Unexpected Ligand Displacement of Ru(cod)(cot) with Trimethylphosphine to Give *fac*-Ru(6-η^1:1-3-η^3-C_8H_{10})(PMe_3)$_3$

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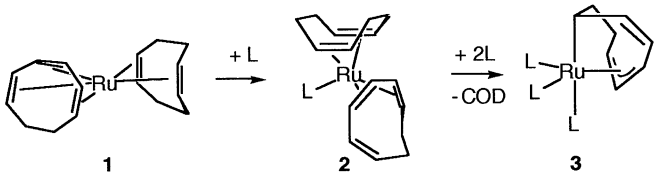
Selective ligand displacement of the cod ligand in Ru(cod)(cot) (**1**) [cod: 1,5-cyclooctadiene, cot: 1,3,5-cyclooctatriene] with trimethylphosphine gives *fac*-Ru(6-η^1:1-3-η^3-C_8H_{10})(PMe_3)$_3$ (**3**) in benzene at 50 °C.

Ru(cod)(cot) (**1**) is nowadays widely used as one of the most versatile zerovalent ruthenium complexes.[1] Combination of **1** with suitable tertiary phosphine ligands especially provides many useful catalytic systems.[2] Although it is known to isomerize to divalent ruthenium complex, Ru(η^5-C_8H_{11})$_2$ upon heating via intramolecular hydrogen migration,[1d-f] the cyclooctatriene ligand (cot) in **1** is expected to be readily removed to give reactive species Ru(cod)L_n in the early stage of the catalytic and non-catalytic reactions promoted by **1**. Indeed, the labile nature of the cot ligand is shown by a series of the reactions of **1** with arenes giving Ru(arene)(1-2:5-6-η^4-cod) under hydrogen.[3] Although the reaction of **1** with one equivalent of CO gives Ru(1-2:5-6-η^4-cod)(1-2:5-6-η^4-cot)(CO), treatment of **1** with an excess amount of CO leads to the formation of Ru(1-2:5-6-η^4-cod)(CO)$_3$.[4] Tertiary phosphine ligands (L) such as trimethylphosphine and trimethylphosphite are also known to react with **1** to give mono-substituted complexes Ru(1-2:5-6-η^4-cod)(1-2:5-6-η^4-cot)(L).[5] Further displacement of the cot ligand by P ligand has been confirmed by the formation of Ru(1-2:5-6-η^4-cod)(η^1-dppm)(η^2-dppm) [dppm = 1,2-bis(diphenylphosphino)methane].[5] Thus the preferential liberation of the cot ligand in **1** is believed to proceed in all the reactions of **1**. Herein we wish to report the first example of the selective displacement of the cod ligand in **1** with trimethylphosphine giving new Ru(6-η^1:1-3-η^3-C_8H_{10})(PMe_3)$_3$ (**3**).

Treatment of **1** with 3-fold amount of PMe_3 at room temperature in benzene or hexane immediately gave a known monophosphine complex Ru(η^4-cod)(η^4-cot)(PMe_3) (**2**).[5a] Although **2** remained unchanged in the prolonged reaction at room temperature, Ru(6-η^1:1-3-η^3-C_8H_{10})(PMe_3)$_3$ (**3**) was obtained by the reaction at 50 °C for 33 h.



1 **2** **3** (L = PMe_3)

Scheme 1.

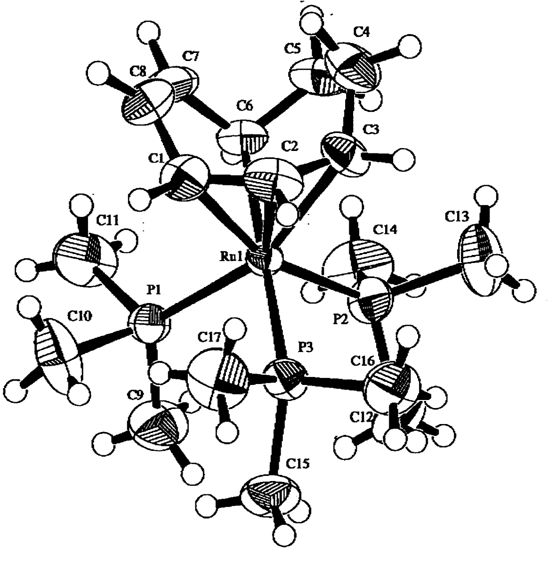
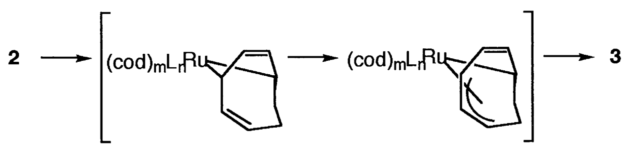


