The importance of cluster fragmentation in the catalytic hydrogenation of phenylacetylene by PtRu$_5$ carbonyl cluster complexes

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Abstract

PtRu$_5$(CO)$_{13}$(PBu$_3^t$)(μ_3-PhC$_2$H)(μ_5-C) (**2**) has been shown to be a catalyst precursor for the hydrogenation of PhC$_2$H to styrene and ethylbenzene. Three new organometallic products have been found in the catalyst solutions. These are Ru$_5$(CO)$_{12}$(μ_5-C)-[PtPBu$_3^t$](μ_3-PhC$_2$H)(μ-H)$_2$ (**4**), Pt(PBu$_3^t$)(PhC$_2$H)(CO) (**5**), and Ru$_5$(CO)$_{11}$(μ_4-CCHCPh)(μ_4-HC$_2$Ph)(μ_3-HC$_2$Ph) (**6**). Compounds **4–6** have been synthesized independently and structurally characterized and each one has been tested independently for its ability to produce hydrogenation of PhC$_2$H catalytically. Compound **4** contains an open square-pyramidal cluster of five ruthenium atoms with one platinum atom bridging an edge of the cluster. It is structurally related to **2** but contains one less CO ligand and two hydrido ligands formed by the addition of one equivalent of hydrogen to the metal cluster. It can be obtained directly from **2** by reaction with hydrogen in the presence of trimethylamine oxide. Compound **5** is a tricoordinated mononuclear platinum complex containing one PBu$_3^t$ ligand, one CO ligand and one μ_2-PhC$_2$H ligand. Compound **5** can be obtained directly from Pt(PBu$_3^t$)$_2$ by reaction with PhC$_2$H under an atmosphere of CO. Compound **6** was obtained from the reaction of Ru$_5$(CO)$_{15}$(μ_5-C) with PhC$_2$H in the presence of UV–Vis irradiation. Compound **6** contains three equivalents of PhC$_2$H; one is present as triply bridging PhC$_2$H ligand; one is a quadruply bridging ligand; the third one has formed a bond to the carbido ligand in the center of the metal cluster to form a novel tetra-metallated allyl ligand. Compound **5** has the highest catalytic activity of all three compounds and is believed to be responsible for the vast majority of the catalytic hydrogenation produced from the solutions of **2**. Compound **4** is transformed into **5** under the conditions of catalysis.
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1. Introduction

Recent studies have shown that metallic cluster complexes can be excellent precursors for highly active metal nanocluster hydrogenation catalysts when they are activated on mesoporous supports [1,2]. There is evidence for synergistic effects in some bimetallic systems [2]. Platinum- and palladium–ruthenium carbonyl cluster complexes have been shown to be among the most effective precursors for these catalysts [1,2]. Some studies have shown the intact cluster complexes containing groups of ruthenium atoms can also perform hydrogenation catalysis homogeneously in solution although the activities are much lower [3]. There is also evidence that some cluster complexes undergo fragmentation in solutions and the catalysis is produced by the metal containing fragments [4].

We have recently prepared the bimetallic tri-*t*-butylphosphine cluster complex PtRu$_5$(CO)$_{15}$(PBu$_3^t$)(C) (**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) [5]

(1)

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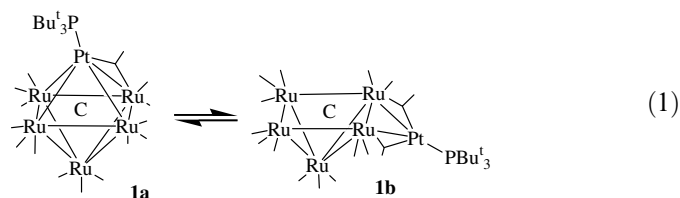
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Compound **1** is able to add alkynes and hydrogen separately and in combination under mild conditions. For example, **1** reacts with PhC_2H to form the complex $PtRu_5$-$(CO)_{13}(PBu_3^t)(\mu_3\text{-}PhC_2H)(\mu_5\text{-}C)$ (**2**) which contains a triply bridging PhC_2H ligand in an open $PtRu_5$ cluster [6]. Compound **1** also reacts with hydrogen at 98 °C to form the dihydride complex $PtRu_5(CO)_{14}(PBu_3^t)(\mu\text{-}H)_2(\mu_6\text{-}C)$ (**3**) [7].

