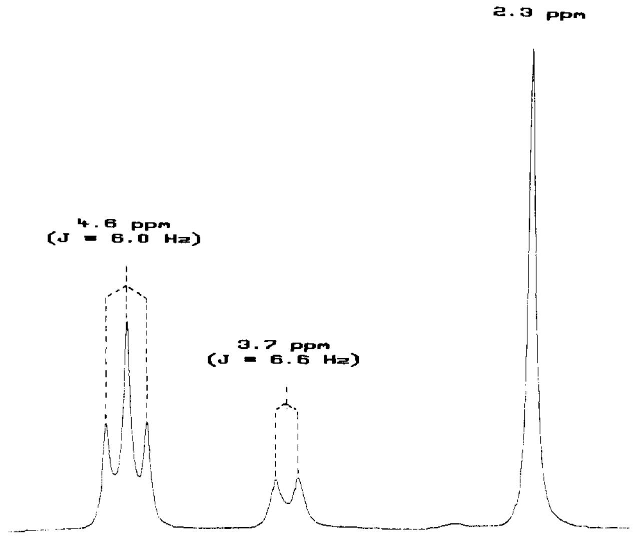

Figure 3. ^{6}Li spectrum (52.99 MHz) of [^{6}Li,^{15}N]-lithium *N*-isopropylanilide (0.5 M) with HMPT (2.0 M) in diethyl ether at −90 °C.

conversion of the dimer to the monomer which, in turn is converted to the triple ion salt with increasing HMPT concentrations (Figure 1b). The ^{31}P spectra of all solutions exhibit only single sharp resonances indicating that exchange between free and bound HMPT is rapid on the ^{31}P NMR time scale. The structure of the triple ion salt is formulated as **1**. The degree of solvation of the triple ion is probably $n = 1$ since the line width of its ^{7}Li resonance is twice that of the monomer, suggesting a trigonal arrangement of ligands. The very narrow line width for ^{7}Li in genenion shows that it is in a tetrahedral environment.

$$[(PhPr\text{-}i\text{-}N)_2Li(HMPT)_n]^-\cdot[Li(HMPT)_4]^+$$
1

$$PhPr\text{-}i\text{-}NLi(THF_{3-n})(HMPT)_n$$
2

$$[Li_5(N{:}CPh_2)_6(HMPT)_3]^-\cdot[Li(HMPT)_4]^+$$
3

Fraenkel and co-workers[9] have used ^{7}Li NMR to show that the addition of THF as a cosolvent to solutions of peralkylcyclohexadienyllithium in cyclopentane induces triple ion formation. They also observe two resonances for the triple ion salt and one for a monomeric ion pair, although in this case all line widths appear similar presumably because the ion pairs are π- rather than σ-types. ^{7}Li NMR has also been used to show that cryptand complexes of ethyl lithioacetoacetate form triple ions.[10] Barr, Clegg, Mulvey, and Snaith[11] have published a number of X-ray structures of HMPT-solvated lithamides. Although none of these corresponds to the type of structure we have found in solution, they do describe a more highly aggregated, polyhedral ate complex[11b] **3** derived from the much less sterically hindered anion of diphenyl ketimine.

In view of the above findings, it appears likely that, in the reactions of lithium enolates, triple ions or more complex ate ions may be better candidates for the reactive species in the presence of HMPT as cosolvent than are tetramers in which the positions of cosolvent and anion are juxtaposed.[12]

Acknowledgment. We gratefully acknowledge support for this research by a grant (CHE85-03502) from the National Science Foundation.

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(8) For a discussion of ^{7}Li quadrupole coupling constants in related systems, see: Jackman, L. M.; Scarmoutzos, L. M.; Debrosse, C. W. *J. Am. Chem. Soc.* **1987**, *109*, 5355.

(9) Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657.

