Does a Metal to Metal "Ligand" Effect Influence the Catalytic Activity of Bimetallic Cluster Complexes? Synthesis and Catalytic Activity of $Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$

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The layer-segregated platinum−ruthenium cluster complex $Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**2**) has been obtained in 51% yield from the reaction of $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**1**) with SMe_2. Compound **2** is structurally analogous to **1** but contains a Me_2S ligand coordinated to one of the ruthenium atoms of the Ru_3 triangle that contains a bridging PhC_2Ph ligand. EXSYS 2D ^1H NMR measurements have shown that the Me_2S ligand is labile and readily exchanges with free Me_2S in solution. Fresh solutions of compound **2** rapidly hydrogenate PhC_2Ph to (*Z*)-stilbene at a turnover frequency TOF of 102 h^{-1}, but the activity is quickly reduced to the level of **1** because **2** is converted to **1** under the conditions of the catalysis. It is proposed that the high catalytic activity of **2** compared to **1** is related to lability of the Me_2S ligand, thus implying that this site on the PhC_2Ph-bridged Ru_3 triangle is catalytically active. It is proposed that all catalytic transformations occur at the ruthenium triangle(s). It is suggested that the enhanced catalytic activity of these bimetallic cluster complexes is due in part to the presence of the platinum layer. The promotional effect may be due to a simple donation of electron density from the platinum to the ruthenium, a metal to metal "ligand" effect.

Introduction

Mixed-metal heterogeneous catalysts have attracted much attention because of their superior properties.[1,2] Synergism between the metal atoms is believed to be responsible for the improved activity of these catalysts. This synergism is believed to assume a variety of forms, although the mechanisms of synergism are generally poorly understood at the atomic and molecular level. For certain mixed-metal catalysts it is believed that the presence of different types of metals in the proximity of an active site can lead to higher catalytic activity.[1k,2,3]

It is possible that studies of the catalytic properties of mixed-metal cluster complexes in solution may provide evidence to develop a deeper understanding of some forms of this metal to metal synergism. However, there have been only a few reports where superior catalytic properties for well-defined polynuclear mixed-metal cluster complexes have been documented.[4−9]

In recent studies we have prepared a number of novel layer-segregated high-nuclearity platinum−ruthenium and platinum−osmium metal carbonyl cluster complexes which have well-defined arrangements of the metal atoms.[10,11 10−11] A diphenylacetylene complex of one of these clusters, $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**1**), has been shown to exhibit an unusually high

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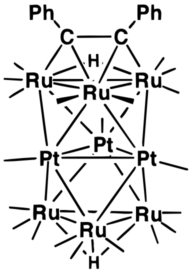

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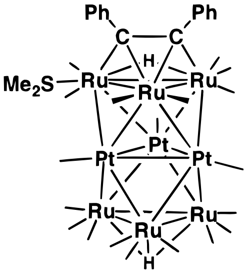

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activity for catalytic hydrogenation of PhC_2Ph to (*Z*)-stilbene[4] and also for the catalytic hydrosilylation of diphenylacetylene to (*E*)-(1,2-diphenylethenyl)triethylsilane.[5] It is believed that a form of synergism between the platinum and ruthenium atoms of **1** leads to this anomalously high catalytic activity, but the details concerning the mechanism for this synergism were not established.

We have now prepared a Me_2S derivative of **1**, $Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**2**) and have found that it has a even higher activity for catalytic hydrogenation of diphenylacetylene to (*Z*)-stilbene than does **1**. Unfortunately, its lifetime is short, but we believe nevertheless that its high activity is a result of lability of the Me_2S ligand; this provides key information about the structural disposition of the catalytically active sites on this mixed-metal complex. Details of this study are provided in this report.

Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Reagent-grade solvents were dried and deoxygenated prior to use. The compound $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**1**) was synthesized as described previously.[11] Diphenylacetylene was purchased from Aldrich and purified by column chromatography. Me_2S was purchased from Aldrich and used as received. Hydrogen (National Welders Supply Co.) and carbon monoxide (SUNOX, Inc.) were used without further purification. IR spectra were recorded on a Nicolet 5XDB FT-IR spectrophotometer. Elemental analysis was performed by Desert Analytics, Tucson, AZ. Chromatographic separations were performed in air on Analtech 0.25 mm silica gel 60 Å F_{254} plates. GC analyses were made using a Perkin-Elmer Sigma 300 chromatograph with a flame ionization detector and an EconoCap SE-30 column (Alltech 2096-14, 0.25 mm, 30 m). Calibrations were made using standardized samples. Reaction rates were obtained by measuring the formation of (*Z*)-stilbene as a function of time. Plots of the kinetic data were prepared using Cricket Graph version 1.3 by Cricket Software on a Macintosh LCIII personal computer.

