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

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Summary: The 46-electron heteronuclear clusters $[Pt_2M(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_5(PPh_3)_2]$ (M = Fe or Ru) are formed in moderate yield by treating $[Pt(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(PPh_3)_2]$ 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≡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 $[\{Co_2(CO)_6\}_2(\mu\text{-diyne})]$[1] and $[\{Ni_2Cp_2\}_2(\mu\text{-diyne})]$[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 $[Os_3(CO)_{10}(\mu_3\text{-}PhC{\equiv}CC{\equiv}CPh)]$, which loses a CO ligand to afford the cluster $[Os_3(\mu_3\text{-}C{\equiv}CPh)(\mu_2\text{-}C{\equiv}CPh)(CO)_9]$.[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 $[Ru_4(\mu_3\text{-}PPh)(CO)_{13}]$.[8] In spite of the scope for transformations of this kind, this study was 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, $[Pt(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(PPh_3)_2]$ 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≡C bond. Unexpectedly, diyne heterometallic clusters in which one C≡C bond remained uncoordinated were obtained and no C−C bond cleavage was observed.

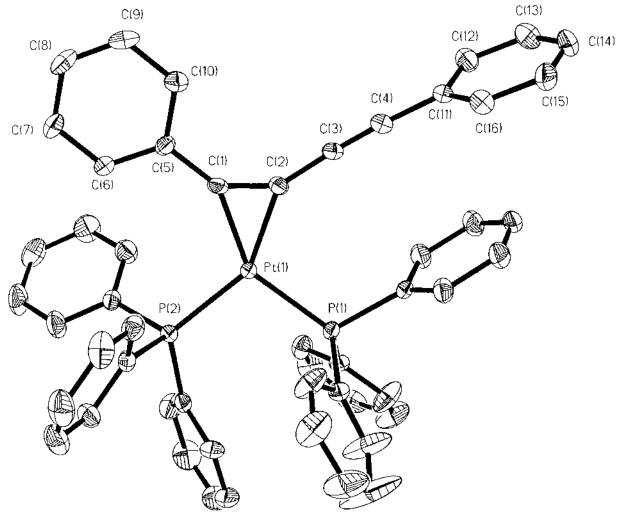

Figure 1. Molecular structure of **1**. Selected distances (Å) and angles (deg): Pt(1)−C(1) 2.036(8), Pt(1)−C(2) 2.041(7), Pt(1)−P(1) 2.273(2), Pt(1)−P(2) 2.279(2), C(1)−C(2) 1.305(11), C(1)−C(5) 1.437(11), C(2)−C(3) 1.389(11), C(3)−C(4) 1.200(11), C(4)−C(11) 1.439(11), C(1)−Pt(1)−C(2) 37.3(3), C(2)−Pt(1)−P(1)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

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≡C bonds, respectively. The single-crystal X-ray structure of **1** confirms the original proposal[9] that only one of the two C≡C bonds is coordinated (Figure 1). The coordination

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(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.

(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.

(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.

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

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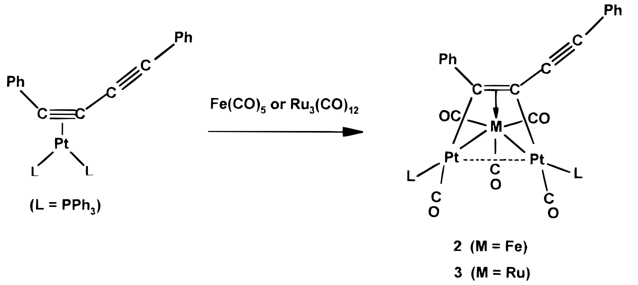
Scheme 1



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 PhC_2 group at C(2) are exerting similar effects.

