Heteronuclear Triangular Clusters of the Type $[Pt_2M(\mu_3-\eta^1:\eta^1:\eta^2-PhC\equiv CC\equiv CPh)(CO)_5(PPh_3)_2]$ (M = Fe or Ru)

Shinsaku Yamazaki,^{*,†} Antony J. Deeming,^{*,‡} and Despo M. Speel[‡]

Chemistry Laboratory, Kochi Gakuen College, 292 Asahi Tenjin-Cho, Kochi 780, Japan, and Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

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Summary: The 46-electron heteronuclear clusters $[Pt_2M_{(\mu_3 \cdot \eta^1 : \eta^1 : \eta^2 \cdot PhC \equiv CC \equiv CPh)(CO)_5(PPh_3)_2]$ (M = Fe or Ru) are formed in moderate yield by treating $[Pt(\eta^2 \cdot PhC \equiv CC \equiv CPh)(PPh_3)_2]$ with $[Fe(CO)_5]$ or $[Ru_3(CO)_{12}]$ in refluxing toluene. The Pt_2Fe and Pt_2Ru clusters are isostructural, being composed of two $Pt(CO)(PPh_3)$ units and a $M(CO)_3$ group linked by two Pt-Fe or Pt-Ru bonds with the μ_3 -diyne coordinated through only one $C \equiv C$ bond.

Introduction

Alkynes can supply up to six electrons to up to four metal centers and can assist in cluster reinforcement. Alkyne clusters can undergo redox processes without a change in cluster nuclearity, and 1,3-diynes, with an even greater capacity to supply electrons, have been used likewise. For example, the complexes [{Co₂- $(CO)_{6}_{2}(\mu\text{-diyne})^{1}$ and $[\{Ni_{2}Cp_{2}\}_{2}(\mu\text{-diyne})]^{2}$ undergo two reversible metal-centered one-electron reductions (CV and ESR studies of frozen solutions).³ It is noted that in using 1,3-diynes with clusters, C-C bond cleavage can occur. Thus, the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with PhC=CC=CPh gives $[Os_3(CO)_{10}(\mu_3-PhC=CC=$ CPh)], which loses a CO ligand to afford the cluster $[Os_3(\mu_3-C=CPh)(\mu_2-C=CPh)(CO)_9]$.⁴ Coupling of alkynyl ligands can also occur. For example, bis(alkynyl) complexes of iron(II),⁵ osmium(II),⁶ or rhodium(III)⁷ can lead to coordinated butenynes or butadiynes by oxidative coupling. A diyne trimer is formed from diyne in a reaction induced by $[Ru_4(\mu_3-PPh)(CO)_{13}]$.⁸ In spite of the scope for transformations of this kind, this study was

[‡] University College London. D.M.S. has previously published under her maiden name Despo M. Michaelidou. A.J.D. may be contacted by e-mail: a.j.deeming@ucl.ac.uk.

- (4) (a) Deeming, A. J.; Felix, M. S. B.; Bates, P. A.; Hursthouse, M.
 B. J. Chem. Soc., Chem. Commun. 1987, 461. (b) Deeming, A. J.; Felix,
 M. S. B.; Nuel, D. Inorg. Chim. Acta 1993, 213, 3.
- (b) B. S. Chen, Soc., Chen, Commun. 1967, 401. (b) Deening, A. S.; Fellx,
 M. S. B.; Nuel, D. Inorg. Chim. Acta 1993, 213, 3.
 (5) Field, L. D.; George, A. V.; Purches, G. R.; Slip, I. H. M. Organometallics 1992, 11, 3019.
- (6) Gotzig, J.; Otto, H.; Werner, H. J. Organomet. Chem. 1985, 287, 247.
- (7) Werner, H.; Gevert, O.; Haquette, P. Organometallics 1997, 16, 803.
- (8) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. Organometallics 1992, 11, 3160.