Preparation of $Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (2). A 13.0 mg amount of **1** (0.006 73 mmol) was dissolved in 15 mL of dichloromethane. A 7.5 μL amount of Me_2S (0.101 mmol) was added to the reaction solution via syringe. The solution was stirred at room temperature for 21 h. The solvent was removed in vacuo and the residue separated by TLC using a hexane/CH_2Cl_2 (2/1) mixture. This yielded, in order of elution, 2.6 mg of unreacted **1** and 6.8 mg of dark brown $Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**2**; 51%). Data for **2**: IR (ν(CO), cm^{-1}, in hexane) 2090 (m), 2057 (vs), 2046 (sh), 2029 (m), 2010 (w), 1996 (w), 1951 (w); ^1H NMR (δ in CD_2Cl_2 at −73 °C) 7.2−7.0 (m, 10H, Ph), 2.27 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), −17.56 (s, 1H). −18.00 (s, 1H). Anal. Calcd (found): C, 21.38 (21.04); H, 0.92 (1.03).

2-D EXSYS Me_2S Ligand Exchange Experiment. A 9.3 mg amount of **2** was dissolved in 0.8 mL of toluene-d_8 in a clean, dry NMR tube and sealed with a septum. A 20 μL amount of Me_2S was dissolved in 1 mL of $CDCl_3$ in a 10 mL round-bottom flask. A 17 μL volume (1 equiv) of the Me_2S solution was added to the sealed NMR tube via syringe. The two-dimensional ^1H EXSYS spectrum was obtained on a Varian Mercury 400 spectrometer at 60 °C using the following parameters: spectrometer frequency 400 MHz, mixing time 100 ms, sweep width 3000 Hz with 2K data points in each dimension, acquisition time 0.331 s with 16 scans per loop and 512 loops.

Reaction of 2 with CO. A 4.5 mg amount of **2** was dissolved in 10 mL of dichloromethane in a three-necked flask. CO (1 atm) was slowly purged through the solution for 1 h. An IR spectrum of the solution at this time showed quantitative conversion to **1**. The solvent was removed, and the residue was separated by TLC using a hexane/dichloromethane (2/1) solvent mixture, yielding 3.1 mg (70%) of **1**. The less than quantitative isolation can be attributed to mechanical loss and partial decomposition in air.

General Procedures for the Hydrogenation Studies. All catalytic studies were conducted in a solvent mixture of CH_2Cl_2 and hexane in a 3/49 v/v ratio.[4] The appropriate amount of catalyst, PhC_2Ph, and a stirbar were placed in a three-necked flask (50 mL) with one neck connected to a vacuum line and nitrogen inlet through a stopcock; another was connected to a water-cooled condenser, and the third was closed with a rubber septum. The system was evacuated and filled with nitrogen five times. The appropriate amount of CH_2Cl_2 was placed in the flask via syringe and stirred at room temperature for 10 min to dissolve the catalyst completely. Then the appropriate amount of hexane was introduced via syringe, and the system was purged with hydrogen at room temperature for 5 min. The flask was then immersed in a thermostated bath at 323 K, and hydrogen was purged slowly through the solution. After the reaction was stopped, the solvent was removed under reduced pressure, and the residue was separated by TLC. The reaction rates per hour were determined by measuring the amount of *Z*-stilbene formed after a period of 1 h, as established by separation of the components from an aliquot of the reaction solution by gas chromatography.

Catalytic Hydrogenation of PhC_2Ph by 2 at a 300/1, PhC_2Ph/2 Ratio. A 138.5 mg amount (0.777 mmol) of PhC_2Ph and 5.1 mg (0.002 59 mmol) of **2** were dissolved in a mixture of 1.5 mL of CH_2Cl_2 and 24.5 mL of hexane. The reaction conditions were as previously described. The formation of (*Z*)-stilbene was followed by GC at 20 min intervals for 2 h. After 1 h, 34% of the PhC_2Ph was converted to (*Z*)-stilbene, corresponding to a TOF of 102 h^{-1} for the formation of (*Z*)-stilbene. After 2 h, the reaction was terminated. GC showed that 50% of the PhC_2Ph was converted to (*Z*)-stilbene and 2.5% to (*E*)-stilbene. The solvent was removed in vacuo, and the residue was separated by TLC using a hexane/CH_2Cl_2 (3/1) solvent mixture. This yielded 1.7 mg of **1**, 0.4 mg of $Ru_6Pt_3(CO)_{15}(\mu_3\text{-}PhC_2Ph)_3(\mu\text{-}H)_6$,[4] 0.9 mg of $Ru_6Pt_3(CO)_{18}(\mu_3\text{-}\eta^6\text{-}PhC_2H_4Ph)(\mu_3\text{-}H)_4$,[4] and 0.5 mg of $Ru_6Pt_3(CO)_{18}(\eta^6\text{-}PhCH_2CH_2Ph)(\mu_3\text{-}H)_4$.[4] A second run using 5.1 mg of **2** conducted under identical conditions was terminated after 20 min. A GC analysis of this reaction mixture showed that 20% (60 turnovers) of the PhC_2Ph was already converted to (*Z*)-stilbene. An IR spectrum of the reaction solution showed that the compound **2** was already completely transformed. Separation of the inorganic residues by TLC subsequently yielded 2.6 mg of **1**, 1.0 mg of $Ru_6Pt_3(CO)_{15}(\mu_3\text{-}PhC_2Ph)_3(\mu\text{-}H)_6$,[4] and 1.1 mg of a mixture of $Ru_6Pt_3(CO)_{18}(\mu_3\text{-}\eta^6\text{-}PhC_2H_4Ph)(\mu_3\text{-}H)_4$[4] and $Ru_6Pt_3(CO)_{18}(\eta^6\text{-}PhCH_2CH_2Ph)(\mu_3\text{-}H)_4$.[4]