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Alkyne Cyclizations at Reduced Tantalum Centers: Synthesis and Molecular Structure of (η^6-C_6Me_6)Ta(O-2,6-*i*-$Pr_2C_6H_3$)$_2$Cl

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Many transition metals are known to catalyze the cyclotrimerization of alkynes[1,2] and thereby provide an elegant strategy for assembling complex organic molecules.[3] The intermediates most often implicated in these cyclizations are metallacyclopentadienes[4,5] (**1**, Scheme I). Arene formation by the addition of a third alkyne is proposed to occur either through an intermediate (a) metallacycloheptatriene (**3**), or (b) Diels–Alder adduct "7-metallanorbornadiene" (**4**). Since $d^{n\geq 2}$ metal centers are required for the oxidative coupling of alkynes, and since certain niobium and tantalum complexes polymerize[6] and cyclize[6c,7] alkynes, we have begun to investigate mid-valent tantalum chemistry with a view to understanding the details of these reactions in the early transition metals.

Yellow Ta(DIPP)$_2$Cl$_3$ (DIPP = 2,6-diisopropylphenoxide),[8] upon reduction with 2 equiv of Na/Hg in the presence of RC≡CR (R = Me, Et; 3 equiv in Et$_2$O, −30 °C), provides blue solutions containing the complex (C_6R_6)Ta(DIPP)$_2$Cl (R = Me (**5**), R = Et (**6**)) (eq 1). The removal of all volatiles from the reaction filtrate provides the blue, thermally sensitive, microcrystalline product in 65% yield. This reaction also produces a quantity of insoluble alkyne polymer and, in the presence of excess alkyne, free hexaalkylbenzene. The ^{1}H NMR spectrum of the C_6Me_6 compound (**5**, C_6D_6, 30 °C) displays diisopropylphenoxide resonances[9] in addition to a singlet at δ 2.02 (18 H, C_6Me_6); in

$$Ta(DIPP)_2Cl_3 + 2Na/Hg + 3RC{\equiv}CR \rightarrow (\eta^6\text{-}C_6R_6)Ta(DIPP)_2Cl \quad (1)$$
5, R = Me
6, R = Et

---

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(2) See, for example: (a) Krüerke, U.; Hübel W. *Chem. Ber.* **1961**, *94*, 2829. (b) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 4729. (c) Hoover, F. W.; Webster, O. W.; Handy, C. T. *J. Org. Chem.* **1961**, *26*, 2234. (d) Jhingan, A. K.; Maier, W. F. *Ibid.* **1987**, *52*, 1161.

(3) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Vollhardt, K. P. C. In *Strategies and Tactics in Organic Synthesis*; Lindberg, T., Ed.; Academic Press: Orlando, 1984; pp 299–324.

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(5) Other intermediates have been suggested, see: (a) Crocker, M.; Green, M.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1141. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

(6) (a) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473. (b) Masuda, T.; Niki, A.; Isobe, E.; Higashimura, T. *Macromolecules* **1985**, *18*, 2109. (c) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Ibid.* **1981**, *14*, 233.

(7) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094.

(8) (a) Synthesized from the reaction of TaCl$_5$ (10.30 g, 28.8 mmol) and LiDIPP·OEt$_2$ (14.86 g, 57.6 mmol) in benzene/ether (50:1/v:v). The compound crystallizes from pentane (−40 °C) as the etherate Ta(DIPP)$_2$Cl$_3$·OEt$_2$ in 82% yield. The ether-free material has been reported, ref 8b. (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575.

(9) Full spectroscopic and analytical details are available as Supplementary Material. Selected ^{13}C NMR data: **5** (C_6D_6, 30 °C) δ 120.6 (s, C_6Me$_6$), 16.2 (q, $C_6\mathit{Me}_6$); **6** (C_6D_6, 30 °C) δ 126.8 (s, C_6Et$_6$), 23.9 (t, $C_6(\mathit{C}H_2CH_3)_6$), 17.7 (q, $C_6(CH_2\mathit{C}H_3)_6$); **7** (tol-d_8, 50 °C) δ 205.1 (s, C_α), 163.1 (s, C_β), 29.2 (t, $C_\alpha\mathit{C}H_2CH_3$), 22.0 (t, $C_\beta\mathit{C}H_2CH_3$), 15.5 (q, $C_\beta CH_2\mathit{C}H_3$), $C_\alpha CH_2\mathit{C}H_3$ is coincident with either isopropyl methyls (δ 24.4) or $C_\beta CH_2\mathit{C}H_3$ (δ 15.5). Typical 2,6-diisopropylphenoxide resonances occur at δ 157 (s, C_{ipso}), 137 (s, C_o), 124 (d, C_m), 123 (d, C_p), 26 (d, CHMe$_2$), 25 (q, CHMe_2).

