further cyclize with EtC≡CEt (72 h, 70 °C). The reaction of $Ta(DIPP)_3Cl_2$ with 2 equiv of Na/Hg and excess MeC≡CMe provides the tetramethylmetallacycle, $(\mathrm{DIPP})_3\overline{\mathrm{Ta(CMe{=}CMeCMe{=}C}}\mathrm{Me})$ (**8**) (this compound has yet to be crystallized).[9,21]

The isolation of both metallacyclopentadienes and 7-metallanorbornadienes in this cyclization system suggests that tantallacyclopentadienes may be immediate precursors to compounds **5** and **6**.[22] Finally, we observe (by $^1H$ NMR) that $(\eta^6\text{-}C_6Me_6)Ta(DIPP)_2Cl$ reacts with a large excess of EtC≡CEt (20 equiv in $Et_2O$, room temperature, 8 h) to provide $C_6Me_6$ (quantitatively), $(\eta^6\text{-}C_6Et_6)Ta(DIPP)_2Cl$ (ca. 93%), and free $C_6Et_6$ (ca. 20%). The fact that no other species are observed throughout the reaction secures the validity of 7-tantallanorbornadienes as one intermediate in this early transition metal cyclization.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also acknowledge support by a Flinn Foundation Grant of the Research Corporation and the financial support of the taxpayers of the State of Arizona.

**Supplementary Material Available:** Analytical and spectral data for compounds **5**–**8** and full details of the structure solution and tables of bond distances and angles and atomic positional and thermal parameters for $(\eta^6\text{-}C_6Me_6)Ta(DIPP)_2Cl$ (13 pages). Ordering information is given on any current masthead page.

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(21) $^1H$ NMR ($C_6D_6$, 30 °C): $CMe_\alpha$, δ 2.16; $CMe_\beta$, δ 1.71.

(22) (a) The difficulty in reducing Ta(V) to Ta(III) makes the reductive retrocyclization of the metallacyclopentadiene to a bis(alkyne) an unlikely process in this early metal cyclotrimerization; tantallacyclopentadienes are the most likely immediate precursors to the arene complexes. For the late metal cobalt systems, a direct *cyclobutadiene*-bis(alkyne) interconversion is probable, ref 22b. (b) Ville, G. A.; Vollhardt, K. P. C.; Winter, M. J. *Organometallics* **1984**, *3*, 1177.

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## Models for Reactions of Acetylene on Platinum(111): The $\mu_3$-$\eta^2$-Acetylene Derivative

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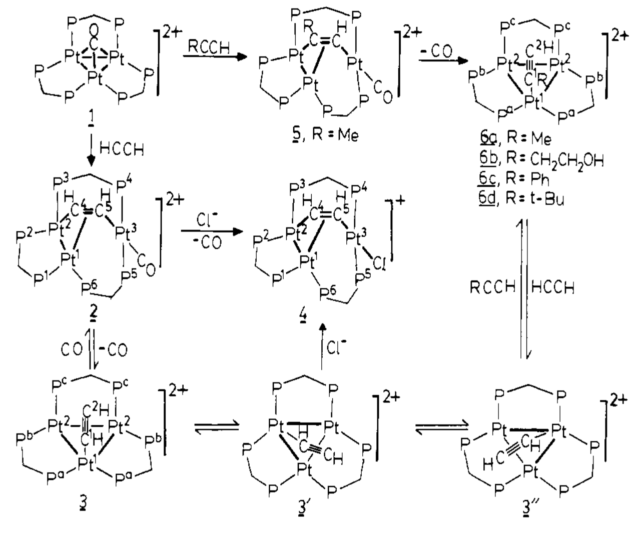
The reactions of acetylene with the Pt(111) surface have been studied in detail;[2] the species $Pt_3(\mu_3\text{-}\eta^2\text{-HCCH})$, $Pt_3(\mu_3\text{-}\eta^2\text{-C}{=}CH_2)$, and $Pt_3(\mu_3\text{-}CCH_3)$ are formed sequentially, and theoretical studies of each species have been carried out.[3] This article reports an attempt to mimic this chemistry[4] by reaction of acetylene with the coordinatively unsaturated cluster $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ (**1**, dppm = $Ph_2PCH_2PPh_2$)[5] and the characterization of the first $Pt_3(\mu_3\text{-}\eta^2\text{-HCCH})$ complexes.[6] The chief chemical results are shown in Scheme I.