Catalytic Hydrogenation of PhC_2Ph by 1 at a 300/1 Ratio. A 138.5 mg amount (0.777 mmol) of PhC_2Ph and 5.0 mg (0.002 59 mmol) of **1** were dissolved in a mixture of 1.5

Table 1. Crystallographic Data for Compound 2

formula	$Pt_3Ru_6SO_{19}C_{35}H_{18}$
fw	1966.27
cryst syst	triclinic
lattice params	
a (Å)	12.219(2)
b (Å)	19.274(3)
c (Å)	10.749(2)
α (deg)	105.74(2)
β (deg)	111.36(1)
γ (deg)	88.71(1)
V (Å^3)	2261.1(8)
space group	$P\bar{1}$ (No. 2)
Z	2
ρ_{calc} (g/cm^3)	2.89
μ(Mo Kα) (cm^{-1})	112.68
temp (°C)	20
2Θ$_{max}$ (deg)	44
no. of obsd rflns ($I > 3\sigma$)	4509
no. of variables	578
goodness of fit (GOF)	1.89
max shift in final cycle	0.00
residuals:[a] R; R_w	0.037; 0.044
abs cor	DIFABS
transmissn coeff, max/min	1.00/0.82
largest peak in final diff map (e/Å^3)	2.15

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

mL of CH_2Cl_2 and 24.5 mL of hexane. The reaction conditions were as previously described. The formation of (*Z*)-stilbene was followed by GC at 20 min intervals for 2 h. After 1 h, 21% of the PhC_2Ph was converted to (*Z*)-stilbene, corresponding to a TOF of 63 h^{-1} for the formation of (*Z*)-stilbene. After 2 h, the reaction was terminated. GC showed that 36% of the PhC_2Ph was converted to (*Z*)-stilbene and 2% to (*E*)-stilbene. The solvent was removed in vacuo, and the residue was separated by TLC using a hexane/CH_2Cl_2 (3/1) solvent mixture. This yielded 2.3 mg of **1**, 0.7 mg of $Ru_6Pt_3(CO)_{15}(\mu_3\text{-}PhC_2Ph)_3(\mu\text{-}H)_6$,[4] 0.7 mg of $Ru_6Pt_3(CO)_{18}(\mu_3\text{-}\eta^6\text{-}PhC_2H_4Ph)(\mu_3\text{-}H)_4$,[4] and 0.7 mg of $Ru_6Pt_3(CO)_{18}(\eta^6\text{-}PhCH_2CH_2Ph)(\mu_3\text{-}H)_4$.[4]

Crystallographic Analysis. Crystals of **2** suitable for X-ray diffraction analysis were grown from a solution in a dichloromethane/hexane (1/1) solvent mixture by slow evaporation of the solvent at 25 °C. The crystal used in intensity measurements was mounted in a thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo Kα radiation. The unit cell was determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analysis are listed in Table 1. All data processing was performed on a Silicon Graphic Indigo^2 computer using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz–polarization (Lp) and absorption corrections were applied to the data. Neutral-atom scattering factors were calculated by the standard procedures.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. Compound **2** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the two hydride ligands were obtained in difference Fourier syntheses. They were partially refined and then fixed in the final cycles of refinement. The hydrogen atoms on the Me_2S ligand and the phenyl rings of the PhC_2Ph ligand were calculated by assuming idealized geometry with C–H distances at 0.95 Å. Their scattering contributions were added to the structure factor calculations, but their positions were not refined.

