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Metallacycles of 1,4-Bis(3-thiophenyl)-1,3-butadiyne in Mixed Metal Clusters Derived by C−C Bond Coupling of Alkynyls

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Reaction of *cis*-Pt(C$\equiv$CTp)$_2$(dppe) (Tp = thiophene) with Ru$_3$(CO)$_{11}$(CH$_3$CN) in refluxing toluene for 1 h resulted in head-to-head C−C bond coupling of the alkynyl ligands forming 1,4-bis(3-thiophenyl)-buta-1,3-diyne, which afforded an extraordinal 1,4-heterodimetalla[5,6-*b*]thienopentalene, [PtRu$_3${μ_4-η^1:η^1:η^1:η^1:η^4:η^4-C$_4$H$_2$S-C=CC(H)=CTp}(μ-CO)$_2$(CO)$_6$(dppe)] (**1**) (Tp = 3-thiophene), in 54% yield. Its crystal structure shows that a hydrogen shift occurs from the thiophene substituent to an end carbon atom of the 1,3-diyne, transforming 1,4-bis(3-thiophenyl)buta-1,3-diene, which results in formations of PtC$_4$ and RuC$_4$ rings, both with metallacyclopenta-2,4-diene. The Ru$_3$(μ-CO)$_2$(CO)$_6$ moiety conforms to an open cluster, and its central ruthenium atom forms a RuCp ring whose carbon atoms bond to two ruthenium atoms by eight Ru−C π-bonds. Reactions of the acetylides with single metal media, Fe(CO)$_5$, gave rise to annealation of alkynyls via both cyclic and acyclic dimerization processes, affording extraordinal metallacycles of 1,3-diyne, a platinacyclobutene consisting of a cyclone, [FePt{μ_2-η^1:η^1:η^4-(C$_4$Tp$_2$-CO)-CO}(CO)$_3$(dppe)] (**2**), and a 1,2-heterodimetallacyclo-3-penten-5-one, [FePt(μ_2-η^1:η^1:η^2-TpCCCCTp-CO)(μ-CO)(CO)$_2$](dppe)] (**3**), in 15 and 16% yields, respectively.

Introduction

A number of metallacyclic compounds have recently been investigated as important intermediates of metal-catalyzed oligomerization of alkynes[1] and syntheses of hetero- and carbocyclic organic molecules.[2] In these studies, five-membered metallacycles that undergo complexation have intriguing bonding features,[3] whose bond multiplicity has been proposed as an intermediate of bond scission of C−C single bond of the 1,3-diyne.[2e,13,14] Mixed dimetallic compounds thus derived principally through the C−C bond coupling of alkynyls have been recently applied toward use as a single-source precursor of chemical vapor deposition of ceramic thin films.[4]

Four-membered metallacycles (A in Figure 1), the first [(η^5-C$_5$H$_5$)Co{(R^{1}C=CR^2)C=NR^3}(PPh$_3$)] (R^1 = Ph, R^2 = CO$_2$-

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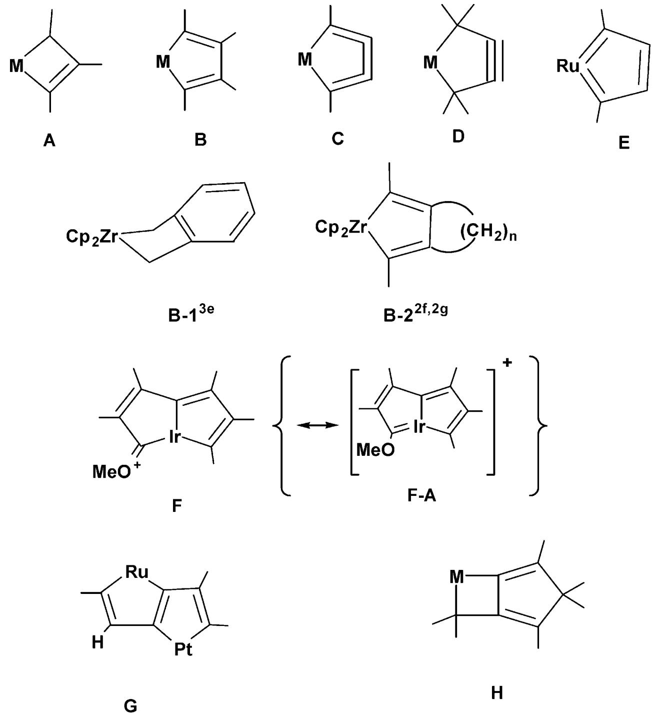


Figure 1.

