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Articles

Some Mixed Transition Metal Compounds of 1,3-Diyne with Metallacycles Derived by Cross-Coupling of Alkynyl Ligands and Sequential C−C Bond Coupling between 1,3-Diyne and Carbon Monoxide

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By treating *cis*-Pt(C≡CPh)$_2$(dppe) (**1**) with $Mn_2(CO)_9(CH_3CN)$ in refluxing toluene, cross-coupling of alkynyl ligands occurs to afford mixed transition metal compound of 3,4-diphenyl-1,3-butadiyne, [$Mn_2Pt(\mu_3$-η^1:η^1:η^2:η^4-PhCCCCPh)(CO)$_6$(dppe)] (**2**) in 19−38% isolated yield. **2** has a structure formed by an unprecedented heterometal complexation of 1-manganacyclo-2,3,4-pentatriene. The Pt(II) acetylide, by treating with $Ru_3(CO)_9(PPh_3)_3$, directly converts into a π-complex of 1,3-diyne, Pt(η^2-PhCCCCPh)(dppe) (**4**), in 38% yield. By reacting π-alkyne compound Pt(η^2-PhCC−C≡CPh)(PPh$_3$)$_2$ with Fe(CO)$_5$ and $Ru_3(CO)_{12}$, bimetallic [FePt(μ_3-η^1:η^1:η^2-COC$_4$Ph$_2$)(CO)$_3$(PPh$_3$)$_2$] (**5a**) and triangular cluster [MPt$_2$(μ_3-η^1:η^1:η^2-PhCC−C≡CPh)-(CO)$_5$(PPh$_3$)$_2$] (**6a**) have successionally been isolated in considerable yields. A dimetallic analogue of alkyne [FePt{μ_2-η^1:η^1:η^2-C(O)C$_2$H$_2$}(CO)$_3$(PPh$_3$)$_2$] (**5b**) and trimetallic **[**MPt$_2$(μ_3-η^1:η^1:η^2-R^{1}CCR^2)(CO)$_{7-n}$(PPh$_3$)$_n$] (**6b**−**f**) {R^1 = Ph, R^2 = C≡CPh, $n = 3$, M = Fe, **6b**; $R^1 = R^2$ = H, $n = 3$, M = Fe, **6c**; $R^1 = R^2$ = Ph, $n = 2$, M = Fe, **6d** and ***iso*-6d**; $R^1 = R^2$ = OCOCH$_3$, $n = 2$, M = Fe, **6e**; M = Ru, **6f**} have consecutively been prepared. Crystal structures of five of the compounds have been determined.

Introduction

Oxidative coupling of alkynyl ligands may be one of the significant reactions studied more recently in the methodical syntheses of one-dimensional allotropes of the polyyne (−C≡C−) unit with nonlinear optical properties.[1] These nanomolecules and macrocyclic organometallic compounds[2] have mostly been derived by the tail-to-tail coupling of the terminal carbon atoms on the metal-assisted alkynyls, intermolecularly, using several oxidizing reagents (e.g., a stoichiometric amount of O_2 in the presence of CuX (X = Cl, I) and primary amines such as diethylamine and piperydine), Eglinton coupling using $Cu_2(OAc)_2$ in pyridine, and Cardiot−Chodkiewicz coupling[3] between lithiated alkynyls and halogenated alkyne.

On the other hand, metallacycles of alkyne(s) may be involved in important reactions such as the syntheses of carbocyclic and heterocyclic compounds.[4e,9] It should be noticed that σ-acetylide is well known to function as a ligand,[5] and many mixed metal clusters composed of

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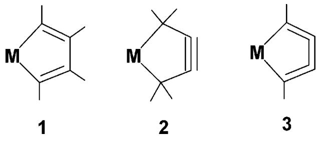
Scheme 1. Five-Membered Metallacycles of 1,3-Diyne

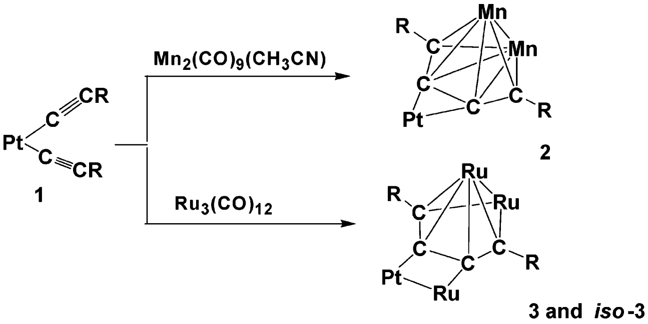


the versatile alkynyls have been prepared.[5] 1,3-Butadiyne can function as a greater electron supplier, which enables formation of up to a four-metal cluster bridged by its unusual linkages.[6] Metallacycles of 1,3-butadiyne formed by the head-to-head C−C bond coupling of σ-acetylides are known in mono- and dinuclear complexes.[4]

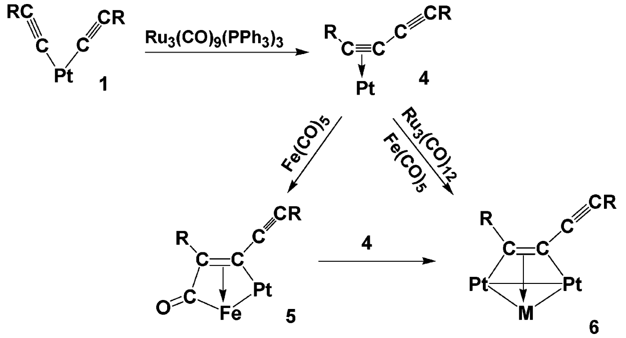
Small cyclic alkynes are usually unstable because of ring strain. 1-Metallacyclo-2,4-diene **1** (Scheme 1) is well known.[4e,6b] 1-Metallacyclo-3-pentyne compound **2**[7] was recently isolated by treating zirconocene dichloride with Bu-Li, followed with cumulenes having bulky substituents, (*Z*)-1,4-bis(trimethylsilyl)-1,2,3-butatriene and (*Z*)-2,2,7,7-tetramethyl-3,4,5-octatriene, or by a photoreaction of zirconocene dichloride in the presence of 1,4-dichloro-2-butyne and magnesium. Titanocene and zirconocene compounds **3** are five-membered metallacyclocumulenes, in which the 1,3-butadiyne compound was derived through an intramolecular C−C bond coupling of bis(σ-acetylide) by sunlight treatment.[8] Owing to the multiple-bond character of the C2−C3 bond, complexation of both **2** and **3** occurs to form heterodinuclear complexes composed of **3** and **1**, respectively. These metallacycles had a planar C_4 unit[6f,7c,8] contributed of hybrid resonance, suggesting an intermediate[9] in the cleavage of the C−C single bond of 1,3-butadiyne, interestingly. These reports of metallacycles that are formed by alkyne(s) are mostly concentrated on mononuclear and dinuclear complexes of titanium and zirconium. However, complexation of **2** or **3** of the electron-rich transition metals (Mn, Ru, Pt) forming tri- and tetranuclear complexes is elusive.

In our goal of alkyne oligomerization,[4d] we have utilized bis(acetylide) Pt(II) complexes and achieved acyclic dimeriztion of alkynyls through the head-to-head C−C bond coupling of acetylides in *cis*-$\mathrm{Pt(C{\equiv}CPh)_2(dppe)}$ (**1**) by using metal carbonyls in refluxing toluene. Simultaneously, mixed metal compounds of 1,3-diyne with unusual metallacycles have been obtained as shown in Scheme 2, in which **3** and ***iso*-3**, $\mathrm{[PtRu_3(PhCCCCPh)(CO)_{10}(dppe)]}$, are in an anomalous form given by complexation of 1-metalla-2,4-pentadiene as published elsewhere.[10] A new compound, $\mathrm{[Mn_2Pt(PhCCCCPh)(CO)_6(dppe)]}$ (**2**), has been prepared by reacting the bis(σ-acetylide)platinum(II) with $\mathrm{Mn_2(CO)_9(CH_3CN)}$. The crystal structure of **2** reveals an unprecedented metallacycle of 1,3-diyne, which is discussed in comparison of **3** and ***iso*-3**, newly determined in this paper. Σ-Acetylides in **1**, by treating with $\mathrm{Ru_3(CO)_9(PPh_3)_3}$ in refluxing toluene for 1 h, directly convert into the π-1,3-diyne compound $\mathrm{Pt(\eta^2\text{-}PhCCCCPh)(dppe)}$ (**4**), in 38% isolated yield,[11] as shown in Scheme 2. Successive reactions of $\mathrm{Pt(\eta^2\text{-}R^1CCR^2)(PPh_3)_2}$ ($\mathrm{R^1 = Ph, R^2 = {-}C{\equiv}CPh; R^1 = R^2 = H}$) with $\mathrm{Ru_3(CO)_{12}}$ and $\mathrm{Fe(CO)_5}$ have led to the isolation of a dimetallacyclic compound, $\mathrm{[FePt(\mu_2\text{-}\eta^1{:}\eta^1{:}\ \eta^2\text{-}C(O)R^1C{=}CR^2)(CO)_3(PPh_3)_2]}$ (**5**) ($\mathrm{R^1 = Ph, R^2 = C{\equiv}CPh}$, **5a**; $\mathrm{R^1 = R^2 = H}$, **5b**), through C−C bond coupling between 1,3-diyne and carbon monoxide, and then a triangular cluster, $\mathrm{[M_2Pt(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}R^1CCR^2)(CO)_5(PPh_3)_2]}$ **(6)** ($\mathrm{M = Fe, R^1 = Ph, R^2 = C{\equiv}CPh; R_1 = R_2 = H, Ph, COOCH_3; M = Ru, R^1 = Ph, R^2 = CCPh}$).