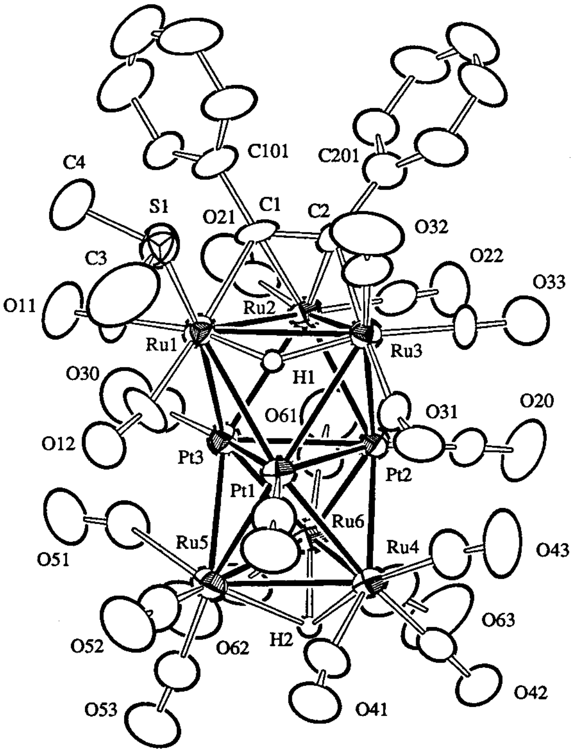

Figure 1. ORTEP diagram of $Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**2**) showing 40% probability thermal ellipsoids.

Results and Discussion

The compound $Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**2**) was obtained in 51% yield from the reaction of **1** with Me_2S at room temperature. Compound **2** was characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analysis. An ORTEP diagram of its molecular structure is shown in Figure 1. Selected bond distances and angles are given in Tables 2 and 3. Like its parent **1**, this complex contains a layered structure of Pt_3 and Ru_3 triangles in a staggered conformation.[11] There is a triply bridging PhC_2Ph ligand coordinated to one of the triruthenium triangles, Ru(1)–Ru(2)–Ru(3), in the parallel coordination mode similar to that found in **1** and commonly observed for triply bridging alkyne ligands at trimetallic centers.[13] Compound **2** contains a Me_2S ligand bonded to one of the ruthenium atoms of the Ru_3 triangle that contains the alkyne ligand. The ruthenium–sulfur distance (Ru(1)–S = 2.409(6) Å) is similar to those found in other ruthenium cluster complexes containing a σ-bound thioether ligand, such as $Ru_3(CO)_7(\mu\text{-}CO)_2((1,1,1\text{-}\eta)\text{-}1,4,7\text{-}$trithiacyclo-

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Table 2. Selected Intramolecular Bond Distances for 2[a]

Pt(1)−Pt(2)	2.6301(8)	Ru(1)−H(1)	1.75
Pt(1)−Pt(3)	2.6349(8)	Ru(2)−H(3)	2.829(2)
Pt(1)−Ru(1)	2.958(1)	Ru(2)−C(1)	2.13(1)
Pt(1)−Ru(3)	2.959(1)	Ru(2)−C(2)	2.11(1)
Pt(1)−Ru(4)	2.754(1)	Ru(3)−C(2)	2.16(1)
Pt(1)−Ru(5)	2.753(1)	Ru(3)−H(1)	1.58
Pt(2)−Pt(3)	2.7097(8)	Ru(4)−Ru(5)	2.868(2)
Pt(2)−Ru(2)	2.712(1)	Ru(4)−Ru(6)	3.066(2)
Pt(2)−Ru(3)	2.991(1)	Ru(4)−H(2)	2.11
Pt(2)−Ru(4)	2.716(1)	Ru(5)−Ru(6)	3.063(2)
Pt(2)−Ru(6)	2.688(1)	Ru(5)−H(2)	2.12
Pt(3)−Ru(1)	2.895(1)	Ru(6)−H(2)	1.86
Pt(3)−Ru(2)	2.717(1)	S(1)−C(3)	1.81(2)
Pt(3)−Ru(5)	2.844(1)	S(1)−C(4)	1.79(2)
Pt(3)−Ru(6)	2.695(1)	O−C (av)	1.14(2)
Ru(1)−Ru(2)	2.781(2)	C(1)−C(2)	1.40(2)
Ru(1)−Ru(3)	3.014(2)	Pt(1)−C(12)	2.71(1)
Ru(1)−S(1)	2.413(4)	Pt(1)−C(31)	2.78(1)
Ru(1)−C(1)	2.18(1)	Pt(3)−C(51)	2.37(1)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Selected Intramolecular Bond Angles for 2[a]