Me; R_3 = p-MeC_6H_4),[5a] [$(\eta^5C_5H_5)Rh\{\kappa(C,C)\text{-}C(=NMe)\text{-}CPh=CPh\}(Sb^iPr_3)$],[5b] and [$(\eta^5C_5H_5)Co(PPh_3)\{\eta^1{:}\eta^1CHCO_2\text{-}Et(SiMe_3)C=C(SO_2Ph)\}$],[5c] were all isolated in incoporation processes of isocyanide, Sb^iPr_3, and diazoacetate into the corresponding π-alkyne complexes, respectively.

Five-membered MC_4 metallacycles of alkyne and 1,3-diyne molecules are intriguing in their structures and bondings,[8] since small cyclic alkynes are unstable owing to ring strain.[9] 1-Metallacyclopenta-2,3,4-triene C and 1-metallacyclo-3-pentyne D recently isolated in electron-poor transition metal compounds of titanocene and zirconocene[10−12] are all planar. On electron-rich transition metals, another intriguing five-membered metallacycle of dicarbene structure has been known. $Cp^*RuCl(=C(Ph)\text{-}CH=)_2$ E has recently been isolated from reaction of $Cp^*RuCl(COD)$ with a 2-fold amount of phenylacetylene, which further reacts with phenylacetylene to afford a cationic cyclotrimerized product.[15e] However, on clusters of electron-rich transition metals, there are only a few reports of five-membered metallcycles of 1,3-diyne.[15a]

We have recently established a new type of dimetallacycles of 1,3-diyne unusually interacting with cluster nuclei, which have been prepared by cross-coupling of alkynyls induced by metal−carbonyl,[16] as shown in I and J in Figure 2. I is a cluster with isomers in which all atoms of the RuC_4 ring of the ruthenacyclopentadiene[12] undergo complexation to three metals by a ($\delta{:}\eta^1{:}\eta^1{:}\eta^4$)-bond. The stable cluster J is another extraordinal type of five-membered metallacycle with 1-metallacyclocumulene, whose structure includes a hybrid resonance of metallacyclo-3-pentyne (J-A).

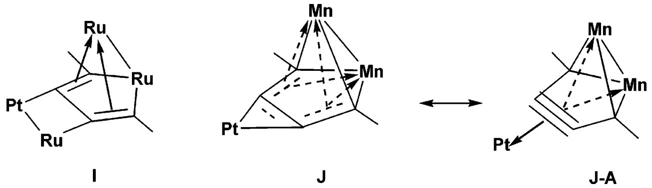
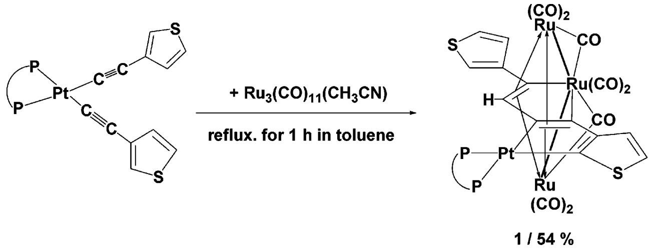


Figure 2.

Scheme 1



1 / 54 %

We have extended the syntheses of the five-membered metallacycles by using acetylides with thiophene substituents. Reactions of *cis*-$Pt(C\equiv CTp)_2(dppe)$ (Tp = 3-thiophene) with metal−carbonyls, $Ru_3(CO)_{11}(CH_3CN)$ and $Fe(CO)_5$, were performed in refluxing toluene for 45 min, which led to the isolation of an extraordinal dimetallapentalene G, [$PtRu_3\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^4{:}\eta^4\text{-}C_4H_2S\text{-}CCC(H)CTp\}(\mu CO)_2(CO)_6(dppe)$] (**1**), and metallacyclobutene H, consisting of condensed ring A with a cyclone ring, [$FePt\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^4\text{-}(C_4Tp_2\text{-}CO)\text{-}CO\}(CO)_3(dppe)$] (**2**), both of which underwent complexation. Despite the many recent studies on π-pentalene complexes,[6] metallapentalene is elusive, except for iridapentalene F,[7] in which the metal occupies a bridge-head position (Figure 1).

