

Mixed Metal Compounds Bridged by 1,4-Diphenylbuta-1,3-diyne Derived by C–C bond Coupling of Alkynyl Ligands

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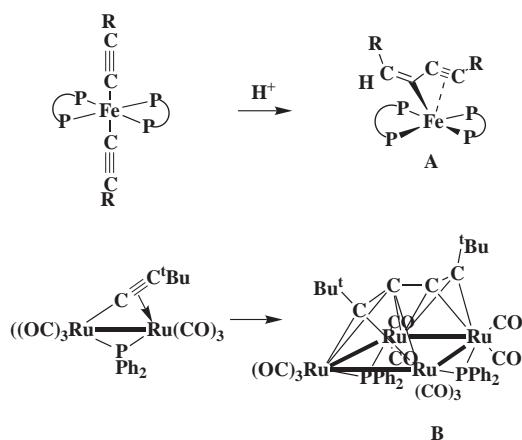
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New mixed-metal compounds, $\text{PtRu}_3(\mu_4\text{-}\eta^1 : \eta^1 : \eta^2 : \eta^4\text{-PhCCCCPh})(\text{CO})_{10}(\text{dppe})$ with isomers **1** and **2**, have been prepared by reacting *cis*-dialkynyl platinum(II) complex, $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppe})$, with $\text{Ru}_3(\text{CO})_{12}$, via a C–C bond coupling of the alkynyl ligands.

Dimerization of alkyne molecules mediated by transition metals have recently attracted much attention as one of the significant alkyne oligomerization.¹ Cyclic dimerization of alkyne molecules readily proceeds on 18 electron complex.² On clusters, extraordinal acyclic dimerization of alkyne molecules and codimerization of alkyne and 1,3-diyne molecules have recently been established for $\text{Ru}_4(\mu_3\text{-PPh})(\text{CO})_{13}$.³



On the other hand, transition metal acetylides can function as a ligand forming clusters,⁴ and many mixed-metal clusters composed of versatile alkynyl(s) are known.⁵ However, there have been only a few reports of transition metal complexes derived from C–C bond coupling reactions of the alkynyls. An example for mononuclear complex is butenyne compound (**A**)⁶ formed by protonation of *trans*- $\text{Fe}(\text{CCPh})_2(\text{dmpe})_2$. Another may be 1,3-diyne compound (**B**) with a Ru_4 -framework,⁷ which is given by an intermolecular C–C bond coupling of the alkynyl ligands.

In the present paper, a new reaction of *cis*-dialkynyl Pt(II) complex, $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppe})$, with $\text{Ru}_3(\text{CO})_{12}$ was carried in refluxing toluene for 40 min, which has lead to isolations of a new mixed metal compound, $\text{PtRu}_3(\mu_4\text{-}\eta^1 : \eta^1 : \eta^2 : \eta^4\text{-Ph-C=C-C=C-Ph})(\text{CO})_{10}(\text{dppe})$ with isomers **1** and **2**, in 61 and 3% isolated yields, respectively.⁸ Each structure of **1** and **2**

reveals that the alkynyl ligands now undergo C–C bond coupling forming a 1,4-diphenylbuta-1,3-diyne which cross-links mixed metal nuclei by a novel ($\mu_4\text{-}\eta^1 : \eta^1 : \eta^2 : \eta^4$)-bond. ^{31}P NMR spectra of **1** showed two resonances at 49.7 ppm ($J_{\text{Pt-P}} = 3171$ Hz) and 49.0 ppm ($J_{\text{Pt-P}} = 1966$ Hz), which suggests that dppe is unsymmetrically arranged. A coupling $^2J_{\text{P,P}}$ by through-metal interaction was not observed in this case, which may be related with a distortion of the bond angle P–Pt–P from an ideal angle 90°. The ^{13}C NMR spectra shows an unsymmetrical arrangement of the two alkynyl groups, and four resonances were observed at 151.6, 152.1, 170.7, and 170.9 ppm, which are rather in the region close to vinyl group. A pale yellow single crystal was obtained from toluene at 253 K and analysed by X-ray structure determination.⁹ The crystal structure of one of two independent molecules is in Figure 1 (phenyl rings of dppe ligands are omitted for clarity). The structure shows that the two alkynyl ligands from $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{dppe})$ now undergoes a head to head coupling forming a 1,4-diphenylbuta-1,3-diyne, which newly cross-links two fragments from $\text{Ru}_3(\text{CO})_{12}$; one, a dimetal system $\text{Ru}_2(\text{CO})_6$ fragment by ($\eta^1 : \eta^1 : \eta^2 : \eta^2$)-bond (bond distance Ru–Ru : 2.721(2), 2.709(2) Å) and the other dimetal system, $\text{PtRu}(\text{CO})_4(\text{dppe})$ group by ($\eta^1 : \eta^1$)-bond {bond distance Pt–Ru 2.7324(15), 2.7393(14) Å}. The geometry around the platinum atom is in good planarity. All bond lengths of Pt–C2 2.101(16), 2.070(14), Ru1–C1 2.130(16), 2.142(18), Ru3–C3 2.09(2), 2.128(18) and Ru3–C4 2.171(16), 2.141(16) Å are consistent with pure M–C σ -bond. The present structure may be viewed as a pentagonal pyramid with the apex occupied by Ru2 atom which