Pt(2)−Pt(1)−Pt(3)	61.95(2)	Pt(3)−Ru(1)−S(1)	171.4(1)
Pt(2)−Pt(1)−Ru(3)	64.40(3)	Ru(2)−Ru(1)−Ru(3)	58.29(4)
Pt(2)−Pt(1)−Ru(4)	60.54(3)	Pt(2)−Ru(2)−Pt(3)	59.89(3)
Pt(3)−Pt(1)−Ru(1)	62.02(3)	Pt(2)−Ru(2)−Ru(3)	65.31(4)
Pt(3)−Pt(1)−Ru(5)	63.66(3)	Pt(3)−Ru(2)−Ru(1)	63.54(4)
Ru(1)−Pt(1)−Ru(3)	61.24(3)	Ru(1)−Ru(2)−Ru(3)	64.98(4)
Ru(4)−Pt(1)−Ru(5)	62.77(4)	Pt(1)−Ru(3)−Pt(2)	52.46(2)
Pt(1)−Pt(2)−Pt(3)	59.11(2)	Pt(1)−Ru(3)−Ru(1)	59.36(3)
Pt(1)−Pt(2)−Ru(3)	63.15(3)	Pt(2)−Ru(3)−Ru(2)	55.46(3)
Pt(1)−Pt(2)−Ru(4)	61.99(3)	Ru(1)−Ru(3)−Ru(2)	56.73(4)
Pt(3)−Pt(2)−Ru(2)	60.14(3)	Pt(1)−Ru(4)−Pt(2)	57.47(3)
Pt(3)−Pt(2)−Ru(6)	59.92(3)	Pt(1)−Ru(4)−Ru(5)	58.60(4)
Ru(2)−Pt(2)−Ru(3)	59.24(3)	Pt(2)−Ru(4)−Ru(6)	54.99(3)
Ru(4)−Pt(2)−Ru(6)	69.13(4)	Ru(5)−Ru(4)−Ru(6)	62.04(4)
Pt(1)−Pt(3)−Pt(2)	58.94(2)	Pt(1)−Ru(5)−Ru(3)	56.14(3)
Pt(1)−Pt(3)−Ru(1)	64.48(3)	Pt(1)−Ru(5)−Ru(4)	58.63(4)
Pt(1)−Pt(3)−Ru(5)	60.20(3)	Pt(3)−Ru(5)−Ru(6)	54.15(3)
Pt(2)−Pt(3)−Ru(2)	59.97(3)	Pt(3)−Ru(5)−C(51)	55.6(5)
Pt(2)−Pt(3)−Ru(6)	59.63(3)	Ru(4)−Ru(5)−Ru(6)	62.15(4)
Ru(1)−Pt(3)−Ru(2)	59.31(3)	Pt(2)−Ru(6)−Pt(3)	60.45(3)
Ru(5)−Pt(3)−Ru(6)	67.08(4)	Pt(2)−Ru(6)−Ru(4)	55.88(3)
Pt(1)−Ru(1)−Pt(3)	53.50(3)	Pt(3)−Ru(6)−Ru(5)	58.77(4)
Pt(1)−Ru(1)−Ru(3)	59.41(3)	Ru(4)−Ru(6)−Ru(5)	55.81(4)
Pt(1)−Ru(1)−C(12)	63.2(5)	Pt−C−O (av)	176(1)
Pt(3)−Ru(1)−Ru(2)	57.16(3)	Ru(1)−C(12)−O(12)	167(1)
Pt(3)−Ru(1)−Ru(3)	88.41(4)	Ru(3)−C(31)−O(31)	165(1)
Ru(5)−C(51)−O(51	155(1)		
Ru−C−O (av)	174(2)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

nonane)[14a] Ru−S$_{av}$ = 2.401(2) Å), Ru$_3$(CO)$_9$(μ-H)(μ_3-η^3-(*C*,*S*,*S*)-1,3-dithiacyclohexane)[14b] (Ru−S$_{av}$ = 2.408(5) Å), Ru$_3$(CO)$_9$(μ_3-η^3-1,3,5-dithiacyclohexane)[14b] (Ru−S$_{av}$ = 2.423(3) Å), Ru$_4$(CO)$_{10}$(μ-H)$_4$(μ_2-η^3-1,3,5-dithiacyclohexane)[14c] (Ru−S$_{av}$ = 2.417(4) Å), Ru$_4$(CO)$_{10}$(μ-H)$_2$(μ_3-η^3-1,3,5-dithiacyclohexane)[14c] (Ru−S$_{av}$ = 2.389(4) Å). There is one edge-bridging hydride ligand on the PhC$_2$Ph-bridged Ru$_3$ triangle and one triply bridging hydride on the other Ru$_3$ triangle. The hydride ligands in **1** occupy similar positions. As expected, the hydride-associated ruthenium−ruthenium distances (Ru(1)−Ru(3) = 3.013(2) Å, Ru(4)−Ru(5) = 2.868(2) Å, Ru(4)−Ru(6) = 3.067(2) Å, Ru(5)−Ru(6) = 3.062(2) Å) are significantly longer than the others due to the presence of the well-known hydride elongation effect.[15] Compound **2** contains 19 carbonyl ligands, distributed as as shown in the figure. Each platinum atom has one CO ligand and each ruthenium atom has three, except for Ru(1), which contains two carbonyls and the Me$_2$S ligand. One of the carbonyl ligands has adopted a semibridging coordination mode from Ru(5) toward Pt(3) (Pt(3)−C(51) = 2.35(2) Å, Ru(5)−C(51)-O(51) = 152(2)°). Two other carbonyl ligands exhibit weak semibridging coordination: one between Ru(1) and Pt(1) (Pt(1)−C(12) = 2.69(1) Å, Ru(1)−C(12)−O(12) = 166(2)°) and one between Ru(3) and Pt(1) (Pt(1)−C(31) = 2.78(1) Å, Ru(3)−C(31)−O(31) = 164(2)°). There are a total of 124 cluster valence electrons, exactly the number predicted by the polyhedral skeletal electron pair theory for a face-shared bioctahedral structure.[16]