Results and Discussion

A head-to-head cross-coupling of alkynyls in *cis*-$Pt(CCTp)_2(dppe)$ (Tp = 3-thiophene) was induced by $Ru_3(CO)_{11}(CH_3CN)$ and proceeded to afford a mixed metal compound of 1,3-diyne, [$PtRu_3(C_2C_4H_3S)_2(CO)_8(dppe)$] (**1**) (Tp = 3-thiophene), in 54% yield (Scheme 1). The crystal structure of **1**, in Figure 3, shows that a hydrogen shift occurs from a ring carbon atom of the substituted thiophene to an end carbon atom of 1,3-diyne, resulting in the formation of 1,4-heterodimetalla[5,6-*b*]thienopentalene (Scheme 1), consisting of RuC_4 and PtC_4 rings both with metallacyclopentadiene. Four carbon atoms in the RuCp ring bond to two ruthenium atoms by eight Ru−C π-bonds {bond lengths Ru1−C3 2.303(8) Å, Ru1−C 42.303(9) Å, Ru1−C1 Ru2−C3 2.333(8) Å, Ru1−C2 2.328(9) Å, Ru2−C1 2.342(9) Å, Ru2−C3 2.292(9) Å, Ru2−C2 2.313(9), and Ru2−C4 2.317(8) Å: mean bond length 2.316 Å} in opposite directions, and the $Ru_3(\mu\text{-}CO)_2(CO)_6$ group conforms to an open cluster {atomic distance Ru1−Ru2 3.7515(11) Å and bond angle Ru1−Ru3−Ru2 88.71(3)°}. Bond lengths Ru3−C3 2.212(8) Å and Ru3−C4 2.202(9) Å in the RuCp ring are comparable with 2.216(4)−2.219(4) Å found for the alkyne-dimerized compounds [$Ru_3(C_4Ph_4)(CO)_8$][17a] and [$Ru_3(CH_3CC^iPr)_2(CO)_8$][17c] and the alkyne-trimerized product [$Ru_3(HCC^tBu)_3(CO)_8$].[17b] In the present case, the C−C double-bond lengths, C1−C3 1.446(11) and C2−C4 1.458(13) Å, are elongated from those of metallacyclopentadiene, and they are longer than the bond length C1−

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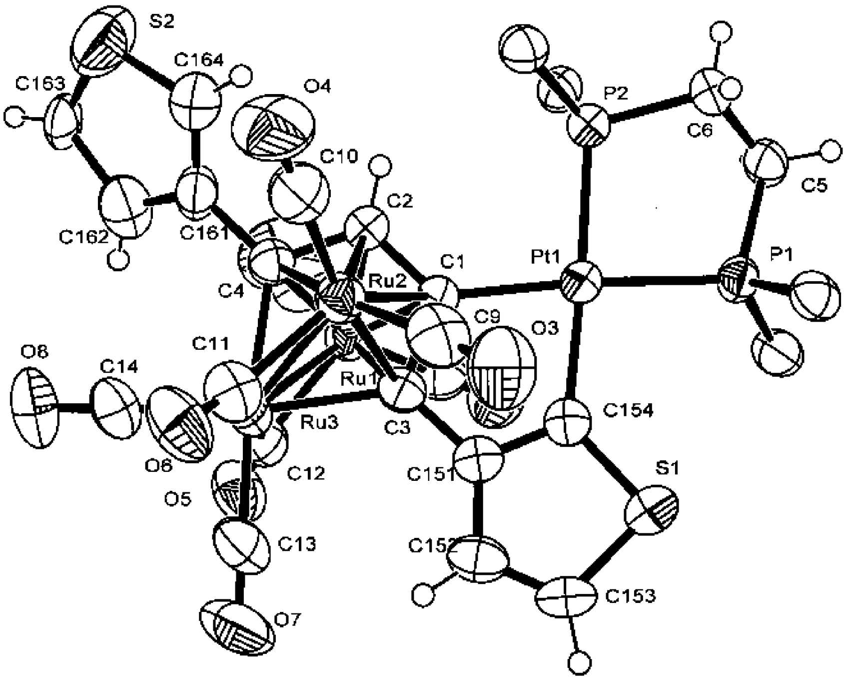
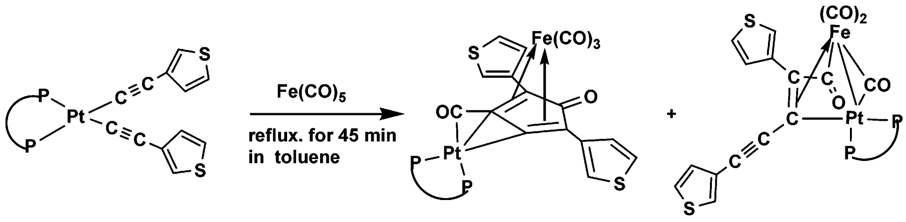