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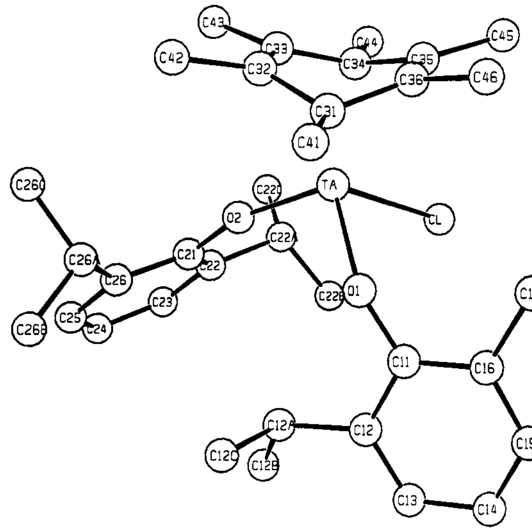
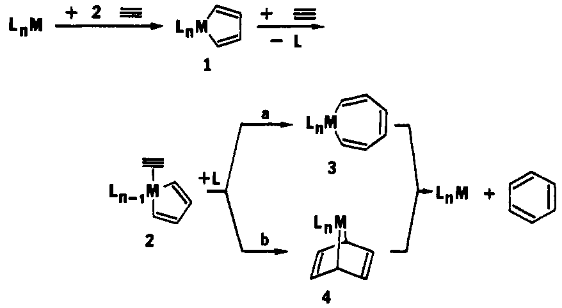


Figure 1. Molecular structure of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl (DIPP = 2,6-diisopropylphenoxide) with atoms shown as arbitrary sized spheres and hydrogen atoms omitted.

Scheme I



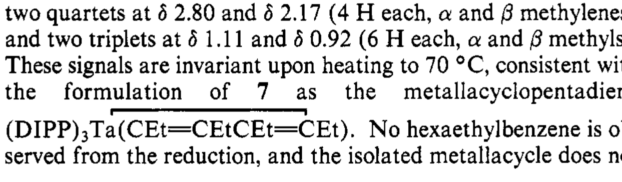
toluene-d_8 these signals are invariant to −80 °C.[10] Compound **5** reacts with PCl_5 (benzene, 25 °C) to quantitatively release hexamethylbenzene. These data are consistent with the cyclotrimerization of alkyne molecules to form the η^6-arene complex (η^6-C_6Me_6)Ta(DIPP)$_2$Cl.[11] Evidence that the arene ligand is assembled at the metal center is provided in the fact that no η^6-C_6Me_6 complex is generated by reducing Ta(DIPP)$_2$Cl$_3$ in the presence of either hexamethylbenzene/EtC≡CEt mixtures or hexamethylbenzene alone.

The molecular geometry of **5** is presented in Figure 1.[12] The pseudotetrahedral tantalum atom (in the simplest possible description) is coordinated to two aryloxide ligands (Ta–O(1) = 1.935 (5) Å and Ta–O(2) = 1.887 (5) Å, with Ta–O–C$_{ipso}$ angles[13] of 146.5 (6)° and 162.6 (6)°, respectively), to a chloride (Ta–Cl = 2.424 (2) Å), and to a highly distorted η^6-C_6Me_6 arene. Ligand bending is severe: the C31–C32–C33–C34 plane assumes an angle 34.4° out of planarity with C34–C35–C36–C31.[14] The arene ring features substantial localization of the π electron system as indicated by the short C32–C33 (1.381 (14) Å) and C35–C36 (1.394(15) Å) bonds. All other carbon–carbon bond lengths within the ring approach C(sp^2)–C(sp^3) single bonds (average 1.462 Å).[15]

Tantalum–carbon bonds also require comment. The Ta–C32 (2.448 (10) Å), Ta–C33 (2.442 (9) Å), Ta–C35 (2.526 (9) Å), and Ta–C36 (2.529 (9) Å) bonds are not unlike tantalum-η^5-pentamethylcyclopentadienyl[16] or niobium-η^6-hexamethylbenzene bond distances.[11b] The anomalous feature is the very close approach of C31 and C34 to the metal (2.158 (10) and 2.218 (9) Å, respectively) which approximates the Ta–C(sp^3) σ bonds of a metal alkyl.[17] Therefore, while bending may be *enhanced* by the bulky DIPP ligands, it seems to *originate* from C31 and C34 being abnormally close to the tantalum for simple η^6-arene coordination.[18]