2   **3**
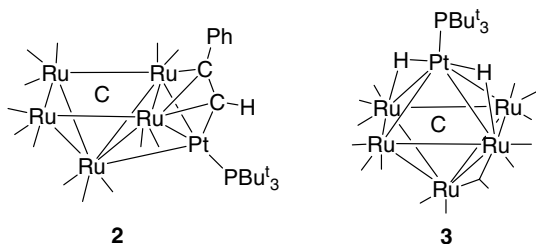
We have found that **2** also reacts with hydrogen in the presence of Me_3NO to form the dihydride complex $Ru_5(CO)_{12}(\mu_5\text{-}C)[PtPBu_3^t](PhC_2H)(\mu\text{-}H)_2$ (**4**), and compounds **1**, **2** and **4** are all catalyst precursors for the hydrogenation of PhC_2H in solution [8]. We have now found that the catalytic activity produced by these complexes is due principally to the mononuclear platinum complex $Pt(PBu_3^t)(PhC_2H)(CO)$ (**5**) that is formed by fragmentation of the $PtRu_5$ cluster complexes under the reaction conditions. The results of our studies of these reactions are reported herein.

2. Experimental

General data. All the reactions were performed under a nitrogen atmosphere by using Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on an AVATAR 360 FT-IR spectrophotometer. ^{1}H NMR and ^{31}P NMR were recorded on a Varian Mercury 400 spectrometer operating at 400 and 162 MHz, respectively. ^{31}P NMR spectra were externally referenced against 85% *ortho*-H_3PO_4. Elemental analyses were performed by Desert Analytics (Tucson, AZ). $Pt(PBu_3^t)_2$ was purchased from Strem, and phenylacetylene and trimethylamine oxide were purchased from Aldrich and were used without further purification. $Ru_5(CO)_{15}(\mu_5\text{-}C)$ [9], $Ru_6(CO)_{17}(\mu_6\text{-}C)$ [9], $PtRu_5(CO)_{15}(PBu_3^t)(C)$ [5], and **2** [6] were prepared according to the published procedures. Toluene-d_8 was purchased from Cambridge Isotopes and was used without further purification. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

2.1. Preparation of $Ru_5(CO)_{12}(\mu_5\text{-}C)[PtPBu_3^t](\mu_3\text{-}PhC_2H)(\mu\text{-}H)_2$ (4)

A 22.5 mg amount of **2** (0.016 mmol) was dissolved in 25 mL CH_2Cl_2. Hydrogen gas was then purged slowly through this solution at 1 atm. A 5.4 mg amount of

$Me_3NO \cdot 2H_2O$ (0.049 mmol) was then added to the flask and the solution was then heated to reflux with stirring under a continuous purge with H_2 for 1 h. The solvent was then removed in vacuo and the product was separated by TLC by using a 4:1 hexane–methylene chloride solvent mixture to give 4.2 mg (20% yield) of dark gray **4**. Spectral data 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). ^{1}H NMR (in toluene-d_8): $\delta = 9.76$ (dd, 1H, CH, $^3J_{H-H} = 1.5$ Hz, $^3J_{P-H} = 4$ Hz, $^2J_{Pt-H} = 42$ 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, $^3J_{P-H} = 13$ Hz), −9.56 (ddd, 1H, hydride on Pt, $^2J_{P-H} = 1.5$ Hz, $^2J_{H-H} = 4$ Hz, $^3J_{H-H} = 1.5$ Hz, $^1J_{Pt-H} = 641$ Hz), −18.55 (d, hydride on Ru, $^2J_{H-H} = 4$ Hz). ^{31}P{^{1}H} NMR (in toluene-d_8): $\delta = 124.0$ (s, 1P, $^1J_{Pt-P} = 3839$ Hz). Anal. Calc.: C, 29.27; H, 2.61. Found: C, 29.63; H, 2.44%.

