

Platinum Participation in the Hydrogenation of Phenylacetylene by $\text{Ru}_5(\text{CO})_{15}(\text{C})[\text{Pt}(\text{PBU}_3)]$

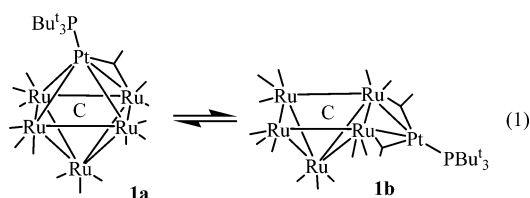
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Recent studies have shown that bimetallic cluster complexes are excellent precursors for highly active nanocluster hydrogenation catalysts when placed on mesoporous supports.¹ In certain cases, these bimetallic catalysts exhibit evidence for strong synergistic effects.^{1,2} Platinum- and palladium-ruthenium carbonyl cluster complexes are among the most effective precursors for these catalysts.² In our previous studies of bimetallic clusters in homogeneous catalysis, we observed promotional effects of platinum, but no evidence for its direct participation in the process.³

We have recently prepared the tri-*tert*-butylphosphine complex $\text{Ru}_5(\text{CO})_{15}(\text{C})[\text{Pt}(\text{PBU}_3)]$, **1**, and have shown that it exists in solution as a mixture of rapidly interconverting isomers having closed (**1a**) and open (**1b**) structures for the metal cluster, eq 1.⁴ We have now investigated the reactions of **1** with hydrogen and phenylacetylene, PhC_2H , and have found evidence for catalytic hydrogenation activity in solutions. We have also isolated bimetallic complexes that show heteronuclear coordination of both of these reagents.



The dihydride complex $\text{Ru}_5(\text{CO})_{14}(\mu_6\text{-C})[\text{Pt}(\text{PBU}_3)](\mu\text{-H})_2$, **2**, was obtained in 68% yield from the reaction of **1** with hydrogen in a heptane solution at reflux.⁵ Compound **2** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 1.⁶ The molecule consists of an octahedral cluster of six metal atoms, PtRu_5 , with a carbido ligand in the center. A PBU_3 ligand is coordinated to the platinum atom, and there are two hydride ligands (refined crystallographically) that bridge two of the Pt-Ru bonds. In contrast to most hydride bridges, these hydride-bridged Pt-Ru bonds, $\text{Pt}(1)\text{-Ru}(4) = 2.8336(3) \text{ \AA}$, $\text{Pt}(1)\text{-Ru}(2) = 2.8497(3) \text{ \AA}$, are significantly shorter than the unbridged Pt-Ru bonds, $\text{Pt}(1)\text{-Ru}(3) = 2.9969(3) \text{ \AA}$, $\text{Pt}(1)\text{-Ru}(1) = 3.1189(3) \text{ \AA}$.⁷ This could be due to influences of the interstitial carbido ligand.⁸ The hydride ligands show strong one-bond coupling to ¹⁹⁵Pt in the ¹H NMR spectrum: $\delta = -13.86$ (d, ¹ $J_{\text{Pt-H}} = 774 \text{ Hz}$, ² $J_{\text{P-H}} = 8 \text{ Hz}$).

The alkyne complex $\text{Ru}_5(\text{CO})_{13}(\mu_5\text{-C})(\text{PhC}_2\text{H})[\text{Pt}(\text{PBU}_3)]$, **3**, was obtained in 41% yield from the reaction of **1** with PhC_2H in a CH_2Cl_2 solution at reflux.⁹ Compound **3** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 2. This molecule consists of a platinum-capped square-pyramidal pentaruthenium cluster of six metal atoms with a carbido ligand in the center of the Ru_5 cluster. A PBU_3 ligand is coordinated to the platinum atom, and a PhC_2H ligand bridges one of the PtRu_2 triangles, $\text{Pt}(1)\text{-C}(3) = 1.980(7)$

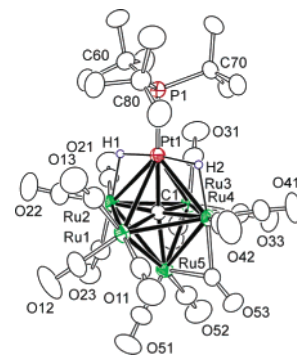


Figure 1. An ORTEP diagram of $\text{Ru}_5(\text{CO})_{14}(\mu_6\text{-C})[\text{Pt}(\text{PBU}_3)](\mu\text{-H})_2$, **2**, showing 40% probability thermal ellipsoids. Selected interatomic distances (\AA) are: $\text{Pt}(1)\text{-Ru}(4) = 2.8336(3)$, $\text{Pt}(1)\text{-Ru}(2) = 2.8497(3)$, $\text{Pt}(1)\text{-Ru}(3) = 2.9969(3)$, $\text{Pt}(1)\text{-Ru}(1) = 3.1189(3)$, $\text{Pt}(1)\text{-H}(1) = 1.67(4)$, $\text{Pt}(1)\text{-H}(2) = 1.71(4)$, $\text{Pt}(1)\text{-P}(1) = 2.3248(9)$.