Scheme 2. Frameworks of Metallacycles of 1,3-Diyne Derived by Cross-Coupling of Acetylides



Scheme 3. Frameworks of Metallacycles of 1,3-Diyne Derived by Cross-Coupling of Acetylides and Successive C−C Bond Coupling between 1,3-Diyne and Carbon Monoxide



Experimental Section

Preparation of $\mathbf{[Mn_2Pt(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}PhCCCCPh)(CO)_6(dppe)]}$, 2. To $\mathrm{Mn_2(CO)_9(CH_3CN)}$ in toluene {in situ prepared by treating $\mathrm{Mn_2(CO)_{10}}$ (0.17 g) in $\mathrm{CH_2Cl_2}$ with $\mathrm{NMe_3{=}O{\cdot}H_2O}$ (0.05 g) and $\mathrm{CH_3CN}$ (0.1 g)} in a two-necked flask with a condenser was added $\mathrm{Pt(CCPh)_2(dppe)}$ (0.15 g). The mixed solution was then refluxed for 45 min, cooled, and evaporated. The residue was separated by column chromatography ($\mathrm{SiO_2}$). A red band was collected and rechromatographed {TLC($\mathrm{SiO_2}$)} using $\mathrm{CH_2Cl_2}$. From an eluent of a deep orange band in $\mathrm{CH_2Cl_2}$, followed by recrystallization of the product from $\mathrm{CH_3CN}$ in 253 K, crystals of deep orange plates were obtained (0.077 g, 38%/

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platinum atom). Anal. Found: C, 53.24; H, 3.40. Calc for $C_{48}H_{34}O_6P_2Mn_2Pt$: C, 53.69; H, 3.19. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) 2020s, 1990vs, 1949vs, 1929vs (M−CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 29.7(CH_2− of dppe), 143.9(Ph*C*C−*C*CPh), 175.2 (PhC*C*CCPh), 223.5 (Mn−CO). ^{31}P NMR ($CDCl_3$): δ (ppm) 53.22 ($J_{Pt,P}$ = 3140 Hz).

Preparation of [Pt(η^2-PhCCCCPh)(dppe)], 4. To $Pt(CCPh)_2$(dppe) (0.24 g) (**1**) in toluene was added $Ru_3(CO)_9(PPh_3)_3$[11] (0.4 g), and the mixed solution was refluxed for 1 h, cooled, and evaporated. The deep red residue was separated by column chromatography (SiO_2) using CH_2Cl_2. From an eluent of a red band, red crystals of unreacted $Ru_3(CO)_9(PPh_3)_3$ were recovered (0.096 g, 24%/Ru atom). An orange band was collected and rechromatographed {TLC(SiO_2)}. A colorless eluent, by recrystallization from toluene, gave pale yellow crystals of Pt(PhCCCCPh)(dppe) (0.09 g, 38% yield/Pt atom). Anal. Found: C, 63.03; H, 4.31. Calc for $C_{42}H_{34}P_2Pt$: C, 63.39; H, 4.31. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) $2108.6_m\{\nu(C{\equiv}C)_{nonbonding}$ of 1,3-diyne}, while $\nu(C{\equiv}C)_{bonding}$ could not be detected. ^{31}P NMR ($CDCl_3$): δ (ppm) 49.93($J_{Pt,P}$ = 3074 Hz), 48.31($J_{Pt,P}$ = 3304 Hz).

Preparation of [FePt{μ_3-η^1:η^1:η^2-C(O)C_4Ph_2}$(CO)_3(PPh_3)_2$], 5a. To Pt(η^2-PhCCCCPh)$(PPh_3)_2$ (0.25 g) in benzene was added $Fe(CO)_5$ (0.053 g). The solution was refluxed for 5 min, cooled, and evaporated. The residue was separated by column chromatography (Al_2O_3) using CH_2Cl_2. An eluent of a deep orange band gave deep orange crystals (0.282 g, 95% yield/platinum atom). Anal. Found: C, 62.36; H, 3.74; P, 5.32. Calc. for $C_{56}H_{40}O_4P_2FePt$: C, 61.72; H, 3.70; P, 5.69. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) $1953.5_{vs}\{\nu(CO)\}$, $1929.5_{vs}\{\nu(CO)\}$, $2011.4_{vs}\{\nu(CO)\}$, 1720.0m{ν(C=O)}. FABMS (*m*-nitrobenzyl alcohol as a matrix): *m/z* 1090(M^+), 1006(M^+ − 3CO), 978(M^+ − 4CO), 775 (M^+ − 4CO − 1,3-diyne)}. ^{31}P NMR ($CDCl_3$): δ (ppm) 25.60{$J_{Pt,P}$ = 3996.2 Hz}, 29.08{$J_{Pt,P}$ = 2782 Hz}. ^{13}C NMR ($CDCl_3$): δ (ppm) 216.6{Fe*C*(O)C(Ph)=C(CCPh)}, 204{$Fe(CO)_3$}, 83.0{PhC(Pt)=C(Pt)−C≡*C*Ph}, 98.4{PhC−(Pt)=C(Pt)−*C*≡CPh}, 147{PhC≡C−*C*(Pt)=C(Pt)−Ph}, 166{PhC≡C−C(Pt)=*C*(Pt)Ph, J_{Pt-C} not well resolved}. An analogous reaction by extending the period in refluxing toluene up to 30 min considerably decreased its yield to 27%.

Preparation of [FePt{μ_2-η^1:η^1:η^2-C(O)C_2H_2}$(CO)_3(PPh_3)_2$], 5b. Into a benzene solution of $Pt(PPh_3)_4$ (1.1 g), acetylene was bubbled for a few minutes, during which the canary yellow solution turned colorless. $Fe(CO)_5$ (0.17 g) was then added into the solution. The mixed solution was refluxed for 30 min, cooled, and evaporated. The residue was separated by column chromatography (Al_2O_3) using CH_2Cl_2. An eluent of a yellow band gave yellow microcrystals (0.37 g, 46% yield/platinum atom). Anal. Found: C, 55.78; H, 4.03. Calc for $C_{42}H_{32}O_4P_2FePt$: C, 55.21: H, 3.53. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) $2014.6_{vs}\{\nu(CO)\}$, $1946.5_{vs}\{\nu(CO)\}$, $1749.5_s\{\nu(C{=}O)\}$. ^{13}C NMR ($CDCl_3$): δ (ppm) 234.335{Fe−(*C*=O)−HCCH}, 221.55{Fe(*C*O)$_3$}, 221.09{Fe(CO)$_3$}, 220.18{Fe(*C*O)$_3$}, 154.376{−C(=O)−C(Pt)H=*C*H(Pt), J_{Pt-C} = 695.8 Hz}, 155.29{−C(=O)−*C*H (Pt)=C(Pt)H}.

Crystallographic Determination of 2, *iso*-3, and 4. Intensity data collected by $\theta/2\theta$ scans at 298 K using a MXC 18 diffractometer (Mac Science) and Mo Kα radiation were corrected for Lorentz and polarization effectes, but not for absorption. Structure solutions were by direct methods using CRYSTAN SIR STAN, with refinement by full-matrix least-squares on F_o^2. All diagrams and calculations were performed using CRYSTAN (MacScience, Japan) or by DIRDIF 99[12] and WinGX 3.0.[13]

Crystal Structure Determination of 6a, 6c, 6d, and *iso*-6d. Intensity data collected by $\omega-2\theta$ scans at 20 °C on a Nicolet R3v/m instrument using Mo Kα radiation (λ = 0.7103 Å) were corrected for Lorentz and polarization effects and for absorption by semiempireral methods based on ψ scans. Structure solutions were performed by direct methods using SHELXL-97,[14] with refinement by full-matrix least-squares on F_o^2. All non-hydrogen atoms were refined anisotropically with H atoms in the calculated positions riding on C atoms with C−H fixed at 0.96 Å.