2.2. Preparation of $Pt(PBu_3^t)(PhC_2H)(CO)$ (5)

A 54.3 mg amount of $Pt(PBu_3^t)_2$ (0.091 mmol) was dissolved in 10 mL toluene and an excess amount of phenylacetylene was added. CO gas was then purged through the solution at 1 atm while stirring. The reaction solution was allowed to stir for 15 min at room temperature. The solvent was then removed in vacuo leaving a thick yellow oil. The product was obtained in a crystalline form by redissolving in diethylether and cooling to −20 °C to yield 39.5 mg of yellow crystals of pure $Pt(PBu_3^t)(PhC_2H)$-(CO) (**5**) (83% yield). Compound **5** is unstable to chromatography on silica gel and cannot be isolated by such a workup. Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane): 1999 (s), 1980 (w). ^{1}H NMR (in toluene-d_8): $\delta = 7.92$ (d, 1H, CH, $^2J_{P-H} = 7$ Hz), 7.46 (d, 2H, Ph, $^3J_{Pt-H} = 60$ Hz), 7.21 (t, 2H, Ph), 7.06 (t, 1H, Ph), 1.29 (d, 27H, CH_3, $^3J_{P-H} = 12$ Hz). ^{31}P{^{1}H} NMR (in toluene-d_8): $\delta = 89.8$ (s, 1P, $^1J_{Pt-P} = 2980$ Hz). Anal. for **5**, Calc.: C, 47.82; H, 6.26. Found: C, 48.19; H, 6.16%.

2.3. Reaction of 2 with PhC_2H

A 10 mg amount of **2** (0.0072 mmol) was dissolved in 25 mL benzene in a 50 mL three-neck flask. Phenylacetylene (36 μL, 0.36 mmol) was added and the solution was heated to reflux for 16 h. ^{31}P NMR spectra of the reaction mixture taken in d_8-toluene showed that the major Pt-containing product was compound **5**. The reaction mixture was separated by TLC by using 5:1 hexane–methylene chloride solvent mixture to yield 0.4 mg (5% yield) of green $Ru_5(CO)_{11}(\mu_4\text{-}CCHCPh)(\mu_4\text{-}HC_2Ph)(\mu_3\text{-}HC_2Ph)$ (**6**). Compound **5** is unstable to chromatography on silica gel and cannot be isolated by such a workup. Spectral data for **6**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2087 (m), 2069 (w), 2046 (s), 2022 (vs), 1996 (m), 1979 (m), 1949(w). ^{1}H NMR (in toluene-d_8): $\delta = 9.05$ (s, 1H, CH, broad), 8.79 (s, 1H, CH, broad), 8.58 (s, 1H, CH,), 6.98–7.52 (m, Ph, broad). Anal. Calc.: C, 38.20; H, 1.59. Found: C, 39.56; H, 1.50%.

2.4. Alternative preparation of 6

A 47.0 mg amount of $Ru_5(CO)_{15}(\mu_5$-C) was dissolved in 20 mL heptane. An excess amount of phenylacetylene was added while stirring, and the solution was irradiated by medium pressure mercury lamp at 1000 W for 2 h. The solvent was removed in vacuo and the product **6** was then separated by TLC by using a 5:1 hexane–methylene chloride solvent mixture to yield 4.8 mg (8%) of **6**.

2.5. Studies of the catalytic hydrogenation of phenylacetylene

The compounds **1**, **2**, **4**, **5**, **6**, $Pt(PBu^t_3)_2$, $Ru_5(CO)_{15}(\mu_5$-C), and $Ru_6(CO)_{17}(\mu_6$-C) were each studied for their ability to produce the hydrogenation of PhC_2H catalytically. Turnover rates were obtained by measuring the amount of the products formed, styrene and ethylbenzene, by integrating the signals of the proton resonances by ^1H NMR spectroscopy. Typical catalytic runs were performed as follows:

1. 5.3 mg amount of **2** (0.00384 mmol), 2.1 µL of PhC_2H (0.192 mmol, 50 equiv.), were dissolved in 2 mL of d_8-toluene solvent in a stainless steel *Parr* pressure reactor. The reactor was pressurized with 30 psi of H_2, placed in an oil bath maintained at 80 °C, and allowed to stir for 1 h. Analysis by ^1H NMR spectroscopy showed that 40% of the PhC_2H (20 turnovers) was converted to styrene. The resonances in the region of the *t*-butyl groups unambiguously showed the presence of three metal complexes: **5**, **2** and **4** in the relative amounts, 83/9/8, respectively, at the end of the 1-h period of this reaction.
2. Similarly, 5.2 mg of **4** (0.00384 mmol) converted 41% of PhC_2H (0.192 mmol, 50 equiv.) to styrene (20.5 turnovers) in 1 h at 80 °C. ^1H NMR analysis of the solution after the 1-h period showed the presence of **5** and **4** in the ratio of 82/18, respectively.
3. 4.2 mg of $Ru_6(CO)_{17}(\mu_6$-C) (0.00384 mmol) was treated with PhC_2H and hydrogen under the same conditions described above. No styrene or ethylbenzene was detected by ^1H NMR spectroscopy.