Figure 3. ORTEP plot (50% probability thermal ellipsoids) of [PtRu$_3$(TpCCC(H)CC$_4$H$_2$S)$_2$(dppe)(μ-CO)$_2$(CO)$_6$], **1**. Phenyl rings of dppe are omitted for clarity. Selected bond distances (Å) and angles (deg): PT(1)−C(1) 2.078(8), C3−C151 1.483(11), Pt1−C154 2.054(9), C151−C154 1.396(13), PT(1)−C(154) 2.054(10), Ru1−C3 2.303(8) Ru1−Ru3 2.6865(12), Ru1−C4 2.303(9), Ru(2)−Ru(3) 2.687(2), Ru1−C1 2.333(8), C1−C2 1.438(11), Ru1−C2 2.328(9), C1−C3 1.466(11), Ru2−C1 2.342(9), C2−C4 1.458(13), Ru2−C2 2.313(9), Ru3−C3 2.212(8), Ru2−C3 2.292(9), Ru3−C4 2.202(9), Ru2−C4 2.317(8), Ru(2)−C(9) 1.891(13), Ru1−Ru3−Ru2 88.71(3), C1−Pt1−C154 78.2(3), Ru3−C3−C1 119.3(5), Pt1−C154−C151 118.6(6), Ru3−C4−C2 117.9(6), C3−C151−C154 114.8(7), C2−C1−C3 112.7(7), C1−C3−C151 111.3(7), C1−C2−C4 116.3(8), Pt1−C1−C3 117.0(5), C3−Ru3−C4 73.8(3), Ru3−C4−C2 117.9(6).

Scheme 2



2 / 14 % **3** / 16 %

C2 1.438(11) Å, owing to the eight Ru−C π-bonds, whose length is rather similar to those of metallacyclopentyne. The PtC$_4$ ring in the present compound is retained as a 1-metallacyclobuta-2,4-diene, and bond lengths Pt1−C1 2.078(8) and Pt1−C154 2.054(9) Å are consistent with a pure Pt−C σ-bond, while the bond length C151−C154 1.396(13) Å in the PtC$_4$ ring is shortened from the corresponding bond length C1−C3 1.466(11) Å in the RuC$_4$ ring, but it is in the range of carbon−carbon double-bond lengths. Three rings of thiophene, the platinacycle, and the ruthenacycle are in good planarity and almost in coplanarity {torsion angles are C1−C3−C141−C144 2.8(11)°, C3−C141−C144−Pt −2.7(11)°, C141−C142−C143−S1 8(11)°, C144−C141−C142−C143−6(12)°; C3−C141−C142−C143 176.1(9)°, Ru3−C3−C141−C142 5.7(15)°, Pt−C1−C2−C4 178.1(16)°}. The hydrogen at the C2 atom was fixed in the X-ray analysis.

Reactions of the acetylides with single metal media, Fe(CO)$_5$, in refluxing touene resulted in both cyclic and acyclic dimerizations through an analogous cross-coupling of alkynyls and succeeding C−C bond coupling of the 1,3-diyne with carbon monoxide from Fe(CO)$_5$. These annealation reactions of 1,3-diyne afforded unusual platinacyclobutenes, the cyclone [FePt{μ_2-η^1:η^1:η^4-(C$_4$Tp$_2$-CO)-CO}(CO)$_3$(dppe)] (**2**) and the 1,2-heterodimetallacyclo-3-pentene-5-one [FePt(μ_2-η^1:η^1:η^2-TpCCCCTp-CO)(μ-CO)(CO)$_2$] (dppe)] (**3**), in 14 and 16% yields, respectively, as shown in Scheme 2.

A single crystal of **2** was obtained from CH$_3$CN−hexane at 253 K, and X-ray analyses were performed.[18] It crystal structure is shown in Figure 2. One carbon monoxide liberated from Fe(CO)$_5$ now couples with an end carbon atom of the 1,3-diyne, affording a π-cyclone compound,[19] while another carbon monoxide of the residual Fe(CO)$_4$ group newly inserted into the Pt−C bond, forming a metallacyclobutene ring.

The ring carbon atoms of the cyclone bond to the Fe(CO)$_3$ group by the four Fe−C π-bonds, and the mean distance of the

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(18) Crystal structure data of C$_{42}$H$_{29}$FeO$_5$P$_2$PtS$_2$, **2**: A single crystal was obtained from a CH$_3$CN−hexane solution; monoclinic, space group $P2_1/n$, a = 11.4350(3) Å, b = 18.3300(7) Å, c = 20.6730(10) Å, α = 89.9980(20)°, β = 82.6960(10)°, γ = 90.00120(10)°, V = 4298(2) Å^3, Z = 4, D_c = 1.551 g·cm^{-3}, R_1 = 0.1060, wR_2 = 0.3447, Goof (S) = 1.5810, for 9827 independent reflections, in the range $0° < 2\theta < 51.54°$ with $F_o > 4\sigma(F_o)$, refining 7211 parameters. Selected bnond lengths (Å) and angles (deg): C1−C2 1.491(19), C1−C3 1.46(2), C2−C4 1.38(2), C4−C10 1.55(2), C3−C10 1.556(18), C11−O5 1.210(17), Pt1−C2 2.0752, C1−C11 1.48(2), Pt1−C11 2.0739, Fe2−C1 2.041(15), Fe2−C2 2.135(14), Fe2−C3 2.137(16), Fe2−C4 2.129(17), Fe2−C10 2.421(15), C2−Pt1−C11 67.97, C1−C2−C4 105.6(13), C2−C1−C3 112.8(12), C1−C3−C10 103.5(12), C2−C4−C10 110.9(14), C3−C10−C4 102.9(12), Pt1−C11−C1 94.80, Pt1−C2−C1 94.31, C2−C1−C11 102.8(12), C2−Pt1−C11 67.97.