Figure 1. Molecular structure of **3**. Selected bond distances (Å) and angles (deg): Ru1-C1, 2.228(5); Ru1-C2, 2.140(5); Ru1-C3, 2.255(5), Ru1-C6, 2.180(5); C1-C2, 1.420(8); C2-C3, 1.387(7); C3-C4, 1.521(8); C4-C5, 1.512(8); C5-C6, 1.506(7); C6-C7, 1.476(7); C7-C8, 1.321(8); P1-Ru1-P2, 98.37(6); P1-Ru1-P3, 93.00(5), P2-Ru1-P3, 95.02(5); P1-Ru1-C1, 95.0(2); P1-Ru1-C3, 160.1(1); P2-Ru1-C1, 162.3(1); P2-Ru1-C3, 95.8(2); P1-Ru1-C6, 89.5(1); P2-Ru1-C6, 89.5(1); P3-Ru1-C6, 174.4(1); C1-C2-C3, 128.3(5).

In the solution, liberation of a quantitative yield of cyclooctadiene was confirmed by ^{1}H NMR analysis. Recrystallization of the yellow solid from pentane afforded fairly air sensitive pale yellow needles of **3** in 42% yield (Scheme 1).[6] Molecular structure of **3** determined by X-ray structure analysis is depicted in Figure 1.[7] The bond distances of Ru1-C1 [2.228(5) Å], Ru1-C2 [2.140(5) Å], Ru1-C3 [2.255(5) Å], C1-C2 [1.420(8) Å] and C2-C3 [1.387(7) Å] show a typical η^3-allyl structure of the C1-C2-C3 linkage. The bond distance of Ru1-C6 is within typical ruthenium-carbon σ bonds.[8] The short C7-C8 bond distance [1.321(8) Å] corresponds to the uncoordinated C=C double bond. The bond angles for P1-Ru1-C6 [89.5(1)°], P2-Ru1-C6 [89.5(1)°], P3-Ru1-C6 [174.4(1)°], P1-Ru1-C1 [95.0(2)°], and P2-Ru1-C3 [95.8(2)°] indicate that **3** basically has an octahedral geometry. Thus, the complex **3** is best regarded as a divalent d^6 complex formulated as Ru(6-η^1,1-3-η^3-C_8H_{10})(PMe_3)$_3$. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows an *ABX* pattern at -11.28 (t, J = 25 Hz), -0.46 (dd, J = 25 Hz, 16 Hz), and -0.36 ppm (dd, J = 25 Hz, 16 Hz), being consistent with the geometry lacking a mirror plane of symmetry among the three P atoms. ^{1}H NMR spectrum shows two uncoordinated olefinic protons at 5.70 and 5.95 ppm. Consistently, IR spectrum of this compound has a medium band at 1634 cm^{-1}, which is assignable to the stretching vibration of the uncoordinated C=C double bond. These spectroscopic data are consistent with the X-ray structure of **3**. Thus, the η^1-η^3-C_8H_{10} fragment is considered to be originated from the η^4-cot ligand in **2**. This result shows *the selective dispalcement of the cod ligand in 2 with PMe*$_3$, accompanied by the change of the coordination mode of the cot ligand. The preferential displacement of the cod ligand rather than cot in **2** is unprecedented.[9] Strong electron donation from PMe_3 ligand to Ru probably causes effective back bonding from ruthenium to the η^4-cot ligand to form a ruthenabicyclic ring.[10,11]



Scheme2.