Figure 1. Molecular structure of **1**. Selected distances (Å) and angles (deg): Pt(1)-C(1) 2.036(8), Pt(1)-C(2) 2.041-(7), Pt(1)-P(1) 2.273(2), Pt(1)-P(2) 2.279(2), C(1)-C(2) 1.305(11), C(1)-C(5) 1.437(11), C(2)-C(3) 1.389(11), C(3)-C(4) 1.200(11), C(4)-C(11) 1.439(11), C(1)-Pt(1)-C(2) 37.3-(3), C(2)-Pt(1)-P(1) 108.2(2), C(1)-Pt(1)-P(2) 110.9(2), C(2)-C(1)-C(5) 140.7(7), C(1)-C(2)-C(3) 146.7(8), C(2)-C(3)-C(4) 176.4(9), C(3)-C(4)-C(11) 176.5(9).

aimed at coordinating one C=C group of a diyne ligand to a metal center and using the remaining one to bind to incoming metallic reagents to give bridging diynes en route to heterometallic clusters. Thus, $[Pt(\eta^2 - PhC \equiv CC \equiv CPh)(PPh_3)_2]$ was treated with reagents such as $[Fe(CO)_5]$, $[Ru_3(CO)_{12}]$, and other carbonyl complexes in an attempt to bind the incoming metal atoms to the free $C \equiv C$ bond. Unexpectedly, diyne heterometallic clusters in which one $C \equiv C$ bond remained uncoordinated were obtained and no C-C bond cleavage was observed.

Results and Discussion

The diyne complex $[Pt(PhC \equiv CC \equiv CPh)(PPh_3)_2]$ (1) is formed quantitatively by treatment of $[Pt(PPh_3)_4]$ with the diyne. IR absorptions at 2161 and 1731 cm⁻¹ are assigned to free and coordinated $C \equiv C$ bonds, respectively. The single-crystal X-ray structure of 1 confirms the original proposal⁹ that only one of the two $C \equiv C$ bonds is coordinated (Figure 1). The coordination

[†] Kochi Gakuen College.

⁽¹⁾ Fronczek, F. R.; Erickson, M. S. J. Chem. Crystallogr. 1996, 25, 737.

⁽²⁾ Tilney-Bassett, J. F. J. Chem. Soc. 1961, 577.

^{(3) (}a) Osella, D.; Rossetti, R.; Nervi, C.; Ravera, M.; Moretta, M.; Fiedler, J.; Pospísil, L.; Samuel, E. *Organometallics* **1997**, *16*, 695. (b) Osella, D.; Milone, L.; Nervi, C.; Ravera, M. *J. Organomet. Chem.* **1995**, *488*, 1.

⁽⁹⁾ Heyns, J. B. B.; Stone, F. G. A. *J. Organomet. Chem.* **1978**, *160*, 337.



geometry at platinum is close to planar, the dihedral angle between the Pt(1)P(1)P(2) and the Pt(1)C(1)C(2) planes being 3.5°. Although the coordinated alkyne is unsymmetrical, the coordination geometry at Pt is essentially symmetrical; the Ph group at C(1) and the PhC₂ group at C(2) are exerting similar effects.