The resemblance between (η^6-C_6Me_6)Ta(DIPP)$_2$Cl (**5**) and the Diels–Alder product (7-metallanorbornadiene (**4**)) of Scheme I is striking. Although it is attractive to postulate that a metallacyclopentadiene is the immediate precursor to compound **5**, tantallacyclopentadienes are unknown and do not form from certain tantalum alkyne complexes.[19] Since tantallacyclopentadienes have yet to be detected in the formation of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl, the coordination sphere of the Ta(V) precursor was tailored in order to "trap" a cyclization product at this stage.

The more sterically congested metal center in Ta(DIPP)$_3$Cl$_2$,[20] upon reduction with 2 equiv of Na/Hg in the presence of EtC≡CEt (≥3 equiv in Et$_2$O, room temperature) provides orange solutions of the complex (DIPP)$_3$Ta(C$_4$Et$_4$) (**7**) (eq 2). Large orange crystals can be isolated in ca. 50% yield by crystallization from pentane at −40 °C. The ^{1}H NMR spectrum of **7** (C_6D_6, 30 °C) reveals, in addition to the diisopropylphenoxide resonances,[9] two quartets at δ 2.80 and δ 2.17 (4 H each, α and β methylenes) and two triplets at δ 1.11 and δ 0.92 (6 H each, α and β methyls). These signals are invariant upon heating to 70 °C, consistent with the formulation of **7** as the metallacyclopentadiene (DIPP)$_3$Ta(CEt=CEtCEt=CEt). No hexaethylbenzene is observed from the reduction, and the isolated metallacycle does not


$$\mathrm{Ta(DIPP)_3Cl_2 + 2RC{\equiv}CR + 2Na/Hg \longrightarrow (DIPP)_3Ta(CR{=}CRCR{=}CR)} \quad (2)$$

7, R = Et
8, R = Me

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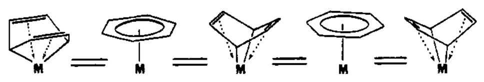
(10) Since simple rotation of the η^6-C_6Me_6 ligand about the Ta–C_6(ring) vector cannot equilibrate the arene methyl groups of a static, bent ring structure, a type of valence tautomerism may be suggested in which three possible bent (localized) ring structures interconvert via planar η^6-C_6Me_6: Free rotation about Ta–O–C$_{ipso}$ would equilibrate isopropyl methyl groups, ref 9.



(11) Few niobium or tantalum arene complexes are known. See: (a) Fischer, E. O.; Röhrscheid, F. *J. Organomet. Chem.* **1966**, *6*, 53. (b) Churchill, M. R.; Chang, S. W.-Y. *J. Chem. Soc., Chem. Commun.* **1974**, 248. (c) Goldberg, S. Z.; Spivack, B.; Stanley, G.; Eisenberg, R.; Braitsch, D. M.; Miller, J. S.; Abkowitz, M. *J. Am. Chem. Soc.* **1977**, *99*, 110. (d) Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938.

(12) Crystal data: space group, triclinic $P\bar{1}$; a = 9.703 (3) Å, b = 11.632 (3) Å, c = 16.023 (4) Å; α = 87.92 (2)°, β = 81.81 (2)°, γ = 74.52 (2)°; V = 1725.0 Å^3 and ρ(calcd) = 1.41 g cm^{-3} for mol wt 733.22 and Z = 2. Structure solution and refinement included 3974 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ of 6819 total (5984 unique) reflections measured for final discrepancy indices are R_F = 4.4% and R_{wF} = 4.6%. Full structural details are available as Supplementary Material.

(13) The steric and electronic factors leading to large metal–oxygen–aryl(C$_{ipso}$) angles have been previously described; see: Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.

(14) Nonplanarity of this type (with two carbons closer to the metal) in η^6-arene ligands has been observed in (a) niobium (ref 11b and 11c), rhodium (ref 14b), and ruthenium compounds (ref 14c), but in no case is bending as severe. (b) Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069. (c) Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 132.