The ^{1}H NMR spectrum of **2** at 25 °C shows two broad singlets for the hydride ligands at δ −17.38, −17.89 ppm and a very broad single resonance at δ 1.94 ppm for the methyl groups of the Me$_2$S ligand. According to the solid-state structure, the methyl groups on the Me$_2$S ligand are diastereotopic, and at −73 °C the methyl resonances are observed as two sharp singlets at δ 2.27 and 1.38 ppm. This is indicative of a dynamic averaging process which could occur by a simple inversion of configuration of the pyramidal sulfur atom. Similar inversions of configuration for thioether ligands have been reported previously.[17] Separate resonances are observed for the free and coordinated Me$_2$S in solutions containing a mixture of Me$_2$S and **2**. This indicates that the averaging of the methyl resonances for the Me$_2$S ligand in **2** occurs without dissociation. At −73 °C, the resonances of the hydride ligands have also sharpened considerably and appear at δ −17.56 and −18.00 ppm. It is likely that the broadness of the hydride resonances at room temperature is also due to a dynamic averaging of these ligands. The hydride ligands in **1** undergo rapid dynamic averaging on the NMR time scale at room temperature.[11]

We have obtained evidence for exchange of the Me$_2$S ligand in **2** with the free Me$_2$S in solution by a 2D EXSYS ^{1}H NMR experiment. Strong magnetization transfer peaks were observed between the methyl resonances of the free Me$_2$S and the Me$_2$S ligand in **2** at 60 °C using a mixing time of 100 ms (see Figure 2). This magnetization transfer indicates that there is a facile intermolecular exchange between the free Me$_2$S and the Me$_2$S ligand in **2,** although this process is occurring more slowly than the intramolecular averaging of the Me$_2$S methyl resonances of **2** described above. Compound **2** is readily converted back to **1** by reaction with CO at room temperature in 70% isolated yield.

Solutions of **2** were found to catalyze the hydrogenation of PhC$_2$Ph to (*Z*)-stilbene at 50 °C. At a PhC$_2$Ph/**2** ratio of 300/1, 102 equiv of (*Z*)-stilbene was formed in the first 1 h at 50 °C. For comparison the reaction was performed similarly using **1** as the catalyst, but in this

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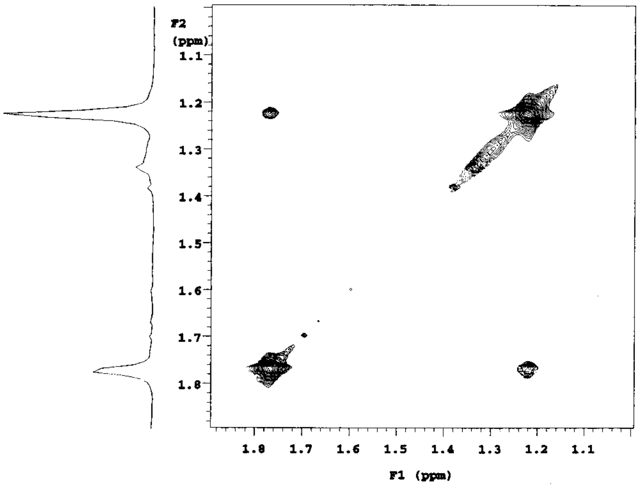

Figure 2. 2D-EXSYS ^1H NMR spectrum of the methyl resonances of a solution of **2** and free Me_2S in toluene-d_8 at 60 °C. The mixing time was 100 ms.