Crystal Structure Data of $C_{48}H_{34}O_6P_2Mn_2Pt$, 2. A single crystal was obtained from CH_3CN−hexane at 248 °C: monoclinic, space group $P12_1/c_1$, $a = 11.0250(50)$ Å, $b = 16.2310(50)$ Å, $c = 24.4320(50)$ Å, $\alpha = 90.000(5)°$, $\beta = 97.889(5)°$, $\gamma = 90.000(5)°$, $V = 4330.65(39)$ Å^3, $Z = 4$, $D_c = 1.65$ g·cm^{-3}, $R_1 = 0.0658$, $wR_2 = 0.3141$, Goof(S) = 1.4790 for 9939 independent reflections, in the range $0° < 2\theta < 54.99°$, with $F_o > 4\sigma(F_o)$ refining 5160 parameters.

Crystal structure data of $C_{52}H_{34}O_{10}P_2PtRu_3$, *iso*-3: orthorhombic, space group *Pcab*, $a = 19.5170(50)$ Å, $b = 23.4600(50)$ Å, $c = 31.0440(50)$, $\alpha = 90.000(5)°$, $\beta = 90.000(5)°$, $\gamma = 90.000(5)°$, $V = 14214(5)$ Å^3, $Z = 8$, $D_c = 1.289$ g·cm^{-3}, $R_1 = 0.047$, $wR_2 = 0.1921$, Goof(S) = 1.5710 for 13 074 independent reflections, in the range $0° < 2\theta < 51.36°$, with $F_o > 4\sigma(F_o)$ refining 9738 parameters.

Crystal structure data of $C_{42}H_{34}P_2Pt$, 4: triclinic, space group $P\bar{1}$, $a = 196(5)$ Å, $b = 21.201(5)$ Å, $c = 9.352(5)$ Å, $\alpha = 93.142(5)°$, $\beta = 111.401(5)°$, $\gamma = 87.661(5)°$, $V = 1878.9(14)$ Å^3, $Z = 2$, $D_c = 1.406$ g·cm^{-3}, $R_1 = 0.0934$, $wR_2 = 2746$, Goof(S) = 1.2490 for 8620 independent reflections, in the range $0° < 2\theta < 55.00°$, with $F_o > 4\sigma(F_o)$, refining 5961 parameters. Selected bond distances (Å) and angles (deg): Pt1−C1 2.02(3), Pt1−C3 1.98(3), C1−C2 1.39(4), C1−C3−C1 1.34(4), C2−C4 1.18(4): C1−Pt1−C3 39.0(11), Pt1−C1−C3 68.8, Pt1−C3−C1 72.1(19), Pt1−C3−C71 148.9(19), C1−C3−C71 139(3), C2−C1−C3 143(3), C1−C2−C4 172(3).

Crystal structure data of $C_{56}H_{40}FeO_4P_2Pt$, 5a: M = 1089.76, orange crystal, 0.50 × 0.25 × 10 mm, triclinic, space group $P\bar{1}$, $a = 11.540(5)$ Å, $b = 12.275(5)$ Å, $c = 21.489\ (12)$ Å, $\alpha = 96.13(3)°$, $\beta = 92.65(3)°$, $\gamma = 117.88(3)°$, $V = 2659(2)$ Å^3, $Z = 2$, $D_c = 1.361$ g·cm^{-3}, $F(000) = 1084$, μ(Mo Kα) = 34.52 cm^{-1}, $R_1 = 0.0584$, $wR_2 = 0.1544$, goof = 1.085 for 7128 reflections in the range $5° < 2\theta < 45°$ with $I > 2\sigma(I_0)$ refining 577 parameters.

Results and Discussion

Dialkynyl compound *cis*-$Pt(CCPh)_2$(dppe) reacts with $Ru_3(CO)_{12}$ to undergo intramolecular C−C bond coupling of alkynyl ligands to afford a mixed metal compound of 1,3-diyne, the racemate [$PtRu_3$(PhCCCCPh)$(CO)_{10}$(dppe)] (**3**) and its isomer ***iso*-3**.[10] Cross-coupling of alkynyl ligands has also been achieved by reacting $Pt(C{\equiv}CPh)_2$(dppe) with $Mn_2(CO)_9(CH_3CN)$ in refluxing toluene for 1 h, and a heterometal compound of 1,3-diyne, [Mn_2Pt(PhCCCCPh)$(CO)_6$(dppe)] (**2**), was obtained in 19−38% yield. ^{31}P NMR of **2** showed a single resonance at 53.22 ppm with $J_{Pt,P}$ = 3140 Hz, suggesting a symmetrical arrangement of the Pt(dppe) group. ^{13}C NMR spectra showed that two alkynyl carbons from $Pt(CCPh)_2$(dppe) are also symmetrically arranged, and two resonances at 143.9 and 175.2 ppm were observed. A single crystal of **2** was obtained from CH_3CN−hexane at 253 K, and its crystal structure was determined. An intriguing molecular structure of **2** is shown in Figure 1 (phenyl rings of dppe are omitted for clarity). A carbon of the alkynyls in $Pt(C{\equiv}CPh)_2$(dppe) undergoes cross-coupling, forming 1,4-diphenylbuta-1,3-diyne, whose alkyne carbons newly bond to the $Mn_2(CO)_6$ group in a (η^1:η^1:η^2:η^4)-fashion and the central carbon of 1,3-diyne

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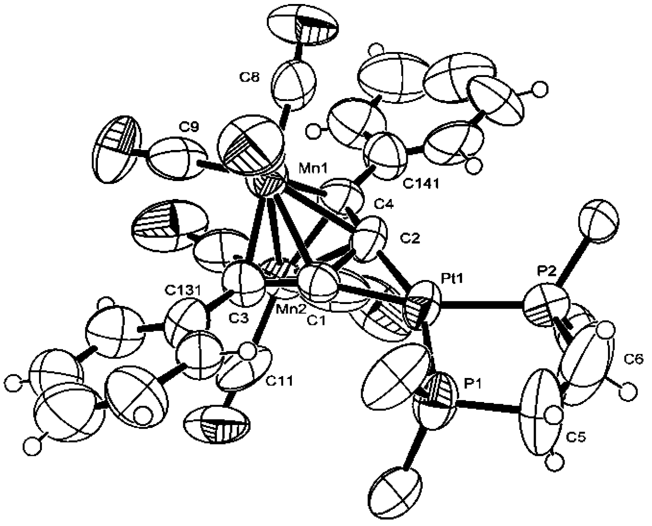

Figure 1. ORTEP plot (50% probability thermal ellipsoids) for $Mn_2Pt(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}PhCCCCPh)(CO)_6(dppe)_4$, **2**. Phenyl rings of dppe are omitted for clarity.

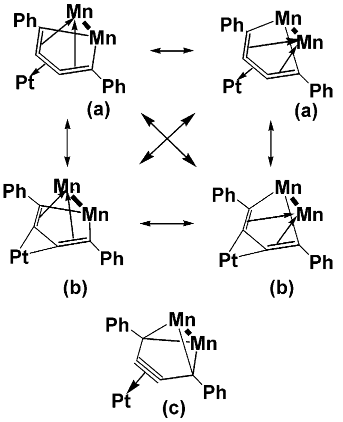

Figure 2. Structure of **2** with complexation of (a) managanacyclocumulene; (b) manganacyclopentadiene; (c) manganacyclopentyne.