Treatment of **1** with $[Fe(CO)_5]$ in refluxing toluene gave the product $[Pt_2Fe(\mu_3-\eta^1:\eta^1:\eta^2-PhC \equiv CC \equiv CPh)$ - $(CO)_5(PPh_3)_2$ (2) as red crystals (62%) (Scheme 1). ¹³C- $\{^{1}H\}$ NMR spectra are consistent with one C=C remaining uncoordinated; two of the four acetylenic carbon atoms give signals at δ 98.7 and 98.3 (free C=C) and two at δ 149.0 and 166.0 (coordinated C=C). Crystals of 2 suitable for XRD were obtained in two forms: triclinic $2 \cdot C_6 H_6$ from a benzene-acetone solution and monoclinic 2. CHCl₃ from a chloroform-hexane solution. Their molecular structures shown in Figures 2 and 3, respectively, are superficially similar with the divne μ_3 -coordinated to a Pt₂Fe triangle in the common parallel manner^{8,10} with two Pt–C σ -bonds and an η^2 interaction to Fe. The system might be considered to result from coordination of the diplatinacyclobutadiene compound, $Pt_2^{I}(CO)_2(PPh_3)_2(\mu - \eta^1: \eta^1 - PhC \equiv CC \equiv CPh)$, to a $Fe(CO)_3$ group to form a 46-electron system. This Pt_2 unit would be closely related to the known platinum(I) compound $[Pt_2(CO)_2(PPh_3)_2(\mu-\eta^1:\eta^1-MeO_2CC \equiv CCO_2-$ Me)].¹¹ There are clear structural differences between the two crystalline forms, $2 \cdot C_6 H_6$ and $2 \cdot CHCl_3$. The PPh₃ ligands have different conformations, and the Fe- $(CO)_3$ groups are twisted in a turnstile manner going from one structure to the other, but most significantly there are pronounced differences in the metal-metal distances. The Pt–Pt distance in $2 \cdot C_6 H_6$ is 2.939(1) Å, which is elongated to 3.072(1) Å in 2. CHCl₃. As the Pt-Pt distance is increased, there is an associated but smaller reduction in the Pt-Fe distances, which are 2.609(3) and 2.606(3) Å in $2 \cdot C_6 H_6$ which are reduced to 2.594(2) and 2.598(2) Å in 2. CHCl₃. The difference in the Pt–Pt distances ($\Delta = 0.133$ Å) indicates that there is either no Pt-Pt bond or that this bond is weak and easily deformed. The values of J_{PtP} are 3500 and 192 Hz for one ³¹P nucleus and 3608 and 208 Hz for the other, the smaller values being couplings between the ³¹P nuclei and the distant ¹⁹⁵Pt nuclei. The corresponding J_{PtP} values for the related dimer $[Pt_2(CO)_2(PPh_3)_2(\mu \eta^1: \eta^1 - \text{MeO}_2\text{CC} \equiv \text{CCO}_2\text{Me}$)] are 2409 and 783 Hz.¹¹ The



Figure 2. Molecular structure of **2** in $2 \cdot C_6 H_6$. Selected distances (Å) and angles (deg): Pt(1)-Fe(1) 2.609(3), Pt-(2)-Fe(1) 2.606(3), Pt(1)-Pt(2) 2.939(2), Pt(1)-C(1) 2.097-(12), Pt(2)-C(2) 2.073(12), Fe(1)-C(1) 2.139(12), Fe(1)-C(2) 2.097(12), Pt(1)-P(1) 2.329(4), Pt(2)-P(2) 2.344(4), Pt(1)-C(21) 1.902(14), Pt(2)-C(31) 1.90(2), C(1)-C(2) 1.43-(2), C(3)-C(4) 1.20(2), C(2)-C(1)-C(301) 129.0(11), C(1)-C(2)-C(3) 127.9(11), C(2)-C(3)-C(4) 170(2), C(3)-C(4)-C(311) 174(2). The structure of $3 \cdot C_6 H_6$ is closely similar with selected distances (Å) and angles (deg): Pt(1)-Ru(1)2.694(2), Pt(2)-Ru(1) 2.699(2), Pt(1)-Pt(2) 2.9595(13), Pt-(1)-C(1) 2.073(14), Pt(2)-C(2) 2.06(2), Ru(1)-C(1) 2.28-(2), Ru(1)-C(2) 2.19(2), Pt(1)-P(1) 2.327(5), Pt(2)-P(2)2.346(4), Pt(1)-C(21) 1.89(2), Pt(2)-C(31) 1.86(3), C(1)-C(2) 1.47(3), C(3)-C(4) 1.22(2), C(2)-C(1)-C(301) 127.6-(13), C(1)-C(2)-C(3) 126(2), C(2)-C(3)-C(4) 166(2), C(3)-C(4)-C(311) 177(2).