2.6. Crystallographic analysis

Dark red crystals of **4** suitable for diffraction analysis were grown by slow evaporation of solvent from a benzene/octane solution at 8 °C. Yellow crystals of **5** suitable for diffraction analysis were grown by slow evaporation of solvent from a diethyl ether solution at −20 °C. Dark red single crystals of **6** suitable for diffraction analysis were grown by slow evaporation of solvent from a dicholoromethane/hexane solution at 8 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The

raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm [10]. Correction for the Lorentz and polarization effects were also applied by SAINT. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS. All three structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, by using the SHELXTL software package [11]. Crystal data, data collection parameters, and results of the analyses for compound **4**–**6** are listed in Table 1.

Compound **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom on the phenylacetylene ligand was located and refined with isotropic displacement parameters. Both hydrido ligands in **4** were located and refined with isotropic displacement parameters. Compound **4** co-crystallized with half a molecule of octane and half a molecule of benzene from the crystallization solvent. The solvent molecules were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and refined as standard riding atoms.

Compounds **5** and **6** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established for both compounds on the basis of the systematic absences observed in the data and confirmed by the successful solution and refinement of the structure. All the nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and refined as standard riding atoms. There was one geometric restraint was used on a hydrogen atom of one of the acetylene ligands in **6**.

3. Results and discussion

The dihydrido-acetylene complex **4** was obtained in 20% yield from the reaction of **2** with hydrogen in a hexane solution in the presence of Me_3NO. Compound **4** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Fig. 1. Like **2**, compound **4** contains a Pt-capped Ru_3 triangle of the Ru_5 cluster, but the Ru_5 cluster is not a square-pyramidal cluster as in **2**. Instead, one of the Ru–Ru bonds in the Ru_5 cluster has been eliminated, Ru(1)–Ru(3) = 3.6574(5) Å in **4** vs. 3.0018(7) Å in **2**. One CO ligand was eliminated in going from **2** to **4** and one equivalent of H_2 was added. The hydrogen was transformed into two hydrido ligands, H(1) and H(2), that bridge the Pt(1)–Ru(1) and Ru(1)–Ru(5) bonds. The resonances of the hydride ligands in the ^1H NMR spectrum are consistent with the solid-state structure, $d = -9.56$ (ddd, 1H, hydride on Pt, $^2J_{P-H} = 1.5$ Hz, $^2J_{H-H} = 4$ Hz, $^3J_{H-H} = 1.5$ Hz, $^1J_{Pt-H} = 641$ Hz), −18.55 (d, hydride on Ru, $^2J_{H-H} = 4$ Hz). Compound **4** contains a PhC_2H ligand that bridges a $PtRu_2$ triangle

Table 1
Crystallographic data for compounds **4–6**

	4	5	6
Empirical formula	$PtRu_5PO_{12}C_{33}H_{35} \cdot \frac{1}{2}C_8H_{18} \cdot \frac{1}{2}C_6H_6$	$PtPOC_{21}H_{33}$	$Ru_5O_{11}C_{36}H_{18}$
Formula weight	1451.19	527.53	1131.85
Crystal system	Triclinic	Monoclinic	Monoclinic
Lattice parameters			
a (Å)	12.3991(9)	10.161(2)	9.9354(10)
b (Å)	12.6807(10)	17.596(4)	20.430(2)
c (Å)	16.5292(12)	12.093(3)	18.048(2)
α(°)	105.157(2)	90	90
β(°)	104.028(2)	92.562(5)	92.862(3)
γ(°)	94.753(2)	90	90
V (Å³)	2403.8(3)	2159.9(9)	3658.9(7)
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
Z value	2	4	4
ρ_{calc} (g/cm³)	2.005	1.622	2.055
μ (Mo Kα) (mm^{-1})	4.517	6.575	2.075
Temperature (K)	296	296	296
$2\Theta_{max}$ (°)	56.6	56.4	50.1
Number of observations ($I > 2\sigma(I)$)	9934	4157	4120
Number of parameters	554	226	481
Goodness-of-fit	1.017	1.032	1.090
Maximum shift in cycle	0.001	0.001	0.001
Residuals:[a] R_1; wR_2	0.0335; 0.0741	0.0359; 0.0927	0.0783; 0.1431
Absorption	SADABS	SADABS	SADABS
Correction (max/min)	1.000/0.698	1.000/0.755	1.000/0.798
Largest peak in final difference map (e$^-$/Å³)	1.523	2.918	1.271