is now also bound to the Pt(dppe) group by an η^2-bond. Bond lengths Mn1−C3 (2.06(2) Å), Mn1−C4 (2.05(3) Å), Mn2−C3 (2.03(2) Å), and Mn2−C4 (2.00(3) Å) are consistent with a Mn−C σ-bond,[13] while all bond lengths Mn1−C1 (2.20(2) Å), Mn1−C2 (2.23(2) Å), Mn2−C1 (2.21(2) Å), and Mn2−C2 (2.28(2) Å) are consistent with η^2-bonds. Bond lengths Pt−C1 (2.04(2) Å) and Pt−C2 (2.03(2) Å) may also be comparable with 2.041(7) and 2.036(8) Å of $Pt(\eta^2\text{-}PhCCCCPh)(PPh_3)_2$,[17] but they do not significantly differ from 2.07 to 2.09 Å of a pure Pt−C σ-bond.[10,11] The geometry around the Pt atom in **2** is in good planarity, and C1, C2, C3, and C4 are coplanar {dihedral angles: C3−C1−C2−C4, 4(4)°, and P1−Pt1−C2−C1, 1.63°}. The structure appears to contain a crystallographically symmetrical plane, through which Mn1 and Mn2 atoms are equivalently positioned with bond length Mn1−Mn2 of 2.5798(60) Å. It should be noticed that the C1−C2 bond distance (1.45(3) Å) is longer than 1.206(7)[7a] and 1.336(4) Å[7c] of the 1-metalla-3-pentyne compounds of zirconocene and 1.33(4) Å of the C−C triple-bond distance in η^2-bonding 1,3-diyne,[10] but rather approaching close to 1.444(8) Å of the C−C double-bond length in a π-bonding stylene compound[15] or 1.45(2) Å of the C−C single-bond distance in **3**.[10] The bond angles C1−C2−C4 (120(2)°) and C2−C1−C3 (127(2)°) in the present case are fairly expanded from 113.7(15)° and 115.6(11)° of the corresponding angles of 1-metallacyclopenta-2,4-diene (**3**), but much narrower than 155.9(7)° and 156.2(6)° of the mononuclear 1-metallacyclopentyne[7a] and 136.78(3)° and 140.6(3)° of the corresponding dinuclear complex.[7c]

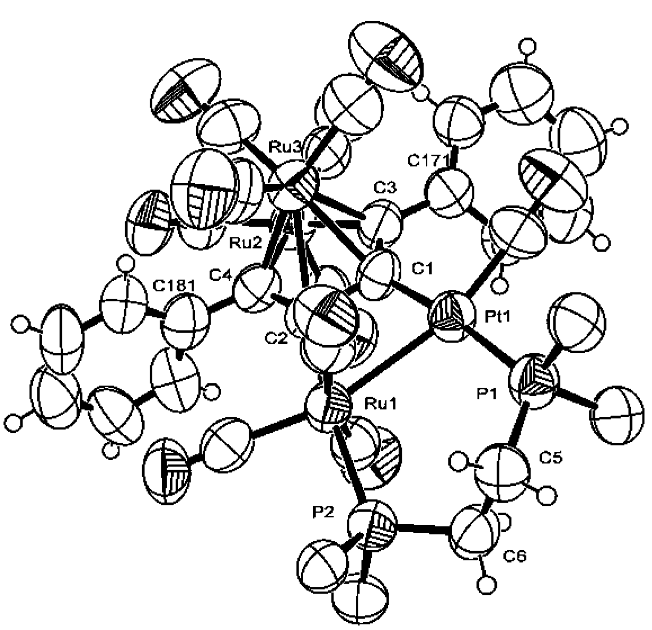

Figure 3. ORTEP plot (50% probability thermal ellipsoids) for $PtRu_3(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^4\text{-}PhCCCCPh)(CO)_{10}(dppe)$, ***iso*-3**. Phenyl rings of dppe are omitted for clarity.

Atomic distances C1−C3 (1.37(3) Å) and C2−C4 (1.40(3) Å), on the other hand, are close to those of vinyl carbons {1.398(18) and 1.404(17) Å of ***iso*-3**, vide infra}, although they are slightly longer than 1.30−1.36 Å of the corresponding distances of the rhodium-cumulene complex $RhCl(P^iPr_3)_2(\eta^2\text{-}H_2CCCCCCPh_2)$,[16] which may be caused by the distortion of the metallacycles. The 1,3-diyne in **2** can, therefore, be viewed as a double complexation form of either a five-membered (a) metallacyclotriene or (b) metallacyclodiene, rather than an electron localized form of (c) 1-metallacyclopentyne geometry.[7−9] The actual structure may be close to (a), which may largely be contributed from (b). The crystal structure of ***iso*-3**, obtained as an isomer of **3**,[10] was newly determined, which is in Figure 3 (phenyl rings of bridging dppe are omitted for clarity). 1,4-Diphenylbuta-1,3-diyne in ***iso*-3** cross-links mixed metal nuclei by a ($\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^4$) bond, forming a 1-ruthenacyclopenta-2,4-diene framework, while dppe in ***iso*-3** bridges over Pt1 and Ru1 atoms and one carbon monoxide now bonds to the Pt1 atom, as expected.[10] The geometry around the platinum atom is in good planarity. Atomic distances of Pt−C, Ru−C, and Ru−Ru bonds in ***iso*-3** do not significantly differ from those of **3**, although the bridging dppe of ***iso*-3** results in formation of fairly expanded bond angles Pt1−P1−C5 (120.9(5)°), Ru1−P2−C6 (117.1(5)°), P1−C5−C6 (111.4(9)°), and P2−C6−C5 (112.8(9)°) from 108.5(7)° {107.8(6)°},

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Table 1. Selected Bond Distances (Å) and Angles (deg) for $Mn_2Pt(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^4\text{-}PhCCCCPh)(CO)_6(dppe)_4$, 2

bond distance		bond angle	
Pt1−C1	2.04(2)	Pt1−C1−Mn1	129.3(11)
Pt1−C2	2.03(2)	Pt1−C2−Mn2	120.8(11)
C1−C3	1.37(3)	Pt1−C2−Mn1	128.4(11)
C1−C2	1.45(3)	C2−C1−C3	127.0(2)
Mn1−C1	2.20(2)	Pt1−C2−C1	69.6(13)
Mn1−C2	2.23(2)	Mn1−C2−C1	69.9(13)
C2−C4	1.40(3)	Mn2−C2−C1	68.5(12)
Mn1−C3	2.06(2)	C1−C2−C4	120.0(2)
Mn1−C4	2.05(3)	Pt1−C1−C2	68.8(13)
Mn2−C1	2.21(2)	Mn1−C1−C2	71.9(13)
Mn2−C2	2.28(2)	Mn2−C1−C2	73.9(13)
Mn2−C3	2.02(2)	Pt1−C1−Mn2	123.8(11)
Mn2−C4	2.00(3)	Mn2−C2−C4	60.5(13)

Table 2. Selected Bond Distances (Å) and Angles (deg) for $PtRu_3(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^4\text{-}PhCCCCPh)(CO)_{10}(dppe)$, *iso*-3 and 3

***iso*-3**		**3**		
Pt1−Ru1	2.7360(14)	Pt1−Ru1	2.732(15)	2.7394(14)
Ru2−Ru3	2.7165(18)	Ru2−Ru3	2.722(2)	2.709(2)
Pt1−C1	2.055(12)	Pt1−C1	2.100(16	2.074(14)
Ru1−C2	2.088(13)	Ru1−C2	2.130(16)	2.137(18)
Ru2−C3	2.105(13)	Ru2−C3	2.09(2)	2.126(18)
Ru2−C4	2.107(16)	Ru2−C4	2.171(16)	2.144(16)
Ru3−C1	2.286(12)	Ru3−C1	2.355(15)	2.387(14)
Ru3−C2	2.3556(12)	Ru3−C2	2.365(17)	2.333(17)
Ru3−C3	2.236(14)	Ru3−C3	2.224(14)	2.289(16)
Ru3−C4	2.253(16)	Ru3−C4	2.262(18)	2.240(17)
C1−C2	1.465(18)	C1−C2	1.45(2)	
C1−C3	1.398(18)	C1−C3	1.44(2)	1.43(2)
C2−C4	1.406(17)	C2−C4	1.41(3)	1.45(2)
Pt1−C1−C2	107.5(8)	Pt1−C1−C2	106.0(12)	104.6(11)
Ru1−Pt1−C1	72.4(3)	Ru1−Pt1−C1	73.4(5)	74.8(4)
Pt1−Ru1−C2	71.2(3)	Pt1−Ru1−C2	71.0(4)	69.0(4)
Ru1−C2−C4	138.2(10)	Ru1−C2−C4	138.1(12	132.5(12)
C1−C2−C4	113.2(11)	C1−C2−C4	113.6(15)	116.8(15)
Ru1−C2−C1	107.2(8)	Ru1−C2−C1	108.3(11)	110.6(11)
C2−C1−C3	115.6(11)	C2−C1−C3	114.9(13)	113.2(13)

107.1(12)°, and 108.1(12)° of the corresponding angles of **3**, respectively (Table 2).