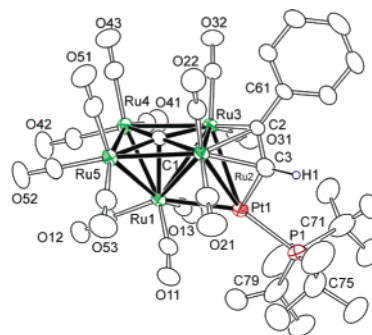


Figure 2. An ORTEP diagram of $\text{Ru}_5(\text{CO})_{13}(\mu_5\text{-C})(\text{PhC}_2\text{H})[\text{Pt}(\text{PBU}_3)]$, **3**. Selected interatomic distances (\AA) are: $\text{Pt}(1)\text{-C}(3) = 1.980(7)$, $\text{Pt}(1)\text{-P}(1) = 2.3122(19)$, $\text{Pt}(1)\text{-Ru}(1) = 2.6787(6)$, $\text{Pt}(1)\text{-Ru}(2) = 2.8476(6)$, $\text{Pt}(1)\text{-Ru}(3) = 2.9979(5)$, $\text{Ru}(1)\text{-Ru}(5) = 2.7705(8)$, $\text{Ru}(1)\text{-Ru}(4) = 2.7949(8)$, $\text{Ru}(1)\text{-Ru}(2) = 2.9856(7)$, $\text{Ru}(1)\text{-Ru}(3) = 3.0018(7)$, $\text{Ru}(2)\text{-Ru}(3) = 2.6666(7)$, $\text{Ru}(2)\text{-Ru}(5) = 2.8926(7)$, $\text{Ru}(3)\text{-Ru}(4) = 2.9037(7)$, $\text{Ru}(4)\text{-Ru}(5) = 2.8898(8)$, $\text{Ru}(2)\text{-C}(3) = 2.210(7)$, $\text{Ru}(2)\text{-C}(2) = 2.214(6)$, $\text{C}(2)\text{-C}(3) = 1.369(10)$.

\AA , $\text{Ru}(2)\text{-C}(3) = 2.210(7) \text{ \AA}$, $\text{Ru}(2)\text{-C}(2) = 2.214(6) \text{ \AA}$, $\text{C}(2)\text{-C}(3) = 1.369(10) \text{ \AA}$.

When compound **3** was treated with hydrogen (30 psi) in the presence of a 50-fold excess PhC_2H at 80°C , styrene was obtained catalytically at a rate of 20(2) turnovers/h.¹⁰ From these solutions, we have isolated the new platinum-ruthenium cluster complex, $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-C})[\text{Pt}(\text{PBU}_3)](\text{PhC}_2\text{H})(\mu\text{-H})_2$, **4**.¹¹ An ORTEP diagram of the structure of **4** is shown in Figure 3. Like **3**, compound **4** contains a platinum-capped Ru_3 triangle of a Ru_5 cluster, but the Ru_5 cluster is not a square-pyramidal cluster as in **3**. Instead, one of the Ru-Ru bonds in the Ru_5 cluster has been eliminated, $\text{Ru}(1)\text{-Ru}(3) = 3.6574(5) \text{ \AA}$ in **4** versus $3.0018(7) \text{ \AA}$ in **3**.¹² One CO ligand was eliminated in going from **3** to **4**, and 1 equiv of H_2 was added. The hydrogen exists in the form of two hydride ligands, H(1) and H(2), that bridge the $\text{Pt}(1)\text{-Ru}(1)$ and $\text{Ru}(1)\text{-Ru}(5)$ metal-metal