Scheme I



The reaction **1** with acetylene to give **2**[7] is very rapid at room temperature, and CO loss to give **3** occurs more slowly (several hours, flushing with acetylene); excess CO reacts rapidly with **3** to give back **2** but does not displace acetylene from platinum. With bulky acetylene derivatives **6** is formed more slowly (several days when R = *t*-Bu), and the intermediate **5** cannot be isolated. Reaction of chloride with **2** or **3** gives **4**.

X-ray analysis[8-10] of $[Pt_3Cl(HC{\equiv}CH)(dppm)_3][PF_6]$, **4**, reveals that the cation has the structure shown in Figure 1. The three platinum atoms define an approximately isosceles triangle whose edges are bridged by the dppm ligands. The $Pt_3$ triangle contains only one metal–metal bond, between Pt(1) and Pt(2), of 2.631 (2) Å; the Pt(1)–Pt(3) and Pt(2)–Pt(3) distances [3.232 (2) and 3.277 (2) Å] lie outside the accepted range (2.6–2.8 Å) for Pt–Pt bond lengths.[11] The HC≡CH ligand lies above the face of the $Pt_3$ triangle. It is σ-bonded to Pt(2) and Pt(3) [Pt–C 2.05 (3), 1.99 (3) Å] and π-bonded to Pt(1) [Pt–C 2.17 (3), 2.21 (3) Å] in such a way that each Pt atom is in a structurally different environment. The $Pt_3(HC{\equiv}CH)$ unit thus contains a distorted example of $\mu_3\text{-}(\eta^2\text{-}\|)$ bonding, which is the typical mode of attachment of alkynes to $M_3$ triangles,[6] although it appears to be

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(4) For a study of HCCH with $[Pt_3(\mu_3\text{-H})(\mu\text{-dppm})_3]^+$ to give $[Pt_3H(\mu_3\text{-}\eta^2\text{-CCH}_2)(\mu\text{-dppm})_3]^+$ see: Rashidi, M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111.

(5) Ferguson, G.; Lloyd, B. R.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 344.

(6) Some $\mu_2\text{-}\eta^2$-alkyne complexes but no μ-HCCH complexes of any kind of platinum are known. Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Thomas, M. D. O.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 2182. Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 862. Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(7) Satisfactory elemental analyses have been obtained for all complexes (as the $PF_6^-$ salts) shown in Scheme I.

(8) Crystal data: $C_{77}H_{68}ClF_6P_7Pt_3$, $M$ = 1944.9, orthorhombic, space group *Pnab* [no. 60, equivalent positions $\pm(x, y, z)$, $\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 - z)$, $\pm(^1/_2 - x, y, -z)$, $\pm(x, ^1/_2 + y, ^1/_2 - z)$], $a$ = 22.987 (4) Å, $b$ = 27.408 (9) Å, $c$ = 25.701 (11) Å, $U$ = 16192 (9) Å$^3$, $Z$ = 8, $D_{calcd}$ = 1.596 g cm$^{-3}$, $F(000)$ = 7520, $\mu$(Mo Kα) = 54.5 cm$^{-1}$, $T$ = 295 K.

The structure is based on 3925 independent absorption corrected intensities [$\theta$(Mo Kα) ≤ 23°, $I \geq 3\sigma(I)$]. Full-matrix least-squares refinement of 301 parameters gave $R$ = 0.059, $R_w$ = 0.069, $S$ = 2.5, $|\Delta\rho| \leq$ 1.1e Å$^{-3}$. Anisotropic displacement parameters were used only for Pt, Cl, and P atoms. Phenyl rings were treated as rigid groups. Contributions for all H atoms, except those of the HC≡CH ligand and of the disordered ring J (vide retro), were included. There are two crystallographically distinct $[PF_6]^-$ sites, both straddling diad axes and both disordered. Ring J is also disordered over two orientations related by an approximately 90° twist about the P–C bond.