Treatment of **1** with $[Fe(CO)_5]$ in refluxing toluene gave the product $[Pt_2Fe(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_5(PPh_3)_2]$ (**2**) as red crystals (62%) (Scheme 1). $^{13}C\{^1H\}$ 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 $\mathbf{2}{\cdot}C_6H_6$ from a benzene–acetone solution and monoclinic $\mathbf{2}{\cdot}CHCl_3$ from a chloroform–hexane solution. Their molecular structures shown in Figures 2 and 3, respectively, are superficially similar with the diyne μ_3-coordinated to a Pt_2Fe 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, $Pt^I_2(CO)_2(PPh_3)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}PhC{\equiv}CC{\equiv}CPh)$, 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 $[Pt_2(CO)_2(PPh_3)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}MeO_2CC{\equiv}CCO_2Me)]$.[11] There are clear structural differences between the two crystalline forms, $\mathbf{2}{\cdot}C_6H_6$ and $\mathbf{2}{\cdot}CHCl_3$. The PPh_3 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 $\mathbf{2}{\cdot}C_6H_6$ is 2.939(1) Å, which is elongated to 3.072(1) Å in $\mathbf{2}{\cdot}CHCl_3$. 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 $\mathbf{2}{\cdot}C_6H_6$ which are reduced to 2.594(2) and 2.598(2) Å in $\mathbf{2}{\cdot}CHCl_3$. 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 ^{31}P nucleus and 3608 and 208 Hz for the other, the smaller values being couplings between the ^{31}P nuclei and the distant ^{195}Pt nuclei. The corresponding J_{PtP} values for the related dimer $[Pt_2(CO)_2(PPh_3)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}MeO_2CC{\equiv}CCO_2Me)]$ are 2409 and 783 Hz.[11] The 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 $[Pt_2(CO)_2(PPh_3)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}MeO_2CC{\equiv}C\text{-}CO_2Me)]$ is 2.6354(8) Å,[11] typically of platinum(I) dimers and considerably less than that for **2**.

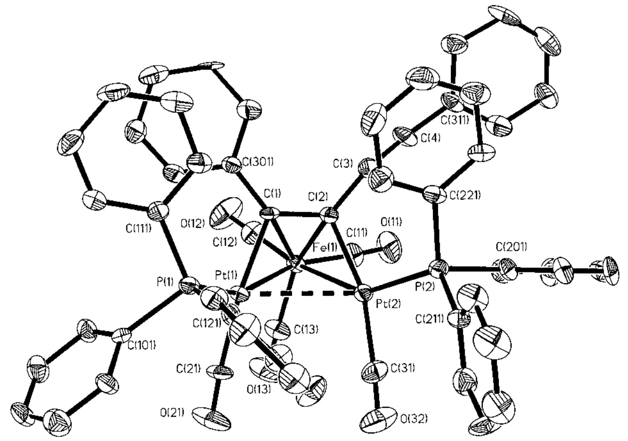


Figure 2. Molecular structure of **2** in $\mathbf{2}{\cdot}C_6H_6$. Selected distances (Å) and angles (deg): Pt(1)–Fe(1) 2.609(3), Pt(2)–Fe(1) 2.606(3), Pt(1)–Pt(2) 2.939(2), Pt(1)–C(1) 2.097(12), Pt(2)–C(2) 2.073(12), Fe(1)–C(1) 2.139(12), Fe(1)–C(2) 2.097(12), Pt(1)–P(1) 2.329(4), Pt(2)–P(2) 2.344(4), 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 $\mathbf{3}{\cdot}C_6H_6$ 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).

The corresponding ruthenium complex $[Pt_2Ru(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_5(PPh_3)_2]$ (**3**) was obtained similarly (19% yield) from **1** and $[Ru_3(CO)_{12}]$ in refluxing toluene. The crystals of $\mathbf{3}{\cdot}C_6H_6$, grown from benzene–acetone, are isomorphous with the corresponding Pt_2-Fe cluster $\mathbf{2}{\cdot}C_6H_6$. 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 $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$ with $[Fe(CO)_5]$ gives, among other products, the complex $[Pt_2Fe(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhC{\equiv}CPh)(CO)_5(PPh_3)_2]$ (**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 $[Pt(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(PPh_3)_2]$ (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 cm^3) was stirred under N_2 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 $C_{52}H_{40}P_2Pt$: C, 67.74; H, 4.37. Found: C, 68.43; H, 4.56. IR (Nujol): ν(C≡C) 2161 m (noncoordinated), 1731 m

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(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.