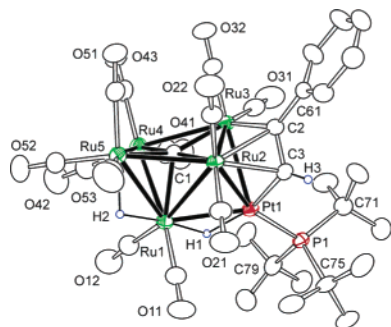
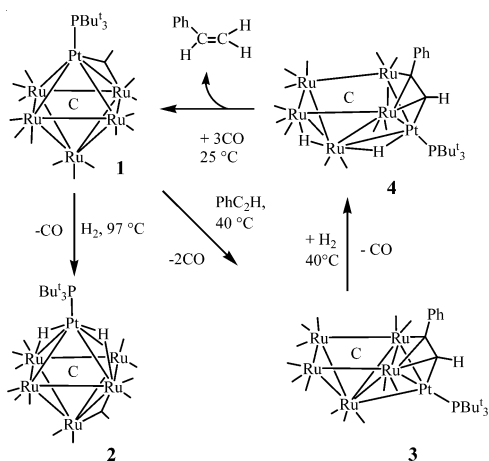


Figure 3. An ORTEP diagram of $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-C})[\text{PtPBu}_3](\text{PhC}_2\text{H})(\mu\text{-H})_2$, **4**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) are: Pt(1)–C(3) = 1.991(4), Pt(1)–P(1) = 2.3146(11), Pt(1)–Ru(1) = 2.6793(4), Pt(1)–Ru(2) = 2.7045(4), Pt(1)–Ru(3) = 2.8143(4), Pt(1)–H(1) = 1.79(5), Ru(1)–Ru(5) = 2.8161(5), Ru(1)–Ru(4) = 2.8609(5), Ru(1)–Ru(2) = 2.9208(5), Ru(1)–Ru(3) = 3.6574(5), Ru(1)–H(1) = 1.79(5), Ru(1)–H(2) = 1.73(5), Ru(2)–C(3) = 2.230(4), Ru(2)–C(2) = 2.289(4), Ru(2)–Ru(3) = 2.6694(5), Ru(2)–Ru(5) = 2.8906(5), Ru(3)–C(2) = 2.050(4), Ru(3)–Ru(4) = 2.9747(6), Ru(4)–Ru(5) = 2.8939(6), Ru(5)–H(2) = 1.79(5), C(2)–C(3) = 1.395(5).

Scheme 1



bonds. The resonances of the hydride ligands in the ^1H NMR spectrum are consistent with the solid-state structure.¹¹ Compound **4** contains a PhC_2H that bridges a PtRu_2 triangle similarly to that in **3**. Interestingly, **4** can be obtained independently in a better yield simply by treating **3** with hydrogen and the decarbonylation agent Me_3NO at 40 °C.¹³

When **4** was treated with CO at 25 °C, both hydrides and the PhC_2H ligand were eliminated in the form of styrene, and compound **1** was formed. When solutions of **4** were treated with hydrogen and an excess of PhC_2H , styrene was formed catalytically, 21(2) turnovers/h. Interestingly, when $\text{Ru}_6(\text{CO})_{17}(\mu_6\text{-C})$ was treated with hydrogen and PhC_2H under similar conditions, no styrene was produced. A summary of these reactions is shown in Scheme 1.

Further studies to establish the mechanism of the catalytic process are in progress, but certain notable features are already apparent: (1) the bimetallic complex **1** is capable of activating both hydrogen and PhC_2H separately and in combination; (2) PhC_2H can be hydrogenated to styrene catalytically, and (3) in all of the species characterized so far, **2–4**, the platinum atom is directly involved in bonding to either the hydride ligands, the PhC_2H ligand, or both. This demonstrates that the platinum atom plays a direct role in the activation of the reagents. This could also help to explain the

synergistic effects observed by these bimetallic clusters when they are used as catalysts on supports.^{1,2}

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy, Grant No. DE-FG02-00ER14980.