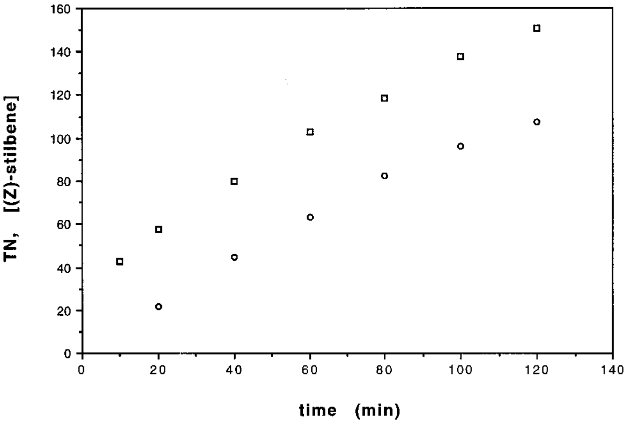

Figure 3. Plot of the formation of (*Z*)-stilbene in turnovers (TN) from the hydrogenation of PhC_2Ph by **1** (○) and **2** (□) as a function of time.

case only 63 equiv of (*Z*)-stilbene was formed.[4] Within the first 20 min of reaction the amount of (*Z*)-stilbene produced by the solutions of **2** is nearly 3 times that of equivalent solutions of **1.** Figure 3 shows a plot of the formation of (*Z*)-stilbene as a function of time for both catalysts. The formation of the larger quantities of (*Z*)-stilbene by **2** is clearly evident. However, it is also seen that after the first 20 min the rate of production of (*Z*)-stilbene for the solutions of **2** is no greater than that for the solutions of **1**. This can be explained by the observation that compound **2** is quickly transformed into other complexes under the conditions of catalysis. For example, even after only 20 min of reaction time all of the **2** has been transformed. The following complexes were recovered from the solution: 2.6 mg of **1**, 1.0 mg of $Ru_6Pt_3(CO)_{15}(\mu_3\text{-}PhC_2Ph)_3(\mu\text{-}H)_6$ (**3**),[4] and 1.1 mg of a mixture of $Ru_6Pt_3(CO)_{18}(\mu_3\text{-}\eta^6\text{-}PhC_2H_4Ph)(\mu_3\text{-}H)_4$ (**4**)[4] and $Ru_6Pt_3(CO)_{18}(\eta^6\text{-}PhCH_2CH_2Ph)(\mu_3\text{-}H)_4$ (**5**).[4] Compounds **3**−**5** are also formed in the catalytic hydrogenation of PhC_2Ph by **1**.[4] These compounds were characterized previously and shown to be poor hydrogenation catalysts. Compound **1** is a good catalyst and is the major component of the solutions of **2**, which explains why the activity of these solutions is so similar to **1** as the catalysis progresses. The CO needed for the formation of **1** from **2** could be obtained in part from the formation of compounds **3**−**5**, in which CO is released. Because of the rapid degradation of **2**, analysis of the kinetics of its catalysis was not possible. Nevertheless, we do feel that some important conclusions can be surmised about the catalytic activity of this family of compounds and about **2** in particular.

It is fairly certain that the alkyne is activated and hydrogenated at one of the Ru_3 triangles. This is established from the crystallographic studies of both **1** and **2**, which show that the alkyne is a triply bridging ligand on one of the Ru_3 triangles, and by the reaction of **1** with CO, which yielded the compound $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}Ph(H)C_2Ph)(\mu\text{-}H)$ (**6**), which contains a partially hydrogenated alkyne ligand coordinated to an edge of one of the Ru_3 triangles.[11] The important remaining question is as follows: which of the nine metal atoms serves as the site for hydrogen activation? Previously, we speculated that this might be one of the platinum atoms.[4] Our studies of **1** showed a first-order inhibition by CO which was interpreted in terms of a mechanism involving a CO dissociation step to generate a "vacant" coordination site for use in the hydrogen activation step. The higher activity of **2** could be an indication that the generation of the vacant coordination site is a more facile process for **2** than for **1**. The lability of the Me_2S ligand, as determined by the 2D EXSYS measurement, is consistent with this notion and could also be a strong indicator of the location of that vacant site, namely the ruthenium atom that contains the Me_2S ligand. A similar mechanism may also be operative for the catalysis observed by **1**. If ruthenium is the location of the vacant site, then it is probably also the site where the hydrogen activation occurs. A number of triruthenium cluster complexes,[18] for example $Ru_3(CO)_9(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)_2$,[18a] have been shown to perform homogeneous hydrogenation of alkenes and alkynes; therefore, there is ample precedent for the ability of ruthenium cluster complexes to activate hydrogen in the absence of platinum.