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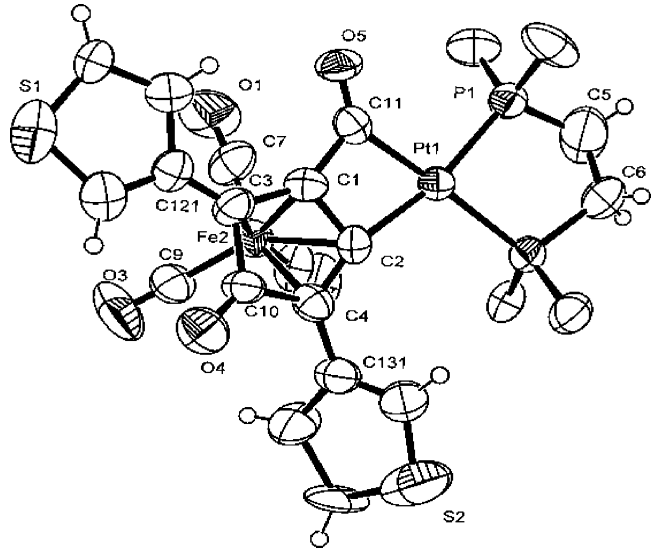
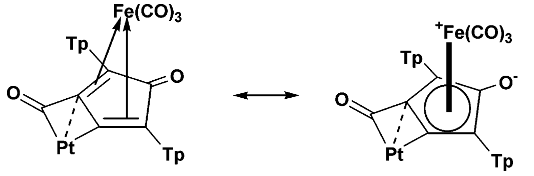


Figure 4. ORTEP plot (50% probability thermal ellipsoids) of [PtFe{μ_2-η^1:η^1:η^4-(TpCCCCTp-CO)-CO}(CO)$_3$(dppe)], **2**. Phenyl rings of dppe are omitted for clarity.

Scheme 3



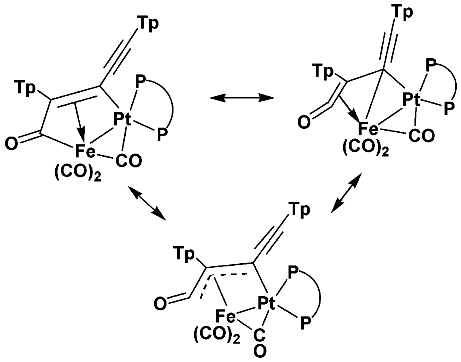
G **G-A**

Fe−C bond (2.11 Å) is slightly shorter than 2.21−2.24 Å of the corresponding cyclone compound, [Ru(η^4-C(O)R^{1}C$_2$R$^2_2$)(CO)$_2$(PPh$_3$)] (R^1 = Ph, R^2 = C≡CPh).[19b] A possible polarized and charge-separated structure is depicted in Scheme 3.

The bond length C1−C2 1.47(3) Å of **2** is noticeably elongated from those of the other two cobalta- and rhodacycles, as shown in Figure 5, which may be due to an electron-delocalized and polarized structure of the π-cyclone moiety.

The crystal structure of [FePt(μ_2-η^1:η^1:η^2-TpCCCCTp-CO)(μ-CO)(CO)$_2$](dppe)] (**3**) is shown in Figure 6, in which an end carbon atom of the 1,3-diyne undergoes C−C bond coupling with one carbon monoxide from the Fe(CO)$_4$ group, and the other carbon atom of the bonding alkyne group links the platinum atom by a pure Pt−C σ-bond {bond distance Pt−C1 2.090(12) Å}, forming a 1,2-dimetalla-3-penten-5-one compound with a metal−metal bond (Pt1−Fe1) of 2.605(2) Å and bridging carbonyl. **3** is evidently formed by incoporation of a Fe(CO)$_4$ group into a π-1,3-diyne in the 16 e$^-$ species [Pt(η^2-C$_4$Tp$_2$)(dppe)], as has been evidenced for the formation of an analogue, [FePt{μ_2-η^1:η^1:η^2-C(O)C$_4$Ph$_2$}(CO)$_3$(PPh$_3$)$_2$].[16b] In the present case, the bond length Fe1−C1 2.052(10) Å is considerably shorter than the bond length Fe1−C3 2.192(12) Å and rather approaches 2.0151(24) and 2.021(3) Å of the Fe−C σ-bond.[20] The bond length C1−C3 1.381(17) Å corresponds to a double-bond length[8,16b] and is much shorter than the corresponding bond length of 1.441(14) Å in [FePt{μ_2-η^1:η^1:η^2-C(O)C$_4$Ph$_2$}(CO)$_3$(PPh$_3$)$_2$]. This may suggest that dimetallacyclopentenone **3** may still consist of resonance structures of a bridging carbene with a ketene substiutuent and an allylic bond, as shown in Scheme 4.