783 Hz coupling is across a full Pt–Pt bond in this case and is approximately 4 times the value for **2**. The Pt– Pt bond length in $[Pt_2(CO)_2(PPh_3)_2(\mu-\eta^{1:}\eta^{1-}MeO_2CC\equiv C-CO_2Me)]$ is 2.6354(8) Å,¹¹ typically of platinum(I) dimers and considerably less than that for **2**.

The corresponding ruthenium complex $[Pt_2Ru(\mu_3-\eta^1:$ $\eta^1:\eta^2$ -PhC=CC=CPh)(CO)₅(PPh₃)₂] (3) was obtained similarly (19% yield) from 1 and $[Ru_3(CO)_{12}]$ in refluxing toluene. The crystals of $3 \cdot C_6 H_6$, grown from benzeneacetone, are isomorphous with the corresponding Pt₂-Fe cluster $2 \cdot C_6 H_6$. The structures are very similar, apart from the longer Pt-Ru distances of 2.694(2) and 2.699(2) Å. These results seem to indicate that the reactions of **1** with $[Fe(CO)_5]$ or $[Ru_3(CO)_{12}]$ do not require a free C=C bond because only one C=C is chemically involved. Consistent with this, the reaction of [Pt(Ph- $C \equiv CPh)(PPh_3)_2$ with $[Fe(CO)_5]$ gives, among other products, the complex $[Pt_2Fe(\mu_3-\eta^1:\eta^2-PhC\equiv CPh)-$ (CO)₅(PPh₃)₂] (4), which is under investigation. Preliminary results indicate that **4** is related to **2**, but the stereochemistries at the two Pt atoms are different in 4.

Experimental Section

Syntheses of [Pt(\eta^2-PhC=CC=CPh)(PPh_3)_2] (1). By a method analogous to that using [Pt(C_2H_4)(PPh_3)_2],⁹ a solution of [Pt(PPh_3)_4] (1.50 g, 1.2 mmol) and PhC=CC=CPh (0.25 g, 1.2 mmol) in CH_2Cl_2 (20 cm³) was stirred under N₂ at 20 °C for 10 min. The volume was decreased by one-half, and addition of hexane gave **1** as orange prisms (0.96 g, 99%). Anal. Calcd for C₅₂H₄₀P₂Pt: C, 67.74; H, 4.37. Found: C, 68.43; H, 4.56. IR (Nujol): ν (C=C) 2161 m (noncoordinated), 1731 m

^{(10) (}a) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **1996**, *49*, 155. (b) Bruce, M. I.; Low, P. J.; Werth, A.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1996**, 1551.
(c) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **1996**, *250*, 129.

^{(11) (}a) Koie, Y.; Shinoda, S.; Saito, Y.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1980**, *19*, 770. (b) Koie, Y.; Shinoda, S.; Saito, Y. *Inorg Chem.* **1981**, *20*, 4408.



Figure 3. Molecular structure of **2** in **2**·CHCl₃. Selected distances (Å) and angles (deg): Pt(1)–Fe(1) 2.594(2), Pt(2)–Fe-(1) 2.598(2), Pt(1)–Pt(2) 3.072(1), Pt(1)–C(1) 2.091(14), Pt(2)–C(2) 2.065(13), Fe(1)–C(1) 2.168(12), Fe(1)–C(2) 2.098(14), Pt(1)–P(1) 2.336(4), Pt(2)–P(2) 2.335(3), Pt(1)–C(21) 1.93(2), Pt(2)–C(31) 1.89(2), C(1)–C(2) 1.43(2), C(3)–C(4) 1.19(2), C(2)–C(1)–C(301) 125.8(12), C(1)–C(2)–C(3) 123.8(13), C(2)–C(3)–C(4) 174(2), C(3)–C(4)–C(311) 177(2).