Complex neutral atom scattering factors were taken from ref 9. All calculations were performed on a GOULD 3227 computer with the GX program package (ref 10).

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

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0002-7863/87/1509-6527$01.50/0

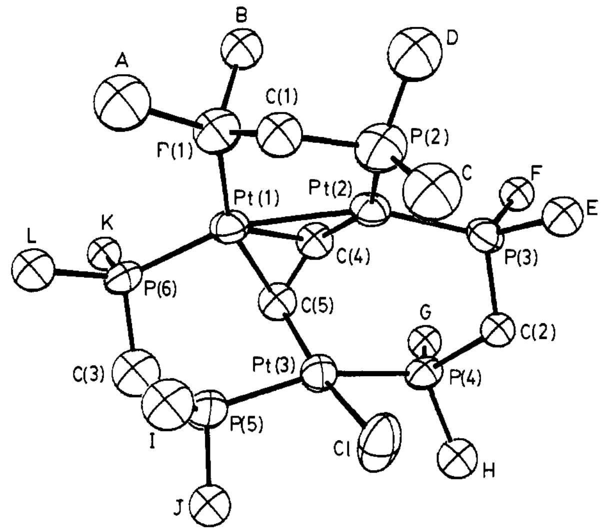

**Figure 1.** A view of the $[Pt_3Cl(HC{\equiv}CH)(dppm)_3]^+$ cation. Selected bond lengths are as follows: Pt(1)-P(1), 2.25 (1); Pt(1)-P(6), 2.28 (1); Pt(2)-P(2), 2.27 (1); Pt(2)-P(3), 2.24 (1); Pt(3)-Cl, 2.41 (1); Pt(3)-P(4), 2.33 (1); Pt(3)-P(5) 2.25 (1) Å. For clarity only the ipso carbon atoms of phenyl rings A-L are displayed, and only one of the two orientations of disordered ring J is shown. Probability ellipsoids (50%) are shown.

unique in being supported by only one M-M bond. The C(4)-C(5) bond length [1.40 (4) Å] is normal],[6] and the Pt(2)-C(4)-C(5) and C(4)-C(5)-Pt(3) angles [119 (2) and 112 (2)°] deviate only slightly from 120° despite the opening of the Pt(2)-C(4)-C(5)-Pt(3) torsion angle to −30 (1)°. The angle between the C(4)-C(5) and Pt(2)-Pt(3) vectors is 17°. The presence of the unsymmetrical $\mu_3$-($\eta^2$-$\|$) alkyne in **2**, **4**, and **5** was confirmed by multinuclear NMR studies. For example, **2** gave six $^{31}P$ resonances and three $^{195}Pt$ resonances, **2*** (prepared from $H^{13}C^{13}CH$) gave two $^{13}C$ resonances each of which was a doublet due to $^1J(CH)$ coupling in the $^1H$ coupled spectrum, and **2**** (prepared from DCCD) gave two $^2H$ resonances.[12]

The complexes **3** and **6** contain the $\mu_3$-($\eta^2$-$\perp$) alkyne as shown by NMR analysis.[13] At low temperature, **3** and **6** each give three $^{31}P$ and two $^{195}Pt$ resonances, showing the presence of a plane of symmetry perpendicular to the $Pt_3$ plane. The $^{13}C$ NMR of **3*** (prepared from $H^{13}C^{13}CH$) and the $^2H$ NMR of **3**** (prepared from DCCD) each contained two resonances, thus ruling out a $\mu_3$-($\eta^2$-$\|$) structure which would contain only one resonance in each case. The NMR data establish the presence of $Pt^1Pt^2$ bonds, but no evidence is present for $Pt^2Pt^2$ bonding.[13] The complexes **3** and **6a** are fluxional at room temperature, indicating that rotation of the alkyne with respect to the $Pt_3$ triangle can occur ($3 \rightleftharpoons 3' \rightleftharpoons 3''$, Scheme I). It is particularly interesting that the bonding mode depends on the electron count of the cluster; there are precedents for the $\mu_3$-($\eta^2$-$\perp$) mode being favored in electron-poor clusters,[14] but we known of no precedent for the easy interconversion with the $\mu_3$-($\eta^2$-$\|$) mode shown in Scheme I.