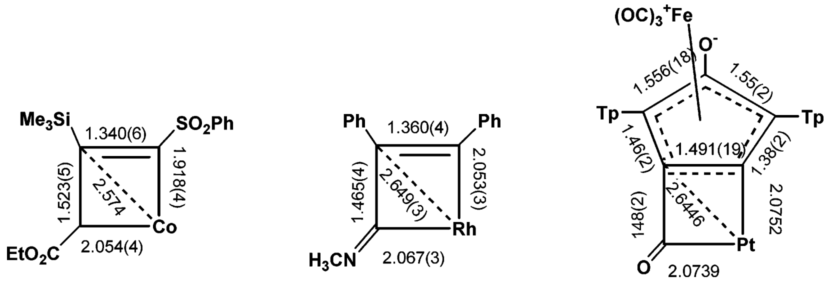
Scheme 4



It should be noted that **2** and **3** were obtained only when the reactions were performed using an excess amount of Fe(CO)$_5$, while neither **2** nor **3** could be obtained when an equivalent amount of Fe(CO)$_5$ was used. This may indicate that the dangling triple bond of an intermediate complex or compound **3** may interact with the iron−carbonyl.

Concluding Remarks

The present work is the first study of the preparation of the unusual heterodimetallapentalene **1** and metallacyclobutene **2** condensed with a cyclone ring that underwent complexation. **1** is formed by the head-to-head cross-coupling of the acetylide. A subsequent C−H bond activation of the thiophene ring accompanied a conversion of the 1,3-diyne into 1,4-bis(thiophenyl)buta-1,3-diene, which newly forms the PtCp and RuCp rings both with 1-metallacyclo-2,4-pentadiene. Cross-coupling of the acetylides was also induced by single-metal media, Fe(CO)$_5$, and succeedingly C−C bond coupling of the 1,3-diyne with carbon monooxide from Fe(CO)$_5$ also proceeded to form **2** and **3**. We have previously established that the acyclic dimerizations of the acetylides with an aryl substituent proceeded via a reductive elimination, first affording a 16-electron species.[16b] Therefore, in the present case, compound **3** may



A-1 **A-2** **A-3**

Figure 5. Bond lengths of the metallacyclobutene ring for CpCo{PhSO$_2$C=C(SiMe$_3$)C(=NCH$_3$)}(PMe$_3$) (A-1), [CpRh{PhC=CPh-C(=NCH$_3$)}(Sb^{i}Pr$_3$)] (A-2), and compound **2** (A-3).

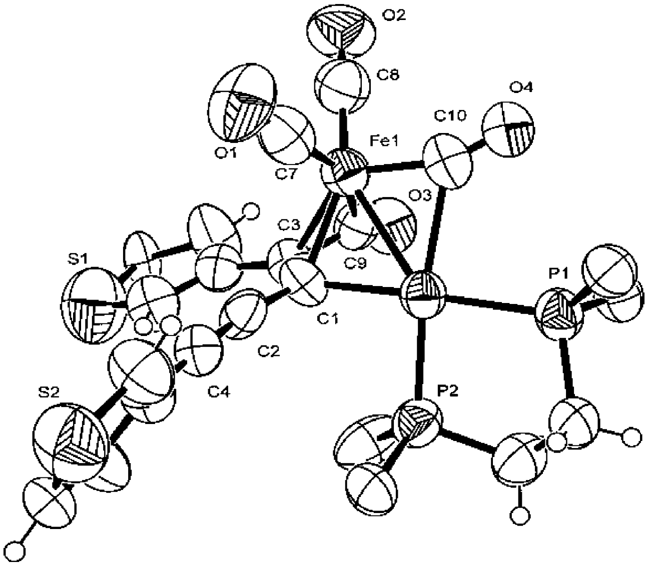


Figure 6. ORTEP plot (50% probability thermal ellipsoids) of FePt(μ_2-η^1:η^1:η^2-TpCCCCTp-CO)(μ-CO)(CO)$_2$(dppe), **3**. Phenyl rings of dppe are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pt1−Fe2 2.605(2), C3−C9 1.451(17), Pt1−C1 2.087(12), Pt1−C10 2.346(15), C1−C2 1.454(18), Fe1−C1 2.052(10), C1−C3 1.381(17), Fe1−C3 2.192(12), O3−C9 1.232(18), O4−C10 1.146(18), C2−C4 1.226(19), Fe1−C9 1.935(14), Fe1−C10 1.795(15), Fe1−Pt1−C1 50.4(3), Fe1−Pt1−C10 42.1(4), Pt1−Fe1−C10 61.2(5), Fe1−C9−C3 79.3(8), C1−C3−C9 108.3(10), Pt1−C1−C3 117.5(9), Pt1−C10−Fe1 76.7(5), C1−Fe1−C3 37.8(5), C9−Fe1−C10 101.8(6).