(15) Distances in Å: C31–C32 = 1.467 (11), C33–C34 = 1.456 (13), C34–C35 = 1.464 (11), C36–C31 = 1.463 (12).

(16) See, for example: McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

(17) (a) Compare σ bonds in (η5-C_5Me_5)Ta(CH$_2$Ph)$_2$(=CHPh) at 2.188 and 2.233 Å, ref 17b. (b) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744.

(18) (a) Butadiene complexes of tantalum exhibit a similar bonding feature and thus are more accurately described as containing a dianionic (metallacyclopent-3-ene) ligand, ref 18b. (b) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

(19) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

(20) (a) Synthesized in 63% yield from the reaction of TaCl$_5$ (5.85 g, 16.3 mmol) with LiDIPP·OEt$_2$ (12.65 g, 48.9 mmol) in benzene/ether (50:1/v:v). The compound crystallizes from pentane (−40 °C) as the etherate Ta(DIPP)$_3$Cl$_2$·1.3OEt$_2$. For the ether-free material see ref 20b. (b) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155.

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, $(DIPP)_3Ta(CMe{=}CMeCMe{=}CMe)$ (**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.

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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_α, δ 2.16; CMe_β, 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.

Models for Reactions of Acetylene on Platinum(111): The μ_3-η^2-Acetylene Derivative

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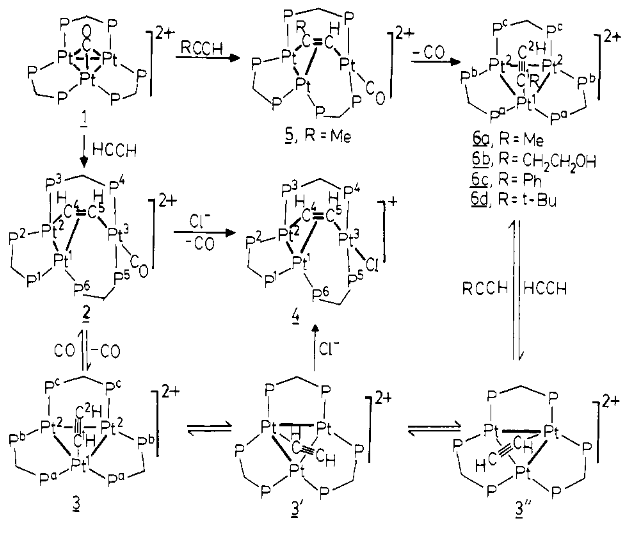
The reactions of acetylene with the Pt(111) surface have been studied in detail;[2] the species $Pt_3(\mu_3\text{-}\eta^2\text{-}HCCH)$, $Pt_3(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)$, and $Pt_3(\mu_3\text{-}CCH_3)$ are formed sequentially, and theoretical studies of each species have been carried out.[3] 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 μ_3-(η^2-∥) bonding, which is the typical mode of attachment of alkynes to M_3 triangles,[6] although it appears to be

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[1] University of Glasgow. (b) University of Western Ontario. (c) On leave from Shiraz University, Iran.

[2] (a) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *J. Chem. Phys.* **1979**, *70*, 2180. (b) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685. (c) Megiris, C. E.; Berlowitz, P.; Butt, J. B.; Kung, H. H. *Surf. Sci.* **1985**, *159*, 184. (d) Bertolini, J. C.; Massardier, J. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1984; Vol. 3, Chapter 3.

[3] (a) Simonetta, M.; Gavezzotti, A. *Theochem* **1984**, *107*, 75. (b) Kang, D. B.; Anderson, A. B. *Surf. Sci.* **1985**, *155*, 639. (c) Silvestre, J.; Hoffmann, R. *Langmuir* **1985**, *1*, 621.

[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 μ_2-η^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, μ(Mo Kα) = 54.5 cm^{-1}, T = 295 K.

The structure is based on 3925 independent absorption corrected intensities [θ(Mo Kα) $\leqslant$ 23°, $I \geqslant 3\sigma(I)$]. Full-matrix least-squares refinement of 301 parameters gave R = 0.059, R_w = 0.069, S = 2.5, $|\Delta\rho| \leqslant$ 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.

[10] Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51–53.

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