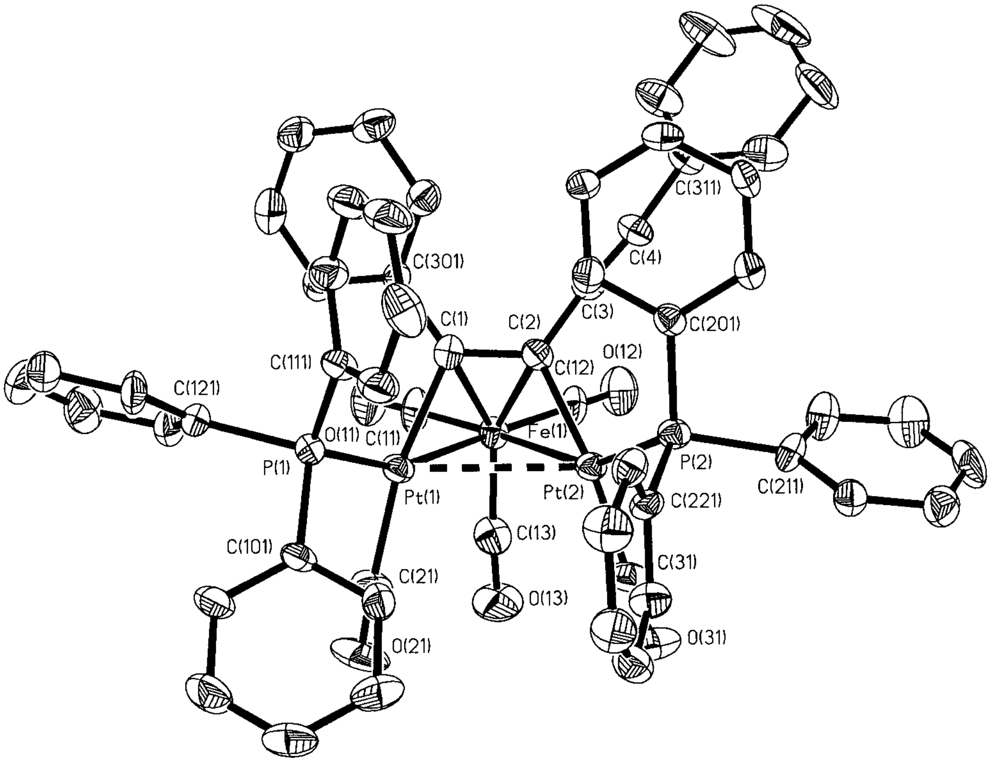

Figure 3. Molecular structure of **2** in **2**·$CHCl_3$. Selected distances (Å) and angles (deg): Pt(1)−Fe(1) 2.594(2), Pt(2)−Fe(1) 2.598(2), Pt(1)−Pt(2) 3.072(1), Pt(1)−C(1) 2.091(14), Pt(2)−C(2) 2.065(13), Fe(1)−C(1) 2.168(12), Fe(1)−C(2) 2.098(14), Pt(1)−P(1) 2.336(4), Pt(2)−P(2) 2.335(3), Pt(1)−C(21) 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}. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 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, C^3), 103.8 (d, J_{PC} = 6.4 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 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 [$Pt_2Fe(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_5(PPh_3)_2$] (2). A mixture of [$Fe(CO)_5$] (0.185 g) and **1** (0.65 g) in toluene (50 cm^3) under N_2 was refluxed for 30 min to give a deep orange solution. TLC (SiO_2; eluent CH_2Cl_2−hexane) gave a deep orange band, which was extracted with CH_2Cl_2. Slow evaporation of a CH_2Cl_2−hexane solution gave orange microcrystals of **2** (0.45 g, 62% based on Pt). Anal. Calcd for $C_{54}H_{40}FeO_5P_2Pt_2\cdot(CH_2Cl_2)_{0.5}$: C, 50.95; H, 3.03. Found: C, 50.44; H, 2.97. IR (Nujol): ν(CO), 2030 vs, 1988 vs, 1941 vs cm^{-1}. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 166.0 (d, J_{PC} = 1.6 Hz, $PhC^1{=}C$, coord), 149.0 (m, $PhC{=}C^2$, coord), 98.7 (dd, $C^3{\equiv}CPh$, uncoord), 98.3 (d, J_{PC} = 1.6 Hz, $C{\equiv}C^4Ph$, uncoord), 216.5 (dd, $J_{PC,cis}$ = 4.1 Hz, J_{PtC} = 10 Hz, FeCO), 196.0 (d, J_{PC} = ca. 8 Hz, FeCO), 194.0 (d, J_{PC} = 8.2 Hz, PtCO, ^{195}Pt coupling undetected). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.8 (J_{PtP} = 3500, 192 Hz), 22.2 (J_{PtP} = 3608, 208 Hz). Recrystallization from benzene−acetone gave single crystals of **2**·C_6H_6 for single-crystal X-ray diffraction. Crystals of **2**·$CHCl_3$ were likewise precipitated from a chloroform−hexane mixture.