support that compound **2** may also be formed via the intermediate of the π-complex of a 1,3-diyne, [Pt(η^2-TpC≡CC≡CTp)(dppe)]. Any further details of the reactions are under further investigation.

Experimental Section

Preparation of Pt(C≡CTp)$_2$(dppe) (Tp = 3-thiophene). To PtCl$_2$(dppe) (0.33 g, 0.5 mmol) in NEt$_2$H and CH$_2$Cl$_2$ (1:1) were added 3-ethynylthiophene (0.12 g, 1.1 mmol) and CuCl (10 mg, 0.1 mmol). The solution was refluxed overnight. After evaporation of the solution, the residue was dissolved in CH$_2$Cl$_2$ and washed by H$_2$O in a separatory funnel. The CH$_2$Cl$_2$ phase, after drying over anhydrous Na$_2$SO$_4$ and filtering the insoluble solid off, was reduced in volume to 10 cm^3, which on addition of hexane and standing at room temperature for several minutes gave colorless crystals (0.35 g, 0.43 mmol; 86% yield/platinum atom). Anal. Found: C, 56.48; H, 3.74. Calc for C$_{38}$H$_{30}$P$_2$PtS$_2$: C, 56.50; H, 3.74. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}) 2122$_s$. ^{31}P NMR (CDCl$_3$): δ (ppm) 41.69 ($J_{\mathrm{Pt,P}}$ = 2282 Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) 103.2 {C$_\alpha$, $J_{\mathrm{P,C}}$(trans) = 146.2 Hz; $J_{\mathrm{P,C}}$(cis) = 15.71 Hz, $J_{\mathrm{Pt,C}}$ = 1131.5 Hz}, 106.4 {C$_\beta$, $J_{\mathrm{P,C}}$(trans) = 35.5 Hz; $J_{\mathrm{Pt,C}}$ = 157.2 Hz}.

Preparation of [PtRu$_3${μ_4-η^1:η^1:η^1:η^1:η^4:η^4-C$_4$H$_2$SCCC(H)-CTp}(μ-CO)$_2$(CO)$_6$(dppe)], 1. To Pt(C≡CTp)$_2$(dppe) (190 mg, 0.24 mmol; Tp = 3-thiophene) in toluene was added Ru$_3$(CO)$_{11}$(CH$_3$CN) {in situ prepared by treating Ru$_3$(CO)$_{12}$ (130 mg, 0.2 mmol) with NMe$_3$=O·H$_2$O and CH$_3$CN}. The solution was refluxed for 45 min. After cooling the solution, the solvent was evaporated to give dark orange products, which were separated by TLC (SiO$_2$) using CH$_2$Cl$_2$. From the eluent of the main dark orange band in CH$_2$Cl$_2$, followed by recrystallization from toluene and CH$_2$Cl$_2$, red crystals were obtained (170 mg, 0.13 mmol: 54% yield/platinum atom). Anal. Found: C, 40.58; H, 2.25. Calc for C$_{46}$H$_{30}$O$_8$P$_2$PtRu$_3$S$_2$·1/2(CH$_2$Cl$_2$): C, 40.54; H, 2.27. IR (Nujol mull): $\tilde{\nu}$ (cm^{-1}), 2049s {ν(CO)}, 2009vs {ν(CO)}, 1974vs {ν(CO)}, 1956vs {ν(CO-Ru)}, 1854s {ν(CO)$_b$}, 1838s {ν(CO)$_b$}. ^{31}P NMR (CDCl$_3$): δ (ppm) 49.4 ($J_{\mathrm{Pt,P}}$ = 3855 Hz), 37.9 ($J_{\mathrm{Pt,P}}$ = 3642 Hz). ^{13}C NMR (CDCl$_3$): δ (ppm) 200.4 (Ru-*C*O), 199.5 (Ru-*C*O), 198.1, 196.9 (Ru-*C*O), 193.3 (Ru-*C*O), 166 (d, $J_{\mathrm{P,C}}$ = 8.3 Hz), 165.0, 151.2.