Reactions of the platinum(II) acetylide with $Ru_3(CO)_9(PPh_3)_3$ in refluxing toluene for 1 h afforded pale yellow $Pt(\eta^2\text{-}PhCCCCPh)(dppe)$ (**4**) in 30−38% yield. From the reaction products, deep red crystals of $Ru_3(CO)_9(PPh_3)_3$ were unexpectedly recovered in 40% yield, while any mixed metal compounds could not be isolated. The details of reductive elimination of the complex are still uncertain. The crystal structure of **4** showed that the geometry around the η^2-bonding 1,3-diyne does not significantly differ from that of the corresponding PPh_3 complex.[17] The corresponding PPh_3 complex, $Pt(\eta^2\text{-}R^1\text{-}CCR^2)(PPh_3)_2$, reacts with an equimolar amount of $Fe(CO)_5$ {and $Ru_3(CO)_{12}$} in refluxing C_6H_6 or toluene to undergo an incorporation of an $Fe(CO)_4$ group with the π-alkyne-Pt complex to afford the heterobimetallic compound $[PtFe(\mu_2\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C(O)C_4Ph_4)(CO)_3(PPh_3)_2]$ in 95% yield and then the heterotrimetallic triangular cluster $[MPt_2(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhCCCCPh)(CO)_5(PPh_3)_2]$ (**6a**) in considerable yields. The dimetallic analogue $[FePt(\mu_2\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}HCC(O){=}CH)(CO)_3(PPh_3)_2]$ (**5b**) and trimetallic $[MPt_2(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}PhCCCCPh)(CO)_{7-n}(PPh_3)_n]$ (n = 3, M = Fe, R^1 = Ph, R^2 = CCPh, **6b**; n = 3, M = Fe, R^1 = R^2 = H, **6c**; n = 2, R^1 = R^2 = Ph, M = Fe, **6d** and ***iso*-6d**; n = 2, R^1 = R^2 = $OCOCH_3$ M = Fe, **6e**; Ru, **6f**) have been correlatively prepared.

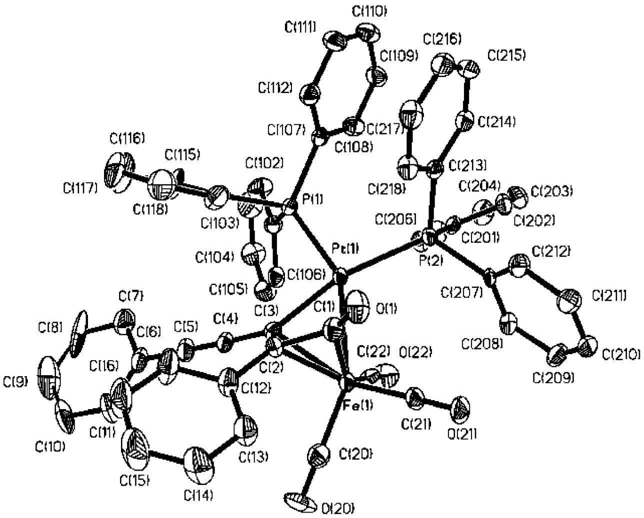

Figure 4. ORTEP plot (50% probability thermal ellipsoids) of $[FePt\{\mu_2\text{-}\eta^1{:}\eta^1{:}\eta^2\text{-}C(O)C_4Ph_2\}(CO)_3(PPh_3)_2]$, **5a**. Phenyl rings of PPh_3 are omitted for clarity.

For **5a**, one alkyne carbon atom of the 1,3-diyne still remains intact as a dangling triple bond,[21] as assesed by ^{13}C NMR spectra: Resonances due to 1,3-diyne were observed by four resonances at 83.9, 98.4, 146, and 166 ppm. The former two resonances are due to nonbonding alkyne carbons, while the other two to a bonding group. A strong stretching band was observed at 1720.0 cm^{-1}, which is due to an organic ketonic carbonyl, and the corresponding ^{13}C NMR resonance appeared at 216.6 ppm.[18,19] ^{31}P NMR resonances were observed at 25.60 $\{J_{Pt,P} = 3996.2$ Hz$\}$ and 29.08 $\{J_{Pt,P} = 2782$ Hz$\}$, suggesting that two phosphorus atoms in the $Pt(PPh_3)_2$ group are unsymmetrically arranged. **5b** may have an analogous structure to **5a**, and a strong IR absorption band due to the organic ketonic carbonyl was observed at 1750 cm^{-1} and ^{13}C NMR resonance at 234.33 ppm, respectively. The acetylene carbons are also unsymmetrically arranged, and two resonances at 154.4 ppm ($J_{Pt,C}$ = 696 Hz) and 166 ppm are consistent with a Pt−C σ bond and an Fe−C σ bond, respectively. The crystal structure of **5a** is shown in Figure 4. An end carbon atom of 1,3-diyne newly undergoes a C−C bond coupling[19,20] with carbon monoxide from the $Fe(CO)_4$ group {Fe−C(1) distance 2.024(12) Å}, resulting in formation of an iron-acyl group. The other carbon atom of the bonding alkyne group also forms a pure Pt−C σ bond {bond distance Pt−C(3) 2.098(10) Å}. Bond distances Fe(1)−C(2) (2.153(10) Å) and Fe(1)−C(3) (2.146(9) Å) are consistent with η^2-bonding. One alkyne group of the 1,3-diyne forms a dimetallacycle in which the bond distance

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Table 3. Selected Bond Distances (Å) and Angles (deg) of [FePt{μ_2-η^1:η^1:η^2-C(O)C$_4$Ph$_2$}(CO)$_3$(PPh$_3$)$_2$], 5a

bond distance		bond angle	
Pt(1)−C(3)	2.098(10)	P(1)−Pt(1)−P(2)	99.64(9)
Pt(1)−Fe(1)	2.608(2)	Fe(1)−Pt(1)−C(3)	52.9(2)
Pt(1)−P(1)	2.309(3)	Pt(1)−Fe(1)−C(2)	75.2(3)
Pt(1)−P(2)	2.350(3)	Pt(1)−C(3)−C(2)	110.2(7)
C(1)−O(1)	1.194(13)	Fe(1)−C(2)−C(3)	70.2(5)
C(2)−C(1)	1.49(2)	Fe(1)−C(3)−C(4)	129.7(7)
C(2)−C(3)	1.441(14)	Fe(1)−C(1)−C(2)	73.7(6)
C(2)−C(12)	1.51(2)	C(12)−C(2)−C(3)	128.8(9)
C(3)−C(4)	1.426(14)	C(2)−C(3)−C(4)	121.0(9)
C(4)−C(5)	1.22(2)	C(3)−C(4)−C(5)	177.3(12)
Fe(1)−C(2)	2.153(10)	C(2)−C(1)−O(1)	140.0(11)
Fe(1)−C(3)	2.146(9)		
Fe(1)−C(1)	2.024(12)		
Fe(1)−C(20)	1.835(14)		
Fe(1)−C(21)	1.793(11)		
Fe(1)−C(22)	1.824(13)		
Pt(1)−Fe(1)	2.608(2)		

Fe(1)−Pt(1) is 2.608(2) Å. The other alkyne of the 1,3-diyne remains intact, as expected. The geometry around the platinum atom is planar.

The C(1)−O(1) bond distance of 1.194(13) Å is considerably shorter than the normal organic ketones (1.215 Å).

Bond distances C(2)−C(1) (1.49(2) Å) and C(3)−C(2) (1.441(14) Å) in **5a** do not significantly differ from the 1.461(5) and 1.423(6) Å of the corresponding distances in [Ru$_2$(CO)(μ-CO){μ-σ:η^2-C(O)C$_2$Ph$_2$}(η-C$_5$H$_5$)$_2$].[20] The structure of **5** could be viewed either as a dimetallacyclopentenone (a) or a bridging carbene with a ketene substituent (b), as depicted in Figure 5. The actual structure may be approaching an electron delocalized form (c) with an allylic bond, but may be rather close to (a).