Synthesis of [$Pt_2Ru(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(CO)_5(PPh_3)_2$] (3). A suspension of **1** (0.25 g) and [$Ru_3(CO)_{12}$] (0.175 g) in toluene (15 cm^3) was refluxed for 10 min to give a deep orange solution. Removal of the solvent and TLC separation (eluent CH_2Cl_2−hexane) gave a deep orange band resulting in **3** as orange microcrystals (0.070 g, 19%). Anal. Calcd for $C_{54}H_{40}O_5P_2Pt_2Ru$: 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}. $^{13}C\{^1H\}$ NMR ($CDCl_3$): broad signals, δ 200.6 (RuCO, ^{195}Pt satellites just apparent), 194.7, 192.4 (PtCO, ^{195}Pt 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·C_6H_6, 2·$CHCl_3$, and 3·C_6H_6. Intensity data collected by $\omega{-}2\theta$ scans at 18 °C on a Nicolet R3v/m instrument using Mo Kα 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 least-squares on F_o^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 × 0.50 × 0.20 mm, triclinic, $P\bar{1}$, a = 12.061(6) Å, b = 13.066(6) Å, c = 15.809(6) Å, α = 68.82(3)°, β = 89.03(4)°, γ = 66.12(3)°, V = 2100(2) Å^3, Z = 2, D_c = 1.458 g cm^{-3}, F(000) = 920, μ(Mo Kα) = 34.52 cm^{-1}, R1 = 0.0519, wR2 = 0.141, goof = 1.037 for 7414 reflections in the range 5° ≤ 2θ ≤ 50° with $I > 2\sigma(I_o)$ refining 496 parameters. (b) Crystal data for **2**·C_6H_6: $C_{63}H_{46}FeO_5P_2Pt_2$, M = 1390.97, red plate, 0.70 × 0.38 × 0.10 mm, triclinic, $P\bar{1}$, a = 13.564(9) Å, b = 13.914(12) Å, c = 15.41(2) Å, α = 79.29(7)°, β = 85.51(7)°, γ = 86.45(6)°, V = 2846(4) Å^3, Z = 2, D_c = 1.623 g cm^{-3}, F(000) = 1352, μ(Mo Kα) = 52.58 cm^{-1}, R1 = 0.0555, wR2 = 0.145, goof = 1.090 for 7131 reflections in the range 5° ≤ 2θ ≤ 45° with $I > 2\sigma(I_o)$ refining 658 parameters. (c) Crystal data for **2**·$CHCl_3$: $C_{58}H_{40}Cl_3FeO_5P_2Pt_2$, M = 1431.22, red plate, 0.63 × 0.40 × 0.12 mm, monoclinic, $P2_1/c$, a = 13.152(5) Å, b = 23.707(13) Å, c = 18.407(10) Å, β = 103.31(4)°, V = 5584(5) Å^3, Z = 4, D_c = 1.702 g cm^{-3}, F(000) = 2764, μ(Mo Kα) = 55.00 cm^{-1}, R1 = 0.0556, wR2 = 0.135, goof = 1.114 for 8107 reflections in the range 5° ≤ 2θ ≤ 47° with $I > 2\sigma(I_o)$ refining 629 parameters. (d) Crystal data for **3**·C_6H_6: $C_{63}H_{46}O_5P_2Pt_2Ru$, M = 1436.19, red triclinic plate, 0.55 × 0.28 × 0.08 mm, $P\bar{1}$, a = 13.581(12)°, b = 14.048(10)°, c = 15.346(9) Å, α = 79.32(5)°, β = 85.49(6)°, γ = 85.88(6)°, V = 2863(3) Å^3, Z = 2, D_c = 1.666 g cm^{-3}, F(000) = 1388, μ(Mo Kα) = 52.37 cm^{-1}, R1

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(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° ≤ 2θ ≤ 45° with $I > 2\sigma(I_o)$ refining 613 parameters.

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Supporting Information Available: Fully labeled diagrams and tables of crystallographic data, data collection, solution, and refinement details, positional and thermal parameters, and bond distances and angles for **1**, **2**, and **3** (50 pages). Ordering information is given on any current masthead page.

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