessful. Under all these conditions, dication **3** was exclusively formed by rapid two-electron oxidation. In contrast, dissolution of valence isomer bissecododecahedradiene **7**[7] in the $CF_3SO_3H:B(O_3SCF_3)_3/SO_2ClF$ system resulted in the desired monoprotonation, as became evident with the independent generation of the same ion by careful ionization[8a] of 2-chlorosecopagodane **4**[8b] in a 5-fold excess of SbF_5 in SO_2ClF at -78 °C. The 50-MHz ¹³C NMR spectrum[9a] of each light yellow colored solution showed the same 12 ¹³C resonances with relative intensities and multiplicities similar to halide progenitor **4**.[9b] This is in accord with the formation of monocation **6** with (retained) C_s symmetry. Seco-cation **6** was also formed on protolytic ionization of seco-

(6) (a) Both in $FSO_3H:SbF_5$ as well as $CF_3SO_3H:SbF_5$ systems. (b) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1984**, *49*, 4591-4594. The oxidizing behavior of $CF_3SO_3H:B(O_3SCF_3)_3$ in the case of pagodane **1** remains unexplained.

(7) Spurr, P. R.; Murty, B. A. R. C.; Fessner, W.-D.; Fritz, H.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 455-456.

(8) (a) Ionizations were carried out with ≈15 mg of **4** in 0.9 mL of SbF_5/SO_2ClF. (b) The chloro derivative **4** was prepared from bissecododecahedrene:[7] Lutz, G.; Hunkler, D.; Rihs, G.; Prinzbach, H. *Angew. Chem.*, in press.

(9) (a) ¹³C and ¹H NMR spectra were obtained on a Varian Associates Model VXR-200 NMR spectrometer equipped with a 5 mm ¹H/¹⁹F broadband variable-temperature probe. (b) ¹³C NMR (CDCl₃, ambient). **8**: δ 104.5 (C2), 76.8 (C1), 70.3 (C11), 59.7 (C6, C17), 58.6 (C7, C16), 54.3 (C12), 53.3 (C3, C15), 45.2 (C10, C18), 44.1 (C8, C20), 39.3 (C5, C13), 36.3 (C9, C19), and 34.8 (C4, C14). **5**: δ 102.2 (C2), 74.5 (C1), 68.8 (C11), 59.8 (C6, C17), 59.4 (C7, C16), 55.1 (C12), 49.6 (OCH₃), 44.7 (C3, C15), 43.1 (C10, C18), 41.7 (C5, C13), 39.9 (C8, C20), 36.5 (C9, C19), 34.2 (C4, C14).