The dimetallacyclopenetenone has recently been established for Os−Ir, Os−Fe, Os−Rh,[18] Fe−Pt,[19] Fe$_2$, and Ru$_2$ systems,[20] which have mostly been obtained by the reactions of dinuclear complexes with alkynes. It is also known that the π-bonding alkyne in the Pt(0) compound displays an acidic nature which is susceptible to an attack of nucleophile such as carbon monoxide or metal-carbonyl to lead to the isolation of clusters.[20,21] Pt(diyne)(PPh$_3$)$_2$ itself did not react with carbon monoxide. Instead, by treatment of **5a** with Pt(diyne)(PPh$_3$)$_2$ in refluxing toluene, **6a**[17] was obtained in 75% yield (/Pt atom of the dimer), while the same reaction in the presence of carbon monoxide gave **6a** in 55% yield. For the transformation of **5a** to **6a**, the primary step may be supposed as a reductive elimination, which may proceed via C−C bond scission of the bridging organic ketonic carbonyl in the Fe(CO)$_4$ group.[22] [FePt$_2$(μ_3-η^1:η^1:η^2-PhCCCPh)(CO)$_4$(PPh$_3$)$_3$] (**6b**)[23] was obtained by treating Pt(η^2-PhCCCPh)(PPh$_3$)$_2$ with Fe(CO)$_5$ directly in refluxing toluene for 30 min in 13% yield, although the main products was **6a** (62% yield). **6b** and **6c**[24] consist of a Fe(CO)$_2$(PPh$_3$) group attached to [Pt$_2$(μ_2-η^1:η^1-C$_4$Ph$_2$)(CO)$_2$(PPh$_3$)$_2$]. For **6b**, a ^{31}P NMR resonance arising from the Fe(CO)$_2$(PPh$_3$) group was observed at 65.7 ppm, while resonances arising from the Pt$_2$(PhCCCPh)(CO)$_2$(PPh$_3$)$_2$ group appeared at 29.94 ($^1J_{Pt,P}$ = 2841.8 Hz) and 25.11 ppm ($^1J_{Pt,P}$ = 3991.5 Hz) with a nuclear spin system A$_2$M$_2$,[25] but $^2J_{Pt,P}$ as observed for **6a** could not be discerned in this case. Clusters with a disymmetrical alkyne, [Pt$_2$M(C$_2$R$_2$)(CO)$_5$(PPh$_3$)$_2$] (M = Fe, R = Ph, **6d** and ***iso*-6d**; R = OCOCH$_3$, M = Fe, **6e**; R = OCOCH$_3$, M = Ru, **6f**) were analogously prepared, except for the cases of **6e** and **6f**, which were prepared by addition reactions of a M(CO)$_3$ (M = Fe, Ru) group to the Pt(I) dimer, [Pt$_2${μ_2-η^1:η^1-C$_2$(CO$_2$CH$_3$)$_2$}(CO)$_2$(PPh$_3$)$_2$].[26] **6d** has already been prepared by Adams et al.[27] We have, however, obtained **6d** as a mixture with isomer ***iso*-6d**,[28] as ^{31}P NMR spectra show with relative intensities (3:2), which could not, however, be separated by the TLC(SiO$_2$) method. The NMR of **6** also suggests that the arrangement of two phosphorus atoms in each Pt$_2$(CO)$_2$(PPh$_3$)$_2$ group is directly related with the long-distance coupling $^2J_{Pt,P}$: the ^{31}P NMR of the *isomer* **6d**

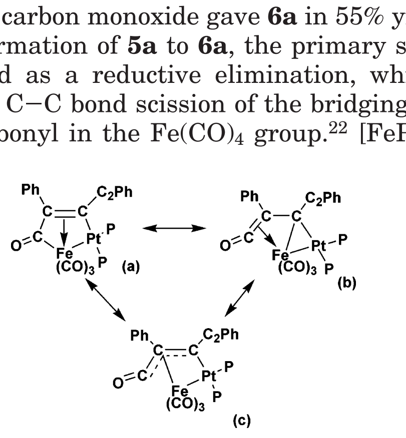

Figure 5. Geometry of **5a** with metallacycle of 1,3-butadiyne in resonante structures of (a) 1,2-dimetalla-3-pentene-4-one; (b) η^2-bonding carbene with a ketene substituent; (c) allylic bond.

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(23) **6b** was prepared as follows: Reactions of Pt(diyne)(PPh$_3$)$_2$ (0.25 g) with Fe(CO)$_5$(0.05 g) in refluxing toluene for 5 min, followed by separation of the products by TLC(SiO$_2$) using CH$_2$Cl$_2$, gave three products, which were respectively identified as **6a** (13% yield/platinum atom); **5a** (27% yield/platinum atom); and [FePt$_2$(μ_3-η^1:η^1:η^2-PhCCCPh)(CO)$_4$(PPh$_3$)$_3$], **6b**. Anal. Found: C, 57.63; H, 3.65. Calc for C$_{74}$H$_{55}$O$_4$P$_3$FePt$_2$: C, 57.44; H, 3.59. FABMS (*m*-nitrobenzyl alcohol as a matrix): *m/z* 1548(M$^+$) 1463(M$^+$ − 3CO) 1239(M$^+$ − 4CO). ^{31}P NMR (CDCl$_3$): δ (ppm) 65.72(Fe−PPh$_3$), 29.94{Pt^1-PPh$_3$, J_{Pt-P} = 2841.8 Hz}, 25.11{Pt^2-PPh$_3$, $J_{Pt,P}$ = 3991.5 Hz}. ^{13}C NMR (CDCl$_3$): δ (ppm) 227.8{Fe−CO}, 220.6{Fe−CO}, 219.7{Pt−CO}, 216.54{Pt−CO}, 83.0{PhC(Pt)=C(Pt)−C≡*C*Ph}, 98.4{PhC(Pt)=C(Pt)−*C*CPh}, 146.0{PhC≡C−*C*(Pt)=C(Pt)-Ph}, 166.0{PhC≡C−C(Pt)=*C* (Pt)Ph}.

(24) **6c** was obtained as follows: In the same TLC separation processes isolating **5b**, an eluent of another deep orange band gave deep orange crystals of Pt$_2$Fe(μ_3-η^1:η^1:η^2-HCCH)(CO)$_4$(PPh$_3$)$_3$, **6c** (0.28 g, 54%/platinum atom). Anal. Found: C, 52.54; H, 3.53. Calc for C$_{60}$H$_{47}$O$_4$P$_2$FePt$_2$: C, 52.56; H, 3.30. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) 2021.9$_{vs}$, 1964.8$_{vs}$, 1916.0$_{vs}$, 1979.9$_{vs}$ cm^{-1}. ^{13}C NMR (CDCl$_3$): δ (ppm) 219.66{Fe(CO)$_2$}, 198.6(Pt−CO, ^{195}Pt satellites not discerned), 150.86(Pt−*C*H=*C*H−Pt, ^{195}Pt satellites not discerned).

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(26) (a) Koie, Y.; Shinoda, S.; Fitzgerald, B. J.; Pierpondt, C. G. *Inorg. Chem.* **1980**, *19*, 770. (b) Koie, Y.; Shinoda, S.; Saito, Y. *Inorg. Chem.* **1981**, *20*, 4408. (c) The starting compound, [Pt{C$_2$(COOMe)$_2$}(PPh$_3$)$_2$], was prepared and characterized as follows. To Pt(PPh$_3$)$_4$ (1.21 g) in C$_6$H$_6$ was added dmad (dimethylacetylene dicarboxylate, 0.138 g). The solution was stirred at room temperature for 5 min and evaporated. The residue, after washing by hexane and diethyl ether, was recrystallized from C$_6$H$_6$−hexane to give colorless crystals (0.43 g, 51%). Anal. Found: C, 59.02; H, 4.10; P, 6.77. Calc for C$_{42}$H$_{36}$O$_4$P$_2$Pt: C, 58.54; H, 4.21; P, 7.19. ^{31}P{^{1}H} NMR (CDCl$_3$): δ (ppm) 24.18(s) ($J_{Pt,\ P}$ = 3727.57 Hz). ^{1}H NMR (CDCl$_3$): δ (ppm) 3.30(Me of dmad). ^{13}C{^{1}H} NMR (CDCl$_3$): δ (ppm) 51.68 (COO*C*H$_3$), 165.60(t, −*C*OOMe; $^3J_{P,\ C}$ = 20.12 Hz). (d) Crystal structure data of C$_{42}$H$_{36}$O$_4$P$_2$Pt: M = 789.70, colorless crystal, 0.35 × 0.3 × 0.2 mm, monoclinic, space group $P2_1/n$, $a = 20.309(9)$ Å, $b = 15.355(7)$ Å, $c = 11.777(3)$ Å, $\beta = 97.89(3)°$, $V = 3637.89$ Å^3, $Z = 4$, $D_c = 0.994$ g·cm^{-3}, $R_1 = 0.032$, $wR_2 = 0.042$, goof(S) = 1.360 for 4410 reflections in the range $1° < \theta < 30°$ with $I > 3.00\sigma(I_0)$ refining 550 parameters. Selected distances (Å) and angles (deg): Pt(1)−P(2) 2.280(3), Pt(1)−P(3) 2.285(3), Pt(1)−C(6) 2.055(12), Pt(1)−C(9) 2.023(13), C(6)−C(9) 1.302(18), C(6)−C(30) 1.433(18), C(9)−C(17) 1.467(19), P(2)−Pt(1)−P(3) 105.2(1), P(2)−Pt(1)−C(9) 107.3(4), C(6)−Pt(1)−C(9) 37.2(5), C(6)−Pt(1)−P(3) 110.6(4), C(9)−C(6)−C(30) 143.4(13), C(6)−C(9)−C(17) 141.2(12).