[a] $R = \sum_{hkl}(\|F_{obs}| - |F_{calc}\|)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.
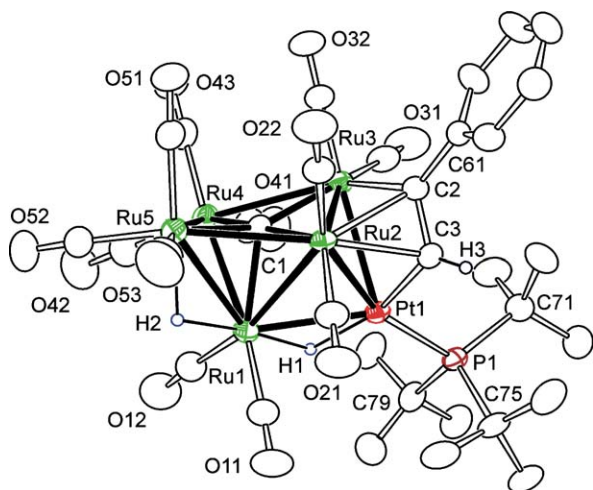

Fig. 1. An ORTEP diagram of $Ru_5(CO)_{12}(\mu_5$-C$)[PtPBu_3^t](\mu_3$-PhC$_2$H)-$(\mu$-H$)_2$ (**4**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) are: Pt(1)–C(3) = 1.991(4), Pt(1)–P(1) = 2.3146(11), Pt(1)–Ru(1) = 2.6793(4), Pt(1)–Ru(2) = 2.7045(4), Pt(1)–Ru(3) = 2.8143(4), 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).

similar to that in **2**. The electron count for compound **4** is 86, which is the number expected for a face-capped square-pyramidal cluster of metal atoms [12]. However, because

Ru(1)–Ru(3) bond in **4** does not exist, it is formally unsaturated by the amount of two electrons. When treated with CO at 1 atm, **4** was converted to **1** by the addition of three CO ligands and the transfer of the two hydrido ligands to the PhC$_2$H ligand which was then eliminated as styrene.

The compound **5** was obtained in 83% yield from the reaction of Pt(PBu$_3^t$)$_2$ with PhC$_2$H under an atmosphere of CO at 25 °C in 15 min. The product was isolated in a crystalline form by cooling solutions in diethylether solvent to −20 °C. Compound **5** is unstable to chromatography on silica gel. Compound **5** was also characterized crystallographically and an ORTEP diagram of its molecular structure is shown in Fig. 2. Compound **5** contains only one metal atom and three ligands, PBu$_3^t$, CO and PhC$_2$H, arranged in a trigonal planar-like structure. The C–C multiple bond of the dihapto PhC$_2$H ligand is parallel to the plane of the molecule. The Pt–C bond lengths, Pt(1)–C(1) = 2.028(6) Å, Pt(1)–C(2) = 2.033(5) Å are typical of platinum coordinated alkynes, as found in structurally related molecules, such as (PPh$_3$)$_2$Pt(PhC$_2$Ph) [13], (PPh$_3$)$_2$Pt(PhC$_2$Me) [14], (Pr$_2^i$PCH$_2$CH$_2$NMe$_2$)Pt(PhC$_2$-Ph) [15], (PPh$_3$)$_2$Pt(HC$_2$CPh$_2$OH) [16]. This C–C bond length, C(1)–C(2) = 1.273(8) Å, has increased as expected, as a result of the coordination. Compound **5** is readily detected in reaction mixtures by the characteristic phosphorus resonance of its PBu$_3^t$ ligand, $\delta = 89.8$ (s, 1P, $^1J_{Pt-P} = 2980$ Hz). In hexane solution, its infrared spectrum in the CO stretching region exhibits two absorptions, 1999 (s) cm^{-1} and 1980 (w) cm^{-1}. This can be explained
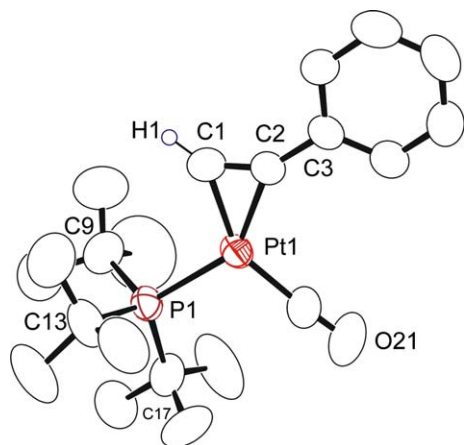
Fig. 2. An ORTEP diagram of Pt(PBu$_3^t$)(PhC$_2$H)(CO) (**5**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) are: Pt(1)–P(1) = 2.3705(13), Pt(1)–C(1) = 2.028(6), Pt(1)–C(2) = 2.033(5), C(1)–C(2) = 1.273(8).