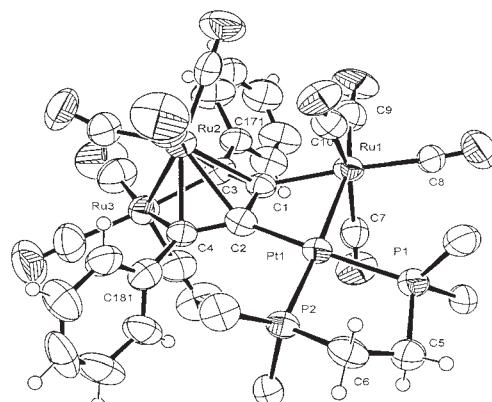
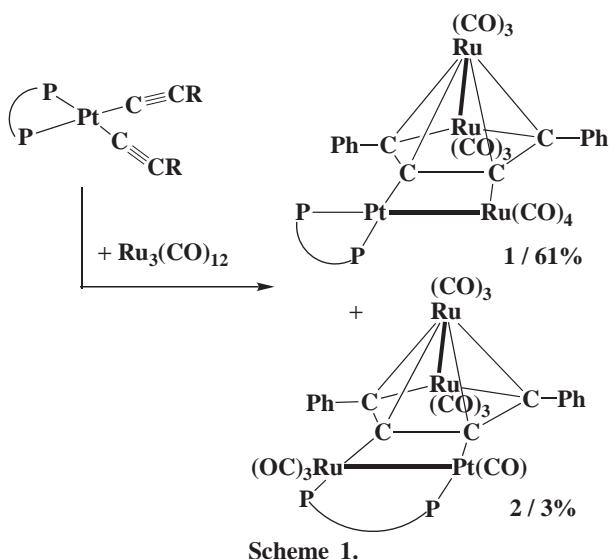


Figure 1. ORTEP plot(50% probability of thermal ellipsoid) for complex $\text{PtRu}_3(\text{PhCCCCPh})(\text{CO})_{10}(\text{dppe})$ **1**.

bonds to C(1), C(2), C(3), and C(4) atoms by η^2 -bonds. The Ru2 atom is bent back from the PtRu(CO)₄(dppe) group in the direction to Ru3 atom, and the bond lengths Ru2–C4 2.222(14), 2.288(16) Å and Ru2–C3 2.262(19), 2.241(17) Å are shorter than the distances Ru2–C1 2.355(15), 2.332(17) Å and Ru2–C2 2.364(17), 2.388(14) Å. The bond angles C2–C4–C181 130.2(15), 128.3(14)° are much more expanded than the angle C1–C3–C171 118.6(17), 124.4(16)°, and the phenyl ring attached to C4 atom is bent in the direction away from the PtRu(CO)₄(dppe) group, which is possibly due to the steric repulsions influenced from the dppe ligand. A bond angle P1–Pt1–P2 85.11(15) 85.15(15) is largely deviated from an ideal angle 90°. ¹³C NMR spectra of **2** showed a resemblance in resonances due to the alkynyl groups to those of **1**, which suggests that **2** may have an analogous structure to **1**. ³¹P NMR spectra of **2**, however, shows that one phosphorous atom of the dppe does not bond to the platinum atom anymore, but it may bridge over to a ruthenium atom, since a resonance at 27.06 ppm was observed by an explicit singlet with no ¹⁹⁵Pt satellites, while the other at 12.17 ppm with $J_{Pt-P} = 1958$ Hz. A bridging dppe is not unusual in cluster as observed for H₄Ru₄(CO)(μ -dppe)₁₀,¹⁰ for which a coupling $^3J_{P,P}$ by through-metal interaction was not also observed. A single crystal of **2** with toluene of solvation was obtained from toluene at 253 K, which readily degrades in air. Therefore, the crystal was carefully sealed in a glass capillary and analyzed by X-ray structure determination ($R(int) = 0.0677$). Unfortunately, owing to disorders of phenyl carbons of the dppe and the solvation by toluene, a desirable final refinement has not been attained. A preliminary structure of **2** is, however, depicted in Scheme 1. Although many clusters bridged by the 1,3-dynes are known,¹¹ the mixed metal compound cross-linked by the 1,3-dyne through a (μ_4 - η^1 : η^1 : η^2 : η^4)-bond is elusive.



Scheme 1.