(27) Adams, R. D.; Wunz, U. H. F.; Captain, B.; Fu, W.; Steffen, W. *J. Organomet. Chem.* **2000**, *614−615*, 75.

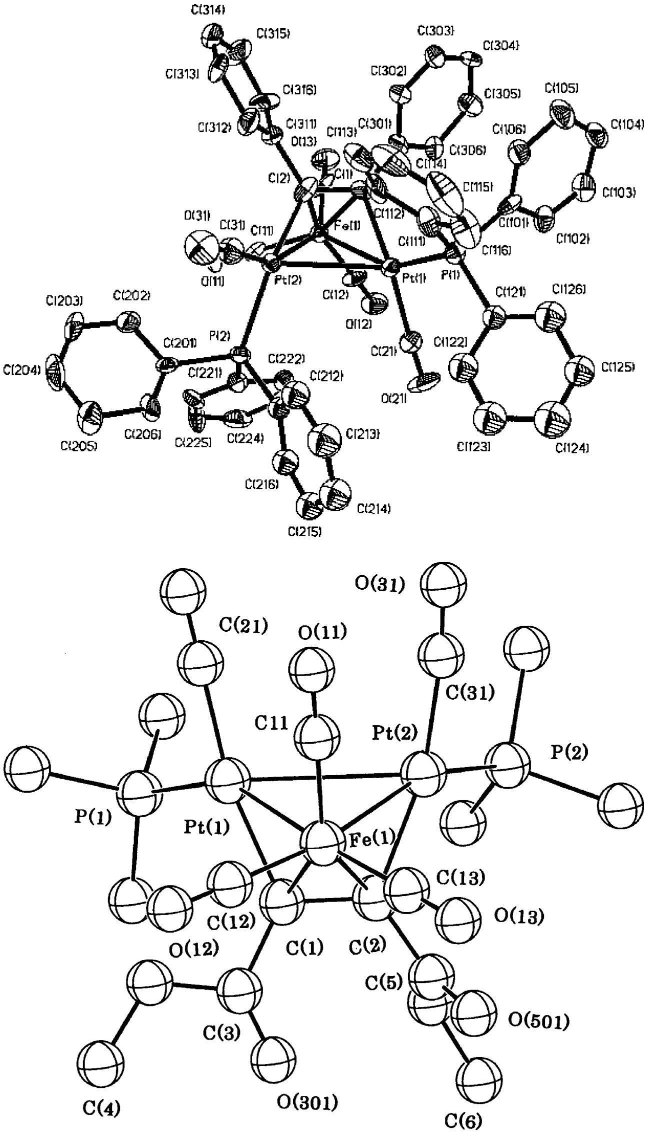

Figure 6. Crystal structures of (μ_3-η^1:η^1:η^2)-bonding alkyne in triangular cluster: [FePt$_2$(μ_3-η^1:η^1:η^2-PhCCPh)(CO)$_5$(PPh$_3$)$_2$], ***iso*-6d**, and [FePt$_2$(μ_3-η^1:η^1:η^2-CH$_3$OCOCCCOOCH$_3$)(CO)$_5$(PPh$_3$)$_2$], **6e**.

consists of nuclear spin system A$_2$MM′ with $^1J_{\mathrm{A,M}}$ = $^1J_{\mathrm{Pt,P}}$ = 3640.9 and $^2J_{\mathrm{A,M'}}$ = $^2J_{\mathrm{Pt,P}}$ = 212.1 Hz at 17.37 ppm, rather than an AA′MM′[26] spin system as observed for [Pt$_2$(μ_2-η^1:η^1-C$_2$(COOMe)(CO)$_2$(PPh$_3$)$_2$).[26] The ^{31}P NMR spectra for the other isomer, ***iso*-6d**, consists of two independent resonances with equal intensities: one due to an AMM′ spin system[25] with $^1J_{\mathrm{Pt,P}}$ = 3757.2 Hz and $^2J_{\mathrm{Pt,P}}$ = 348.9 Hz appearing at 22.33(s) ppm; the other an AM spin system with $^1J_{\mathrm{Pt,P}}$ = 2415.3 Hz at 17.68(s) ppm. Therefore, **6d** with the AMM′ spin sytem may correspond to a symmetrical structure with two phosphine ligands positioned mutually *trans* along the Pt–Pt bond, while ***iso*-6d** is an unsymmetrical structure in which one phosphine ligand with AM spin system is positioned perpendicular to the Pt–Pt bond, for which long-distance $^2J_{\mathrm{Pt,P}}$ could not be detected. A deep orange single crystal of **6d** was preferentially formed from C$_6$H$_6$ solution of these mixtures; however the other single crystal of ***iso*-6d**[28] was obtained from C$_6$H$_6$–acetone solution. The crystal structure of ***iso*-6d** is shown in Figure 6. The two phosphorus atoms in ***iso*-6d** are unsymmetrical, and one Pt–PPh$_3$ bond is perpendicular to the Pt- - -Pt bond {bond length Pt^1–Pt^2 2.998(2) Å}, which does not significantly differ from 2.981(1) Å of **6d** and **6e**, but these are longer than 2.6345(8) Å found in [Pt$_2${μ_2-η^1:η^1-C$_2$(CO$_2$Me)$_2$}(CO)$_2$(PPh$_3$)$_2$].[21] The other selected bond lengths and angles around the (μ_3-η^1:η^1:

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(28) (a) **6d** and ***iso*-6d** were prepared as follows: To Pt(PhCCPh)(PPh$_3$)$_2$ (0.25 g) in toluene was added Fe(CO)$_5$. The mixed solution was refluxed for 30 min, cooled, and evaporated. The deep orange residue was separated by column chromatography (Al$_2$O$_3$) in CH$_2$Cl$_2$. An eluant of a deep orange band was collected and recrystallized from C$_6$H$_6$ to give deep orange crystals (0.29 g, 81% yield/platinum atom). Anal. Found: C, 54.24; H, 3.31. Calc for C$_{55}$H$_{40}$O$_5$P$_2$FePt$_2$-(C$_6$H$_6$): C, 53.59; H, 3.39. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) 2036.2$_{\mathrm{vs}}$, 2010.9$_{\mathrm{vs}}$, 1980.8$_{\mathrm{vs}}$, 1930.4$_{\mathrm{vs}}$, 1900.7$_{\mathrm{vs}}$ cm^{-1}. FABMS (*m*-nitrobenzyl alcohol as a matrix): *m/z* 1288.6(M$^+$), 1203.6(M$^+$ − 3CO), 1176(M$^+$ − 4CO), 1147.7(M$^+$ − 5CO). ^{31}P NMR (CDCl$_3$): δ (ppm) 17.37{**6c**, $^1J_{\mathrm{Pt,P}}$ = 3640.9 Hz, $^2J_{\mathrm{Pt,\ P}}$ = 212.1 Hz}, 17.676{***iso*-6c**, $^1J_{\mathrm{Pt-P}}$ = 3757.2 Hz, $^2J_{\mathrm{Pt-P}}$ = 348.9 Hz}, 22.332{***iso*-6c**, $^1J_{\mathrm{Pt,P}}$ = 2415.3 Hz, $^2J_{\mathrm{Pt,P}}$ not observed}. ^{13}C{^{1}H} NMR (CDCl$_3$): δ (ppm) 217.05{Fe(CO)$_3$, **6c** or ***iso*-6c**}, 216.7{Pt–CO, **6c** or ***iso*-6c**}, 165.2{(Pt)–*C*(Ph)=C(Ph)–(Pt), **6c** or ***iso*-6c**}, 150{(Pt)–C(Ph)=*C*(Ph)–(Pt), **6c** or ***iso*-6c**}. (b) Crystal structure data of C$_{55}$H$_{40}$FeO$_5$P$_2$Pt$_2$, ***iso*-6d:** A single crystal of ***iso*-6d** was obtained from acetone–C$_6$H$_6$: M = 1288.84, deep orange crystal, 0.46 × 0.35 × 0.20 mm, monoclinic, space group P2(1), a = 13.827(10) Å, b = 11.825(4) Å, c = 18.198(9) Å, α = 90°, β = 110.92 (5)°, γ = 90°, V = 2779(3) Å^3, Z = 2, D_{c} = 1.540 g·cm^{-3}, F(000) = 1244, μ(Mo Kα) = 34.52 cm^{-1}, R_1 = 0.0635, wR_2 = 0.1550, goof = 1.093 for 5385 reflections in the range 5° < 2θ < 50° with $I > 2\sigma(I_0)$ refining 521 parameters. Selected bond distances (Å) and angles (deg): Pt(1)–Pt(2) 2.998(2) Pt(1)–Fe(1) 2.640(3) Pt(2)–Fe(1) 2.605(4) Pt(1)–C(1) 2.09(2) Pt(2)–C(2) 2.04(3) Fe(1)–C(1) 2.10(2) Fe(1)–C(2) 2.11(2) C(1)–C(2) 1.44(4) Pt(1)–Pt(2)–C(2) 66.3(7) Pt(2)–Pt(1)–C(1) 69.2(7). (c) A single crystal of **6d** was obtained from C$_6$H$_6$. Crystal structure data for **6d**: C$_{55}$H$_{40}$FeO$_5$P$_2$Pt$_2$, M = 1288.84, deep orange crystal, 0.40 × 0.35 × 0.10 mm, orthorhombic, space group $Pcab$, a = 20.337(9) Å, b = 121.664(14) Å, c = 24.651(8) Å, α = β = γ = 90.0°, V = 10857(9) Å^3, Z = 8, D_{c} = 1.575 Mg/m^3, F(000) = 14976, μ(Mo Kα) = 34.52 cm^{-1}, R_1 = 0.0991, wR_2 = 0.2580, goof = 1.115 for 6889 reflections in the range 5.00° < 2θ < 45.06° with $I > 2\sigma(I_0)$ refining 561 parameters at 293(2) K. Selected bond distances (Å) and angles (deg): Pt(1)–Pt(2) 3.056(2) Pt(1)–Fe(1) 2.567(4) Pt(2)–Fe(1) 2.643(4) Pt(1)–C(1) 2.08(3) Pt(2)–C(2) 1.98(2) Fe(1)–C(1) 2.10(3) Fe(1)–C(2) 2.04(3) C(1)–C(2) 1.42(4) Pt(1)–Pt(2)–C(2) 68.4(8) Pt(2)–Pt(1)–C(1) 63.7(8).