Fig. 3. An ORTEP diagram of Ru$_5$(CO)$_{11}$(μ_4-CCHCPh)(μ_4-HC$_2$Ph)(μ_3-HC$_2$Ph) (**6**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) are: Ru(1)–Ru(2) = 2.7809(14), Ru(1)–Ru(3) = 2.7362(14), Ru(1)–Ru(4) = 3.902(1), Ru(1)–Ru(5) = 2.8183(14), Ru(1)–C(1) = 3.145(12), Ru(1)–C(61) = 2.147(12), Ru(1)–C(62) = 2.179(12), Ru(1)–C(81) = 2.256(13), Ru(1)–C(82) = 2.342(12), Ru(2)–Ru(3) = 2.8892(15), Ru(2)–Ru(5) = 2.7914(13), Ru(2)–C(1) = 2.197(12), Ru(2)–C(71) = 2.189(13), Ru(2)–C(72) = 2.367(11), Ru(2)–C(62) = 2.079(12), Ru(3)–Ru(4) = 2.8315(15), Ru(3)–C(1) = 2.106(12), Ru(3)–C(61) = 2.017(14), Ru(3)–C(81) = 2.185(13), Ru(4)–Ru(5) = 2.8333(15), Ru(4)–C(1) = 2.047(12), Ru(4)–C(81) = 2.258(14), Ru(4)–C(82) = 2.372(13), Ru(5)–C(1) = 2.176(11), Ru(5)–C(72) = 2.109(12), Ru(5)–C(82) = 2.171(12), C(61)–C(62) = 1.385(17), C(71)–C(72) = 1.373(16), C(81)–C(82) = 1.391(17).

by the existence of two isomers; the strong absorption being due to the isomer having Ph group proximate to the CO ligand as found in the structure in the solid state and a second less favorable isomer formed by a 180° rotation of the PhC$_2$H ligand where the Ph group would be proximate to the PBu$_3^t$ ligand.