There are several interesting analogies with surface chemistry. First, it is possible to arrange reagents in order of affinity for the $Pt_3$ unit, $H_2S$ > HCCH > CO. Thus acetylene will displace CO (**1** → **3**) and $H_2S$ will displace both CO from **1** or acetylene from **3** to give $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$, **7**,[15] but the reverse reactions do not occur. The same series applies to the Pt(111) surface.[2] One acetylene can displace another reversibly, as in the reaction of excess propyne with **3** to give **6a**.

Next, coordination of acetylene leads to cleavage of Pt-Pt bonds, with there being three such bonds in the 42e complex **1**,[5] probably two in the 44e complex **3**; and only one Pt-Pt bond in the 46e complexes **2** and **4**.[16] This is an extreme analogy for the weakening of Pt-Pt bonding predicted when acetylene binds to the Pt(111) surface.[3c] In these model compounds, the alkyne can bind in a $\mu_3$-($\eta^2$-$\|$) or $\mu_3$-($\eta^2$-$\perp$) bonding mode, whereas the $\mu_3$-($\eta^2$-$\|$) mode is favored on the Pt(111) surface.[2,3]

**Acknowledgment.** We thank NSERC (Canada) and SERC (U.K.) for support.

**Supplementary Material Available:** Details of X-ray analysis and tables of fractional coordinates, anisotropic displacement parameters, and selected bond distances and angles (10 pages); tables of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(12) NMR data (refs $Me_4Si$, $H_3PO_4$, $K_2PtCl_4$) for **2** in $CD_2Cl_2$: $^1H$ $\delta$ 11.80 [*m*, $^2J(Pt^2H)$ 54, $^3J(Pt^3H)$ 66, $^3J(Pt^1H)$ 16, $^3J(HH)$ 8, $C^4\mathit{H}$], 7.85 [observed in $^2H$ NMR of **2****, obscured in $^1H$, $C\mathit{H}^5$]; $^{13}C$ of **2*** 201 [*m*, $^1J(Pt^2C)$ 650, $^1J(CH)$ 152, $\mathit{C}^4$], 88 [*m*, $^1J(Pt^3C)$ 530, $^1J(CH)$ 163, $\mathit{C}^5$]; $^{13}C$ of **2** ($^{13}CO$) 174 [*s*, $^1J(PtC)$ 1000, *C*O]; $^{31}P$ −12.6 [$\mathit{P}^1$], −6.6 [$\mathit{P}^2$], 9.1 [$\mathit{P}^3$], 10.3 [$\mathit{P}^4$], 12.1 [$\mathit{P}^5$], 2.6 [$\mathit{P}^6$]; $^{195}Pt$ −3300 [*m*, $^1J(PtP^6)$ 3350, $^1J(PtP^1)$ 4050, $^1J(Pt^1Pt^2)$ 2100, $\mathit{Pt}^1$], −2840 [*m*, $^1J(PtP^2)$ 2400, $^1J(PtP^3)$ 3450, $^1J(Pt^1Pt^2)$ 2100, $J(Pt^2Pt^3)$ 900, $^2J(PtP^6)$ 600, $J(Pt^2P^5)$ 170, $\mathit{Pt}^2$], −2920 [*m*, $^1J(PtP^4)$ 2850, $^1J(PtP^5)$ 3000, $\mathit{Pt}^3$]; all PtP and PtC couplings were confirmed by recording both $^{31}P$ and $^{195}Pt$ or $^{13}C$ and $^{195}Pt$ spectra; IR $\nu$(CO) 2090 $cm^{-1}$.