The resultant η^1-allyl fragment would rearrange to the thermodynamically stable η^3-allyl complex **3** as outlined in Scheme 2. Contrary to the highly basic alkyl phosphine ligands, η^4-cot ligands in Ru(η^4-cod)(η^4-cot)(CO) and Ru(η^4-cod)(η^4-cot)[P(OMe)$_3$] are labile toward ligand displacement because of less contribution of canonical ruthenacycle structure. Thus the further displacement of the cot ligand with CO would take place to give Ru(cod)(CO)$_3$.[4] Neither DMPE [1,2-bis(dimethylphosphino)ethane], DEPE [1,2-bis(diethylphosphino)ethane], nor DPE [1,2-bis(diphenylphosphino)ethane] gave monophosphine adduct, Ru(η^4-cod)(η^4-cot)(η^1-diphosphine) and a complex having η^1-η^3-C_8H_{10} ligand, but gave Ru(η^4-cod)(η^2-diphosphine)(η^1-diphosphine) in the reaction with **1**.[12] Chelation effect of diphosphine ligand probably gives Ru(η^4-cod)(η^2-cot)(η^2-diphosphine), from which the η^2-cot ligand is smoothly replaced by another diphosphine.

Complex **3** shows unexpected thermal stability [mp = 193 °C (dec)] and is relatively insensitive to the chemical reactions such as ligand displacement as well as to C-O bond cleavage reactions of esters or ethers, although Ru(cod)(cot)/PR$_3$ system is reactive.[13,14]

The present results may indicate the importance of delicate balance of the employed ligands in the Ru(cod)(cot) assisted catalyses and reactions.

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6 Physical and spectroscopic data for **3**: yield 43%/**1**; mp 193 °C (dec); ^{1}H NMR (300 MHz, C_6D_6): δ 0.67 (d, J = 5.7 Hz, axial-PMe_3, 9H), 1.23 (d, J = 7.5 Hz, equatorial-PMe_3, 9H), 1.25 (d, J = 7.2 Hz, equatorial-PMe_3, 9H), 1.7-2.5 (m, aliphatic protons of cot, 5H), 3.64 (m, allylic protons, 2H), 3.98 (m, allylic proton, 1H), 5.70 (m, uncoordinate CH=, 1H), 5.95(m, uncoordinate CH=, 1H); ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ -11.28 (t, J = 25 Hz, apical PMe$_3$, 1P), -0.46 (dd, J = 25, 16 Hz, equatorial PMe$_3$, 1P), -0.36 (dd, J = 25, 16 Hz, equatorial PMe$_3$, 1P), ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): δ 18.9 (d, J = 16 Hz, apical PMe_3), 23.2 (br.t, equatorial PMe_3), 25.7 (d, J = 4 Hz, CH_2), 44.8 (dt, J = 63.4, 9.8 Hz, Ru-CH), 47.6 (s, CH_2), 68.4 (ddd, J = 5, 5, 25 Hz, allylic CH), 71.4 (ddd, J = 5, 5, 24 Hz, allylic CH), 94.9 (s, allylic CH), 129.3 (dd, J = 8, 3 Hz, uncoordinated CH=), 146.0 (dd, J = 8, 3 Hz, uncoordinated CH=); IR (KBr, cm^{-1}): 1634 (m), 1426 (m), 1417 (m), 1293 (m), 1278 (m), 956 (s), 933 (s), 845 (m), 705 (m), 658 (m); Anal. Found: C, 47.13; H, 8.97%. Calcd for $C_{17}H_{37}P_3Ru$: C, 46.89; H, 8.56%.

7 Crystallographic data for **3**: $C_{17}H_{37}P_3Ru$, Fw = 435.47, monoclinic, space group $P2_1/n$ (#14), a = 8.409(4)Å, b = 16.668(2) Å, c = 15.300(2) Å, β = 97.25(2) °, V = 2127.4(10) Å^3, Z = 4, D_{calc} = 1.360 g/cm^3, R (R_w) = 0.038 (0.034) for 3905 unique reflections.

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