The tris–PhC$_2$H complex Ru$_5$(CO)$_{11}$(μ_4-CCHCPh)(μ_4-HC$_2$Ph)(μ_3-HC$_2$Ph) (**6**) was obtained in 5% yield from the reaction of **2** with PhC$_2$H when solutions in benzene solvent were heated to reflux for 16 h. It was also obtained in a slightly higher yield (8%) from the reaction of Ru$_5$(CO)$_{15}$(μ_5-C) with PhC$_2$H in the presence of UV–Vis irradiation. It was also obtained in small amounts from the reactions of **2** with PhC$_2$H and hydrogen under the conditions of catalysis, see below. Compound **6** was characterized crystallographically and an ORTEP diagram of its molecular structure is shown in Fig. 3. The compound contains three equivalents of PhC$_2$H. One of these, C(61)–C(62), is a triply bridging PhC$_2$H ligand, while the other, C(81)–C(82), is a quadruply bridging PhC$_2$H ligand. Both exhibit no unusual structural features. The third one has formed a bond to the carbon atom C(1), formerly the carbido ligand in the center of the metal cluster, to form a sort of tetra-metallated allyl ligand, C(1)–C(71) = 1.466 (18)Å, C(71)–C(72) = 1.373(16) Å. The carbon atom C(1) is bonded to four ruthenium atoms: Ru(2)–C(1) = 2.197 (12) Å, Ru(3)–C(1) = 2.106(12) Å, Ru(4)–C(1) = 2.047(12) Å and Ru(5)–C(1) = 2.176(11) Å. The coupling of an alkyne to the carbido ligand of Ru$_5$(CO)$_{15}$(μ_5-C) has not been observed previously although the reaction of the tetraruthenium complex Ru$_4$(CO)$_{12}$(μ_4-C)(μ-H)$_2$ with PhC$_2$Ph yields the complex Ru$_4$(CO)$_{11}$[μ_4-CCPhC(H)-Ph](μ-H) formed by the formation of a C–C bond between the PhC$_2$Ph molecule and the transfer of one of the hydrido ligands to the PhC$_2$Ph molecule, but which step occurred first was not established [17].
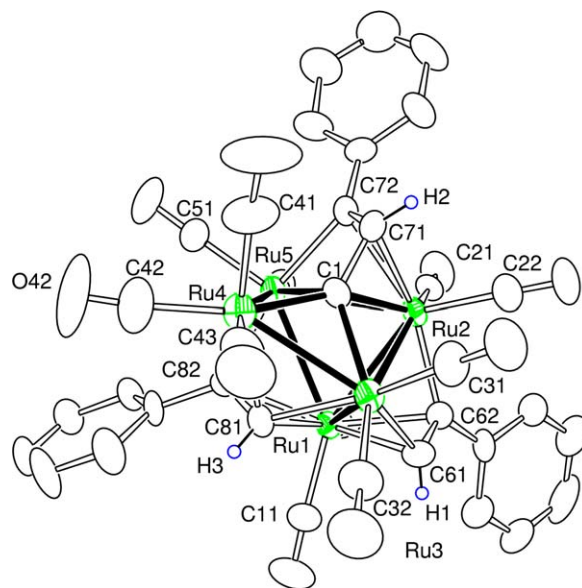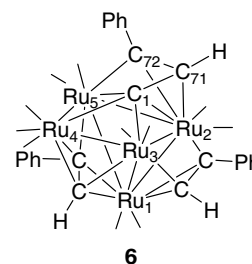

6

The Ru(1)–C(1) distance in **6**, 3.145(12) Å, is too long to have any significant bonding interaction. The Ru$_5$ cluster does not have the usual square-pyramidal structure, because one of the Ru–Ru bonds, Ru(1)–Ru(4) = 3.902(14) Å, has been cleaved. The existing Ru–Ru bonds have normal bond lengths: Ru(1)–Ru(2) = 2.7809(14) Å, Ru(1)–Ru(3) = 2.7362(14) Å, Ru(1)–Ru(5) = 2.8183(14) Å, Ru(2)–Ru(3) = 2.8892(15) Å, Ru(2)–Ru(5) = 2.7914(13) Å, Ru(3)–Ru(4) = 2.8315(15) Å, Ru(4)–Ru(5) = 2.8333(15) Å. The PhC$_2$H group of the μ_4-CCHCPh ligand is σ-bonded to the metal atom Ru(5), and η^2-π bonded to Ru(2), to serve as a 3e$^-$ donor. The carbon atom C(1) of the μ_4-CCHCPh ligand can be viewed as an alkylidyne group which donates 3e$^-$ to the cluster. Hence, the μ_4-CCHCPh ligand serves for-

mally as a 6e$^-$ donor, and the total electron count for the cluster is 76, as expected for a square-pyramidal pentanuclear metal cluster with one missing metal–metal bond [12]. The hydrogen atoms H(1), H(2) and H(3) exhibit low-field resonances in the ^{1}H NMR spectrum: $\delta = 9.05$ (s, 1H, CH, broad), 8.79 (s, 1H, CH, broad), 8.58 (s, 1H, CH,) as expected.