Supporting Information Available: Details of the synthesis and characterizations of the products (PDF), and CIF files for the structural analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Here, 9.3 mg of **1** (0.0070 mmol) in 10 mL of heptane was heated to reflux under a slow purge with hydrogen for 1.5 h. Separation by TLC (4:1 hexane–methylene chloride solvent) yielded 6.3 mg (68%) of dark gray $\text{Ru}_5(\text{CO})_{14}(\mu_6\text{-C})[\text{PtPBu}_3](\mu\text{-H})_2$, **2**. Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2087 (m), 2052 (s), 2015 (s), 1971 (w, sh), 1821 (w, br). ^1H NMR (in toluene- d_8): δ = 1.22 (d, 27H, CH_3 , $^3J_{\text{P-H}} = 13$ Hz), –13.86 (d, 2H, $^1J_{\text{Pt-H}} = 774$ Hz, $^2J_{\text{P-H}} = 8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (in toluene- d_8): δ = 85.3 (s, 1P, $^1J_{\text{Pt-P}} = 4739$ Hz). Anal. Calcd: C, 24.77; H, 2.22. Found: C, 25.13; H, 2.50. Crystal data for **2**: orthorhombic, space group = $Pccn$, $a = 20.5414(9)$ Å, $b = 21.3611(9)$ Å, $c = 18.4550(8)$ Å, $Z = 8$. For 8493 reflections, $R_1 = 0.0241$, $wR_2 = 0.0556$.
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- Here, 16 mg of **1** (0.012 mmol) was dissolved in 20 mL of CH_2Cl_2 . Phenylacetylene (0.010 mL, 0.090 mmol) was added and then heated to reflux for 1 h. Separation by TLC (6:1 hexane–methylene chloride solvent) yielded 6.8 mg of a $\text{Ru}_5(\text{CO})_{13}(\mu_5\text{-C})(\text{PhC}_2\text{H})[\text{PtPBu}_3]$, **3** (41%). Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2076 (vs), 2044 (vs), 2027 (s), 2014 (vs), 1985 (w, sh), 1955 (vw, sh). ^1H NMR (in CDCl_3): δ = 8.58 (d, 1H, CH, $^3J_{\text{P-H}} = 16$ Hz), 7.3–7.4 (m, 5H, Ph), 1.50 (d, 27H, CH_3 , $^3J_{\text{P-H}} = 13$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (in CDCl_3): δ = 113.4 (s, 1P, $^1J_{\text{Pt-P}} = 4545$ Hz). Anal. Calcd: C, 29.57; H, 2.39. Found: C, 28.47; H, 2.15. Crystal data for **3**: triclinic, space group = $P-1$, $a = 12.6218(5)$ Å, $b = 13.3776(5)$ Å, $c = 14.3654(5)$ Å, $\alpha = 92.6780(10)^\circ$, $\beta = 91.0510(10)^\circ$, $\gamma = 109.9580(10)^\circ$, $Z = 2$. For 9150 reflections, $R_1 = 0.0454$, $wR_2 = 0.1139$.
- (10) For comparison, the nine-metal cluster $\text{H}_2\text{Pt}_3\text{Ru}_6(\text{CO})_{20}(\mu_3\text{-PhC}_2\text{H})$ was shown to catalyze the hydrogenation of diphenylacetylene to (*Z*)-stilbene at a rate of 47 turnovers/h at 50 °C.^{3b}
- (11) For **4**, IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2083 (s), 2047 (s), 2023 (vs), 2004 (w, sh), 1977 (w, sh), 1948 (vw, sh). ^1H NMR (in toluene- d_8): δ = 9.76 (dd, 1H, CH, $^3J_{\text{H-H}} = 1.5$ Hz, $^3J_{\text{P-H}} = 4$ Hz, $^2J_{\text{Pt-H}} = 42$ Hz), 7.72 (d, 2H, Ph–H), 7.18 (t, 2H, Ph–H), 7.05 (t, 1H, Ph–H), 0.99 (d, 27H, CH_3 , $^3J_{\text{P-H}} = 13$ Hz), –9.56 (ddd, 1H, hydride on Pt, $^2J_{\text{H-H}} = 4$ Hz, $^3J_{\text{H-H}} = 1.5$ Hz, $^1J_{\text{Pt-H}} = 641$ Hz), –18.55 (d, hydride on Ru, $^2J_{\text{H-H}} = 4$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (in toluene- d_8): δ = 124.0 (s, 1P, $^1J_{\text{Pt-P}} = 3839$ Hz). Anal. Calcd: C, 29.27; H, 2.61. Found: C, 29.63; H, 2.44. Crystal data for **4**: triclinic, space group = $P-1$, $a = 12.3991(9)$ Å, $b = 12.6807(10)$ Å, $c = 16.5292(12)$ Å, $\alpha = 105.157(2)^\circ$, $\beta = 104.028(2)^\circ$, $\gamma = 94.753(2)^\circ$, $Z = 2$. For 9934 reflections, $R_1 = 0.0335$, $wR_2 = 0.0741$.
- (12) Compounds **3** and **4** have the same number of valence electrons; however, **4** is unsaturated because it has one less Ru–Ru bond than **3**.
- (13) Here, 22.5 mg of **3** (0.016 mmol) was dissolved in 25 mL of CH_2Cl_2 . Under a purge with H_2 , 5.4 mg of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.049 mmol) was added, and the solution was then heated to reflux for 1 h. Separation by TLC (4:1 hexane–methylene chloride solvent) yielded 4.2 mg of dark gray $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-C})[\text{PtPBu}_3](\text{PhC}_2\text{H})(\mu\text{-H})_2$, **4** (19%).

JA049955Y