A possible catalytic cycle for hydrogenation by **2**, shown in Scheme 1, is an update of the one we proposed previously.[4] This scheme is very similar to the one proposed earlier, except that the vacant site and hydrogen activation site (step a) are now on one of the ruthenium atoms that contains the PhC_2Ph ligand. Note that a similar process was proposed to account for our recent investigations of the catalytic hydrosilylation of PhC_2Ph by **1**.[5] The remainder of the transformations shown in Scheme 1 are identical with those proposed previously for the catalysis by **1**, but we want to

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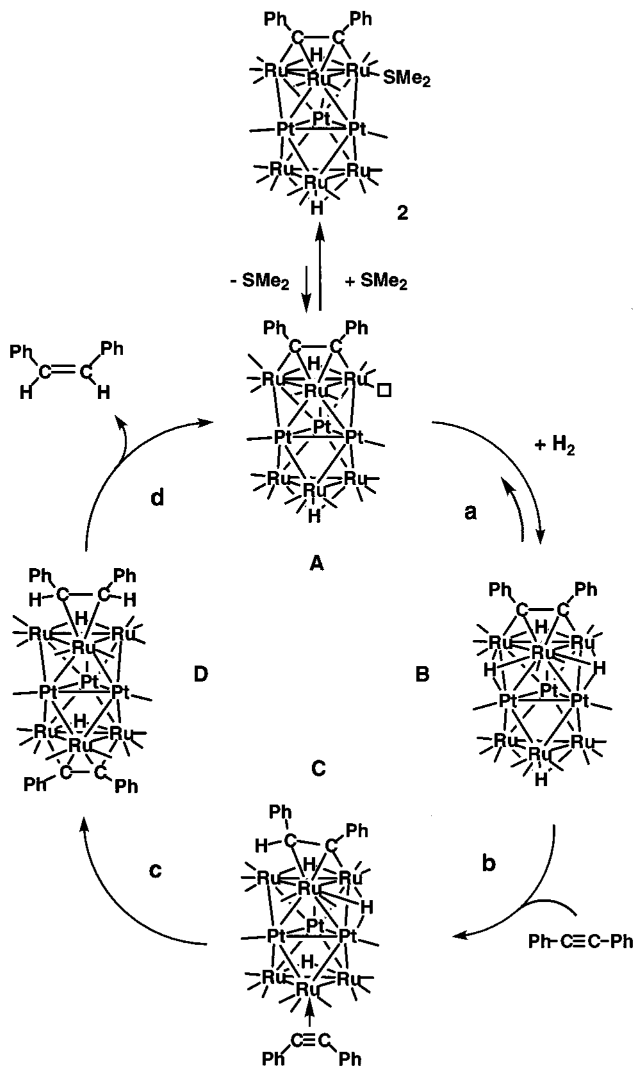
Scheme 1



emphasize that the PhC_2Ph addition (step b) could occur at the same ruthenium triangle that contains the PhC_2Ph ligand.

An important question which has not yet been definitively answered by our series of studies of the catalysis by the layer segregated platinum–ruthenium cluster complexes is “What is the role of the platinum, if any?”. Clearly, these clusters do exhibit higher activity than the pure ruthenium clusters.[18] It seems likely that the platinum is contributing to the enhancement of the activity, but the mechanism for this may be more subtle and indirect than we previously suspected.[4] One way by which the platinum could influence the ruthenium could be viewed as a simple donation of electron density from the platinum triangle to the ruthenium triangle, or even the reverse of this process. A similar concept, known as the “ligand” effect, has been proposed to explain modifications in the activity of certain bimetallic heterogeneous catalysts where, for example, an inactive metal donates electron density (as a ligand would donate to a metal) to a catalytically active metal.[1n,o] This mechanism might be relatively small and minor in the chemistry of the extended surfaces of heterogeneous catalysts,[1h] but it might have a much larger influence on the chemistry of small bimetallic cluster complexes. Recent studies have indicated that thin layers of palladium or platinum on metallic supports transfer electron density from the palladium or platinum layers to the metal supports.[19] In the present case, the electron density donation from platinum to ruthenium might stabilize the unsaturated intermediate **A** shown in Scheme 1. This could result in a greater population of **A** in solutions and in turn a higher catalytic activity.

Recent studies of phosphido-bridged heterobimetallic carbonyl complexes have shown that the formation of a metal–metal bond can promote ligand substitution reactions.[20] This occurs through the mechanism of donation of electron density from one metal to the other, which in turn can lead to the formation of semibridging carbonyl ligands. When the semibridging CO ligands are present, CO ligand substitutions occur more readily than in the presence of terminal CO ligands only.[20] Interestingly, compound **2** contains three semibridging carbonyl ligands. Further studies will be needed to clarify the details and validity of this hypothesis.

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Supporting Information Available: Tables giving final positional parameters and *B*(eq) values, intramolecular distances and angles, and anisotropic thermal parameters for **2** (17 pages). Ordering information is given on any current masthead page.

OM980208H

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