Preparation of [FePt{μ_2-η^1:η^1:η^4-(C$_4$Tp$_2$-CO)-CO}(CO)$_3$(dppe)], 2. To Pt(CCC$_4$H$_3$S)$_2$(dppe) (200 mg, 0.25 mmol) in toluene was added Fe(CO)$_5$ (0.18 g, 0.9 mmol), and the mixed solution was refluxed for 45 min. The solution, after cooling, was evaporated, and the products were purified by TLC (SiO$_2$). An eluent of the yellow band, followed by recrystallization from toluene, gave orange crystals (37 mg, 0.037 mmol; 15% yield/platinum atom). Anal. Found: C, 50.94; H, 3.14. Calc for C$_{42}$H$_{29}$FeO$_5$P$_2$PtS$_2$: C, 51.46; H, 3.01. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ (cm^{-1}), 2016vs, 1955vs {ν(CO)}, 1719m {ν(CO)$_b$}, 1606m {ν(C=O)}. ^{31}P NMR (CDCl$_3$): δ (ppm) 55.67 ($J_{\mathrm{Pt,P}}$ = 2637 Hz), 50.35 ($J_{\mathrm{Pt,P}}$ = 3684 Hz).

Preparation of [FePt(μ_2-η^1:η^1:η^2-TpCCCCTp-CO)(CO)(CO)$_2$(dppe)], 3. In TLC separation processes of compound **2**, an eluent of another orange band, followed by recrystallization from toluene, gave orange crystals (39 mg, 0.038 mmol; 15.2% yield/platinum atom). Anal. Found: C, 53.39; H, 3.56. Calc for C$_{42}$H$_{30}$FeO$_4$P$_2$PtS$_2$·1/2(C$_6$H$_5$CH$_3$): C, 53.48; H, 3.35. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ (cm^{-1}) 2120s {ν(C≡C)$_{\mathrm{nonbonding}}$}, 2016vs, 1956vs, 1819w {ν(CO)$_b$}, 1720m {ν(C=O)}, 1605m {ν(C=O)}. ^{31}P NMR (CDCl$_3$, δ): 55.70 ($J_{\mathrm{Pt,P}}$ = 2608 Hz), 50.30 ($J_{\mathrm{Pt,P}}$ = 3704 Hz). The same reaction was carried out for 30 min, and the yield of **3** was slightly increased to 20%. **3**, by leaving in toluene, CH$_3$CN, or CH$_2$Cl$_2$ for several days, at room temperature underwent decomposition.

Crystal Structural Determinations. Intensity data were collected by $\theta/2\omega$ scans at 298 K using a INST_DIP2000 diffractometer (Mac Science) on an imaging plate for compounds **1** and **3**, and an AFC 7 four-circle diffractometer for compound **2**, with Mo Kα radiation (λ = 0.7103 Å), and were corrected for Lorenz and polarization effects. Structure solutions were performed by the direct method using DIRDIF 99[21] and WinGX 3.0[22] and by full-matrix least squares on F_o with SHELXL.[23] All non-hydrogen atoms were refined anisotropically with H atoms in calculated positions riding on C atoms with C−H fixed at 0.93 Å.

Crystal Structure Data of C$_{46}$H$_{30}$O$_8$P$_2$PtRu$_3$S$_2$, 1. A single crystal was obtained by recrystallizing from CH$_3$CN at 253 K; monoclinic, space group $P2_1/c$, a = 12.8680(0) Å, b = 15.6720(0) Å, c = 25.2910(0) Å, α = 90.0000(0)°, β = 79.6770(0)°, γ = 90.0000(0)°, V = 5017.81(0) Å^3, Z = 4, D_c = 1.767 g·cm^{-3}, R_1 = 0.0512, wR_2 = 0.1727, Goof (S) = 1.0680 for 8555 independent reflections, in the range $0° < 2\theta < 51.41°$ with $F_o > 4\sigma(F_o)$, refining 7115 parameters.

Crystal Structure Data of C$_{42}$H$_{30}$FeO$_4$P$_2$PtS$_2$, 3. A single crystal was obtained from a CH$_3$CN−hexane solution at 253 K; monoclinic, space group $P2_1/n$, a = 14.6080(50) Å , b = 23.7690(50) Å, c = 11.9860(50) Å, α = 90.000(5)°, β = 90.564(5)°, γ = 90.000(5)°, V = 4161.55(24) Å^3, Z = 4, D_c = 1.557 g·cm^{-3}, R_1 = 0.0431, wR_2 = 0.1401, Goof (S) = 1.1490 for 6571 independent reflections, in the range $0° < 2\theta < 51.36°$ with $F_o > 4\sigma(F_o)$, refining 5855 parameters.

Supporting Information Available: Tables giving full crystallographic details, positional and thermal parameters, and bond distances and angles for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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