(coordinated) cm⁻¹. ¹³C{¹H} NMR (CDCl₃): diyne δ 108.1 (d, $J_{PC} = 67.9$ Hz, $J_{PtC} = 281.2$ Hz, $C^{1.2}$), 82.2 (dd, J_{PC} , trans = 12.7 Hz, J_{PC} , cis = 6.7 Hz, C³), 103.8 (d, $J_{PC} = 6.4$ Hz). ³¹P-{¹H} NMR (CDCl₃): δ 23.9 ($J_{PP} = 24.7$ Hz, $J_{PtP} = 3598$ Hz), 23.6 ($J_{PP} = 24.7$ Hz, $J_{PtP} = 3377$ Hz).

Synthesis of $[Pt_2Fe(\mu_3-\eta^1:\eta^1:\eta^2-PhC\equiv CC\equiv CPh)(CO)_5-$ (**PPh₃**)₂] (2). A mixture of [Fe(CO)₅] (0.185 g) and 1 (0.65 g) in toluene (50 cm³) under N₂ was refluxed for 30 min to give a deep orange solution. TLC (SiO₂; eluent CH₂Cl₂-hexane) gave a deep orange band, which was extracted with CH₂Cl₂. Slow evaporation of a CH₂Cl₂-hexane solution gave orange microcrystals of 2 (0.45 g, 62% based on Pt). Anal. Calcd for C₅₄H₄₀FeO₅P₂Pt₂·(CH₂Cl₂)_{0.5}: C, 50.95; H, 3.03. Found: C, 50.44; H, 2.97. IR (Nujol): v(CO), 2030 vs, 1988 vs, 1941 vs cm⁻¹. ¹³C{¹H} NMR (CDCl₃): δ 166.0 (d, $J_{PC} = 1.6$ Hz, PhC1=C, coord), 149.0 (m, PhC=C2, coord), 98.7 (dd, C3=CPh, uncoord), 98.3 (d, $J_{PC} = 1.6$ Hz, C=C⁴Ph, uncoord), 216.5 (dd, J_{PC} , cis = 4.1 Hz, $J_{\text{PtC}} = 10$ Hz, FeCO), 196.0 (d, $J_{\text{PC}} = ca. 8$ Hz, FeCO), 194.0 (d, $J_{PC} = 8.2$ Hz, PtCO, ¹⁹⁵Pt coupling undetected). ³¹P{¹H} NMR (CDCl₃): δ 14.8 (J_{PtP} = 3500, 192 Hz), 22.2 ($J_{PtP} = 3608$, 208 Hz). Recrystallization from benzene-acetone gave single crystals of 2.C6H6 for singlecrystal X-ray diffraction. Crystals of 2·CHCl₃ were likewise precipitated from a chloroform-hexane mixture.

Synthesis of [Pt₂Ru(μ_3 - η^1 : η^1 : η^2 -PhC=CC=CPh)(CO)₅-(PPh₃)₂] (3). A suspension of 1 (0.25 g) and [Ru₃(CO)₁₂] (0.175 g) in toluene (15 cm³) was refluxed for 10 min to give a deep orange solution. Removal of the solvent and TLC separation (eluent CH₂Cl₂-hexane) gave a deep orange band resulting in **3** as orange microcrystals (0.070 g, 19%). Anal. Calcd for C₅₄H₄₀O₅P₂Pt₂Ru: C, 50.41; H, 2.97. Found: C, 50.27; H, 2.91. IR (Nujol): ν (CO) 2044 vs, 2010 vs, 1964 s, 1944 cm⁻¹. ¹³C{¹H} NMR (CDCl₃): broad signals, δ 200.6 (RuCO, ¹⁹⁵Pt satellites just apparent), 194.7, 192.4 (PtCO, ¹⁹⁵Pt satellites unresolved), 100.5, 98.0 (uncoordinated C=C), other signals unassigned. Single crystals suitable for XRD were obtained from benzene-acetone.