3.1. Studies of the catalytic hydrogenation of PhC$_2$H

When **2** was treated with hydrogen in the presence of a 50-fold excess of PhC$_2$H at 80 °C, styrene was obtained catalytically in 40% yield (20 turnovers) within 1 h. The resonances in the region of the *t*-butyl groups unambiguously showed the presence of three metal complexes at the end of this period. These compounds were **5**, **2** and **4** in the relative amounts: 83%/9%/8%, respectively. In addition, small amounts of compound **6** (<5% yield) could be isolated chromatographically from the reaction solutions. We have been able to synthesize each of the compounds of **4**, **5** and **6** independently, and have thus been able to evaluate independently the catalytic activity of each one, see Table 2. Solutions of each compound showed activity for hydrogenation of phenylacetylene to styrene but the solutions of **5** were considerably more active than the solutions of **4**. Significantly, it was found that the solutions of **4** contained large amounts of **5** after the catalysis was completed. In a typical run the ratio of **5** to **4** was 82/18. Compound **6** was also tested for its ability to produce catalytic hydrogenation of PhC$_2$H. Compound **6** produced styrene from PhC$_2$H at a rate of 11 turnovers/h, but since the catalyst solutions derived from **2** contain only very small amounts of **6**, its activity cannot explain the large amounts of styrene that are formed. No additional discrete ruthenium complexes could be isolated from the catalyst solutions, so in order to investigate the possible activity of carbido ruthenium clusters further we tested the compounds Ru$_6$(CO)$_{17}$-(μ_6-C) and Ru$_5$(CO)$_{15}$(μ_5-C). Ru$_6$(CO)$_{17}$(μ_6-C) exhibited no measurable activity under our conditions. Ru$_5$(CO)$_{15}$(μ_5-C) did show activity, but it had no more than about 19% of the activity of **5**. We also tested Pt(PBu$_3^t$)$_2$ although there was no evidence for the presence of it in the solutions derived from the PtRu$_5$ complexes. Pt(PBu$_3^t$)$_2$ did indeed have the highest activity of all of the precursors that we tested, see Table 2, and it was even more active than **5**. Notably, it appears to be more active toward the hydrogenation of styrene to ethylbenzene than **5**.

Except for Pt(PBu$_3^t$)$_2$ which was not detected in the catalyst solutions derived from the PtRu$_5$ clusters, our studies show that **5** is the most active hydrogenation catalyst of all of the compounds studied. In addition, it is formed from all of the PtRu$_5$ cluster precursors under the catalysis conditions, and it is the dominant species in these solutions. Although there is evidence that styrene can be obtained from **4** (e.g., from the addition of CO to **4**) and **6**, our conclusion is that compound **5** is responsible for the vast majority of styrene by the catalytic hydrogenation of phenylacetylene in these solutions. Details of the mechanism of the activity of this new mononuclear platinum catalyst have not been established at this time. Although styrene can be formed from the Ru$_5$ fragments including species like **6** formed by the fragmentation of these PtRu$_5$ clusters, we cannot quantitatively assess the contributions of the ruthenium fragments to the catalysis other than to say that we feel that it is small compared to that produced by **5**.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 234532, 290610 and 290611 for compounds **4**, **5** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [fax (int. code): +44 1223 336 033, email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

Table 2
Results of the catalytic activity for hydrogenation of PhC$_2$H by various metal complexes[a]

Catalytic precursor	% Conversion	% Styrene	% Ethylbenzene	Temperature and time period
2	42	40	2	80 °C, 1 h
2	15	15	0	80 °C, 30 min
4	42	41	1	80 °C, 1 h
5	100	94	6	80 °C, 1 h
5	1	1	0	60 °C, 2 h, 100 eq.
6	11	11	0	80 °C, 1 h
1	45	43	2	80 °C, 1 h
1	100	45	55	80 °C, 3 h
Ru$_6$(CO)$_{17}$(μ_6-C)	0	0	0	80 °C, 1 h
Ru$_5$(CO)$_{15}$(μ_5-C)	19	17	2	80 °C, 1 h
Pt(PBu$_3^t$)$_2$	100	50	50	80 °C, 1 h
Pd(PBu$_3^t$)$_2$	100	41	59	80 °C, 30 min, 1 atm
Control (no cat.)	0	0	0	80 °C, 1 h

[a] Conditions: 2.0 mL toluene-d_8 solvent, 50 eq. PhC$_2$H, 30 psi hydrogen, values are average of at least two consistent runs.

Acknowledgment

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