(13) NMR data for **3** in $CD_2Cl_2$ at −80 °C: $^1H$ 12.67 [*m*, $^2J(Pt^1H)$ 128, $^3J(Pt^2H)$ 70, $C^1H$]; 7.15 [$C^2\mathit{H}$, obscured in $^1H$, confirmed by $^1H$–$^1H$ correlation]; $^{13}C$ of **3*** 171.1 [*m*, $^1J(Pt^1C)$ 440, $^1J(Pt^2C)$ ~ 80, $^1J(CC)$ 40, $^1J(CH)$ 187, $\mathit{C}^1$], 73.4 [m, $^1J(Pt^2C)$ ~ 120, $^1J(CH)$ 188, $\mathit{C}^2$]; $^{31}P$ −9.8 [*m*, $^1J(Pt^1P)$ 2680, $^3J(P^aP^c)$ 80, $\mathit{P}^a$], −18.6 [*m*, $^1J(Pt^2P)$ 3750, $\mathit{P}^b$], 7.30 [*m*, $^1J(Pt^2P)$ 4240, $^2J(Pt^1P$ 490, *P*c]; $^{195}Pt$ −2278 [*m*, $^1J(Pt^1Pt^2)$ 2010, $^1J(PtC)$ 440, $^1J(PtP)$ 2680, $\mathit{Pt}^1$], −3471 [*m*, $^1J(Pt^1Pt^2$ 2010, $^1J(PtP^b)$ 3750, $^1J(PtP^c)$ 4240, $\mathit{Pt}^2$]. NMR at 20 °C: $^1H$ 9.91 [br, $C^1\mathit{H}$ + $C^2\mathit{H}$], 5.11 [*m*, $^2J(HH)$ 13, $^3J(PtH)$ 76, $P_2C\mathit{H}^aH^b$], 3.56 [*m*, $^2J(HH)$ 13, $P_2CH^a\mathit{H}^b$]; $^{13}C$ 122 [br, $\mathit{C}^1$ + $\mathit{C}^2$]; $^{31}P$ −7.3 [br, $^1J(PtP)$ 3580, *P*]. An account of the fluxionality, which is intramolecular, will be given elsewhere.

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(16) We consider that acetylene oxidatively adds to the cluster **1** (i.e., we consider it as $C_2H_2^{2-}$). Under these conditions, $Pt^1$ and $Pt^2$ are platinum(I) while $Pt^3$ is square planar platinum(II), though $Pt^3$ in **4** is tetrahedrally distorted [P-Pt(3)-P, 159 (1)°; C-Pt(3)-Cl, 165 (1)°]. The complex **7** and $[Pd_3(CN)(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$ can be considered similarly (4e S versus 4e HCCH ligand) but have higher symmetry. However, coordination of Lewis bases does not disrupt Pt-Pt bonds, for example, in the 46e cluster $[Pt_3(\mu\text{-}CO)(\mu\text{-}Me_2PCH_2PMe_2)_4]^{2+}$. Ferguson, G.; Lloyd, B. R.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4190–4197. Ling, S. S. M.; Hadj-Bagheri, N.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1987**, *26*, 231–235.

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# Interconversion of Bicyclooctadienes and Cyclooctatrienes Formed by Intramolecular Photocycloaddition of Phenyl Ketones Containing Remote Double Bonds

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We recently reported that *o*- and *p*-alkenoxyphenyl ketones undergo a rare[1] intramolecular 2 + 2 *ortho* photocycloaddition of the remote double bond to the benzene ring to yield bicyclooctadienes that rearrange thermally to cyclooctatrienes.[2] We now find that the major stable photoproduct from these reactions is a bicyclo[4,2,0]octa-2,7-diene, which is a secondary photoproduct of the initial 2 + 2 adduct, a bicyclo[4.2.0]octa-2,4-diene. Both bicyclooctadienes rearrange thermally to cyclooctatrienes, the stability of which depends on substitution.

Chart I illustrates the compounds that we have studied. Irradiation (313 or 365 nm) of any of the compounds (except *o*-$AP_2$d) in a variety of solvents (benzene, acetonitrile, methanol)

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(1) (a) Double bond: Sket, B.; Zupancic, N.; Zupan, M. *Tetrahedron* **1986**, *42*, 753. (b) Triple bond: Lippke, W.; Ferree, W.; Morrison, H. *J. Am. Chem. Soc.* **1974**, *96*, 2134.

(2) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4404.