X-ray Structure Detennination of 1, 2·C₆H₆, 2·CHCl₃, and $3 \cdot C_6 H_6$. Intensity data collected by $\omega - 2\theta$ scans at 18 °C on a Nicolet R3v/m instrument using Mo K α radiation (λ = 0.710 73 Å) were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on Ψ scans. Structure solutions were performed by direct methods using SHELXL-93,12 with refinement by full-matrix leastsquares on F_0^2 . All non-H atoms were refined anisotropically with H-atoms in calculated positions riding on C-atoms with C-H fixed at 0.96 Å. (a) Crystal data for 1: $C_{52}H_{40}P_2Pt$, M =921.87, colorless crystal, $0.65 \times 0.50 \times 0.20$ mm, triclinic, $P\overline{1}$, a = 12.061(6) Å, b = 13.066(6) Å, c = 15.809(6) Å, $\alpha = 68.82$ -(3)°, $\beta = 89.03(4)°$, $\gamma = 66.12(3)°$, V = 2100(2) Å³, Z = 2, $D_c =$ 1.458 g cm⁻³, F(000) = 920, $\mu(Mo K\alpha) = 34.52 \text{ cm}^{-1}$, R1 = 0.0519, wR2 = 0.141, goof = 1.037 for 7414 reflections in the range $5^{\circ} \le 2\theta \le 50^{\circ}$ with $I > 2\sigma(I_0)$ refining 496 parameters. (b) Crystal data for $2 \cdot C_6 H_6$: $C_{63} H_{46} FeO_5 P_2 Pt_2$, M = 1390.97, red plate, $0.70 \times 0.38 \times 0.10$ mm, triclinic, $P\bar{1}$, a = 13.564(9)Å, b = 13.914(12) Å, c = 15.41(2) Å, $\alpha = 79.29(7)^{\circ}$, $\beta = 85.51^{\circ}$ (7)°, $\gamma = 86.45(6)$ °, V = 2846(4) Å³, Z = 2, $D_c = 1.623$ g cm⁻³, F(000) = 1352, $\mu(Mo K\alpha) = 52.58 \text{ cm}^{-1}$, R1 = 0.0555, wR2 =0.145, goof = 1.090 for 7131 reflections in the range $5^{\circ} \leq 2\theta \leq$ 45° with $I > 2\sigma(I_0)$ refining 658 parameters. (c) Crystal data for **2**·CHCl₃: C₅₈H₄₀Cl₃FeO₅P₂Pt₂, *M* = 1431.22, red plate, 0.63 \times 0.40 \times 0.12 mm, monoclinic, P2₁/c, a = 13.152(5) Å, b = 23.707(13) Å, c = 18.407(10) Å, $\beta = 103.31(4)^{\circ}$, V = 5584(5)Å³, Z = 4, $D_c = 1.702$ g cm⁻³, F(000) = 2764, μ (Mo K α) = 55.00 cm^{-1} , R1 = 0.0556, wR2 = 0.135, goof = 1.114 for 8107 reflections in the range $5^{\circ} \leq 2\theta \leq 47^{\circ}$ with $I > 2\sigma(I_0)$ refining 629 parameters. (d) Crystal data for 3·C₆H₆: C₆₃H₄₆O₅P₂Pt₂-Ru, M = 1436.19, red triclinic plate, $0.55 \times 0.28 \times 0.08$ mm, $P\bar{1}$, $a = 13.581(12)^{\circ}$, $b = 14.048(10)^{\circ}$, c = 15.346(9) Å, $\alpha =$ 79.32(5)°, $\beta = 85.49(6)$ °, $\gamma = 85.88(6)$ °, V = 2863(3) Å³, Z = 2, $D_{\rm c} = 1.666 \text{ g cm}^{-3}$, F(000) = 1388, $\mu({\rm Mo \ K\alpha}) = 52.37 \text{ cm}^{-1}$, R1

⁽¹²⁾ Sheldrick, G. M. SHELXL-93; University of Göttingen: Göttingen, Germany, 1993.

= 0.0539, wR2 = 0.138, goof = 1.005 for 5275 reflections in the range $5^{\circ} \leq 2\theta \leq 45^{\circ}$ with $I > 2\sigma(I_0)$ refining 613 parameters.

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