(29) (a) **6e** was prepared as follows: To a C$_6$H$_6$ solution of **2** (0.26 g) was added Fe(CO)$_5$ (0.10 g). The solution was refluxed for 30 min, cooled, and evaporated. The residue was separated by column chromatography (Al$_2$O$_3$) in CH$_2$Cl$_2$–hexane (1:1). An orange band was collected and recrystallized from toluene to give reddish-orange crystals (0.06 g, 21%/Pt atom). Anal. Found: C, 45.32; H, 3.09. Calc for C$_{47}$H$_{36}$O$_9$P$_2$FePt$_2$: C, 45.06; H, 2.90. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) 2045.6vs, 2010.2vs, 1967.5vs, 1939.8vs{ν(CO)}, 1713.2m 1693.7m{ν(C=O)}. ^{1}H NMR (CDCl$_3$): δ (ppm) 2.86(CH$_3$ of dmad). ^{13}C(^{1}H) NMR (CDCl$_3$): δ (ppm) resonances due to conformation A: 50.92 (s, C*H$_3$*OCOCC–COOC*H$_3$*), 51.16(s, *CH$_3$*OCOCCCOOC*H$_3$*), 152.29 (s, CH$_3$OCO*C*(Pt^1)–C(Pt^2)–COOCH$_3$), 174.45(s, CH$_3$O*C*OC–(Pt^1)–C(Pt^2)*C*OOCH$_3$), 174.48(s, CH$_3$O*C*O–C(Pt^1)–C(Pt^2)*C*OOCH$_3$), 193.46(s, Pt–CO), 215.24 {t, Fe–CO, $J_{\mathrm{P,C}}$ = 5.95 Hz}. Resonances due to conformation B: 50.92(s, C*H$_3$*OCOCCCOO*CH$_3$*), 51.16(s, *CH$_3$*OCOCCCOOC*H$_3$*), 152.32(s, CH$_3$OCO*C*(Pt^1)–C(Pt^2)–COOCH$_3$), 174.50(s, CH$_3$O*C*OC(Pt^1)–C(Pt^2)–*C*OOCH$_3$), 174.54(s, CH$_3$O*C*OC(Pt^1)–C(Pt^2)–*C*OOCH$_3$), 193.54(s, Pt–CO), 215.24{t, Fe–CO, $J_{\mathrm{P,C}}$ = 5.95 Hz}. (b) A single crystal of **6e** was obtained from toluene at 253 K. Crystal structure data for C$_{47}$H$_{36}$O$_9$P$_2$FePt$_2$, **6e**: M = 1252.8, orange crystal, 0.35 × 0.3 × 0.2 mm, monoclinic, space group $P2_1/a$, a = 21.284(6) Å, b = 18.822(6) Å, c = 11.320(3) Å, β = 104.61(2)°, V = 4388.44 Å^3, Z = 4, D_{c} = 1.896 g·cm^{-3}, μ(Cu Kα) = 156.07 mm^{-1}, R = 0.0455, wR = 0.0665, goof(S) = 1.1911 for 6354 refelections in the range 1° < θ < 25° with $I > 2.00\sigma(I_0)$ refining 550 parameters. Selected bond distances (Å) and angles (deg): Pt(1)–Pt(2) 2.981(1), Pt(1)–Fe(1) 2.579(3), Pt(2)–Fe(1) 2.567(3), Pt(1)–C(1) 2.014(17), Pt(2)–C(2) 2.021(17), Fe(1)–C(1) 2.069(17), Fe(1)–C(2) 2.053(17), C(1)–C(2) 1.42(3), Pt(1)–Pt(2)–C(2) 67.7(5), Pt(2)–Pt(1)–C(1) 66.9(5).

(30) **6f** was prepared as follows: To a C$_6$H$_6$ solution of **2** (0.20 g) was added Ru$_3$(CO)$_{12}$ (0.11 g), and the solution was refluxed for 30 min, cooled, and evaporated. The residue was separated by TLC(SiO$_2$). An eluant of the yellow band gave orange microcrystals (0.08 g, 34% yield/Pt atom). Anal. Found: C, 43.79; H, 3.04. Calc for C$_{47}$H$_{36}$O$_9$P$_2$Pt$_2$Ru: C, 43.49; H, 2.80. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) 2049.6vs, 2023.1vs, 2005.5vs, 1985.1vs, 1960.1vs{ν(CO)}, 1710.4s, 1695.7vs{ν(C=O)}. ^{1}H NMR (CDCl$_3$): δ (ppm) 2.86(CH$_3$ of dmadc). ^{13}C NMR (CDCl$_3$): δ (ppm) 50.98(s, C*H$_3$*OCOCCCOO*CH$_3$*), 51.18(s, *CH$_3$*OCOCCCOOC*H$_3$*), 152.3(s, CH$_3$OCO*C*(Pt^1)=*C*(Pt^2)–COOCH$_3$), 174.13 (s, CH$_3$O*C*OC(Pt^1)=C(Pt^2)-*C*OOCH$_3$), 192.13{d, Pt–CO, $J_{\mathrm{P,C}}$ = 5.82 Hz, $J_{\mathrm{Pt,C}}$ not well resolved}, 199.36 {t, Ru–CO, $J_{\mathrm{P,C}}$ = 4.52 Hz}.

η^2)-bonding alkyne do not significantly differ from those of **6a**,[17] **6d**,[28] and **6e**.[29]

The structure of **6e** in solution was consistent with the crystal structure (Figure 6). Two ^{13}C NMR resonances due to the methylcarboxylate substituents were distinct at around 51.0 and 152.3 ppm, respectively, at 293 K. These signals, however, collapsed to coalescence at 308 K due to an allowance of free rotation of the substituents. For **6e** and **6f**, ^{13}C NMR resonances arising from the $M(CO)_3$ group (M = Fe, Ru) were unexpectedly observed as a single triplet pattern at 215.2 ppm ($^3J_{P,C} = 6$ Hz) and 199.36 ppm ($^3J_{P,C} = 4.52$ Hz), respectively, suggesting that the $M(CO)_3$ group in **6e** and **6f**,[30] in addition to **6d** and ***iso*-6d**, may undergo fluxional motion in a turnstyle manner as observed for **6a**,[12] which is in contrast to the stereochemical rigidity of the corresponding group in **5a** and **6b**.

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Supporting Information Available: Tables giving full crystallographic details, positional and thermal parameters, and bond distances and angles for **2**, ***iso*-3**, **5a**, ***iso*-6d**, and **6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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