The crystallographic data for the compound PtRu₃(PhCCCCPh)(CO)₁₀(dppe) **1** have been deposited in the Cambridge Crystallographic Data Centre, CCDC No. 184934. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK

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References and Notes

- See for review of cyclotrimerization; e.g. "Comprehensive Organometallic Chemistry II," ed. by E. W. Abel, F. G. A. Stone, and G. Wilkinson (1995), Vol. 12; "Transition metal Organometallics," in "Organic Syntheses: 7.3," ed. by L. S. Hegedus; D. B. Grotjahn, "Transition metal alkyne complexes: Transition metal catalyzed cyclotrimerization," Pergamon, Oxford.
- a) M. Crocker, M. Green, K. R. Nagle, A. G. Orpen, C. M. Thomas, H. P. Newman, C. E. Morton, and C. J. Schaverien, *Organometallics*, **9**, 1422 (1990). b) S. Yamazaki and Z. Taira, *J. Organomet. Chem.*, **578**, 61 (1999).
- J. F. Corrigan, S. Doherty, N. J. Taylor, and A. J. Cart, *Organometallics*, **11**, 3160 (1992).
- a) K. Yasufuku and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **45**, 2664 (1972). b) K. Yasufuku, K. Aoki, and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **48**, 1616 (1975).
- a) M. I. Bruce and P. J. Low, *Adv. Organomet. Chem.*, **48**, 71 (2001). b) M. Akita, A. Sakurai, and Y. Moro-oka, *Chem. Commun.*, **1999**, 101. c) S. Yamazaki, D. M. Speel, and A. J. Deeming, *Chem. Commun.*, **1997**, 177.
- L. D. Field, A. V. George, G. R. Purches, and I. H. M. Slip, *Organometallics*, **11**, 3019 (1992).
- M. I. Bruce, N. N. Zaitseva, B. W. Skelton, and A. H. White, *Inorg. Chim. Acta*, **250**, 129 (1996).
- Satisfactory elemental analyses for **1** and **2** with toluene of solvation were obtained. Spectral data of **1**: IR(nujol mull) $\tilde{\nu}_{max}$ (cm⁻¹): 2062(vs), 2041(vs), 1984(vs), 1965(vs), 1950(vs). ¹³C NMR (CDCl₃, δ): 32.7 (m: -CH₂- of dppe) 36.1 (m, -CH₂- of dppe). 151.6, 152.1 {C(Ph)=C-C=C(Ph)} 170.7, 170.9, {C(Ph)=C-C=C(Ph)} 180.0, 189.3, 192.2, 194.1, 196.3, 197.8, 200.0, 203.3, 204.7, 206.1 (M-CO). Spectral data of **2**: IR(nujol mull). $\tilde{\nu}_{max}$ (cm⁻¹): 2063(vs), 2038(vs), 2028(vs), 1976(vs), 1955(vs); ¹³C NMR (CDCl₃, δ): 25.49 (d, -CH₂- of dppe, $J_{P,C} = 26.5$ Hz) 26.79 (m, -CH₂- of dppe) 151.8, 152.4 (PhC=C-C=CPh) 171.1, 172.2 (PhC=C-C=CPh) 174.1, 181.2, 194.5, 195.0, 196.1, 197.4, 199.9 (d, $J_{P,C} = 10.7$ Hz) 201.1, 203.4 (d, $J_{P,C} = 10.7$ Hz) 205.0 (M-CO).
- Crystal data for C₅₂H₃₄O₁₀P₂PtRu₃ **1**: pale yellow crystal, orthorhombic, space group *Pc21b*, $a = 13.8980(19)$ Å, $b = 26.2400(11)$ Å, $c = 27.4270(20)$ Å, $V = 10002.17$ Å³, $Z = 8$, $D_{calcd} = 1.832$ g cm⁻³, $R_1 = 0.0586$, wR_2 (ref) = 0.1619, goof = 1.128 for 9525 independent reflections in the range 1° ≤ θ ≤ 25.76°, 1 > 2σ(I₀), refining 1227 parameters: Crystal data for C₅₉H₄₂O₁₀P₂PtRu₃. (C₇H₈) **2**: yellow crystal, orthorhombic, space group *Pcab*, $a = 19.5170(0)$ Å, $b = 23.4955(0)$ Å, $c = 31.0440(0)$ Å, $V = 14214.08$ Å³.
- M. R. Churchill, R. A. Lashewycz, J. R. Shapley, and S. A. I. Richter, *Inorg. Chem.*, **19**, 1277 (1980).
- a) M. I. Bruce, N. N. Zaitseva, B. W. Skelton, and A. H. White, *Inorg. Chim. Acta*, **250**, 129 (1996). b) M. I. Bruce, P. J. Low, A. Werth, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, **1996**, 1551. c) S. Yamazaki, D. M. Speel, and A. J. Deeming, *Organometallics*, **17**, 775 (1998). d) R. D. Adams, U. H. F. Wunz, W. Fu, and G. Riidl, *J. Organomet. Chem.*, **578**, 55 (1999). e) Y. Chi, A. J. Cart, P. Blenkiron, E. Delgado, G. D. Enright, W. Wang, S.-M. Peng, and G.-H. Lee, *Organometallics*, **15**, 5269 (1996).