Catalytic Hydrosilylation of Diarylalkynes by Layer-Segregated Platinum−Ruthenium Cluster Complexes $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}RC_2R)(\mu_3\text{-}H)(\mu\text{-}H)$

Richard D. Adams* and Thomas S. Barnard

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received February 19, 1998

It has been found that the layer-segregated platinum−ruthenium cluster complex $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$, **2a**, is an effective catalyst for the hydrosilylation of diphenylacetylene by triethylsilane to yield (*E*)-[(1,2-diphenyl)ethenyl]triethylsilane at a turnover frequency, TOF (TON/h), of 29 h^{-1}. The activation parameters, $\Delta H^{\ddagger} = 17(2)$ kcal/mol and $\Delta S^{\ddagger} = -18(5)$ eu, were established. Small amounts of *cis*-stilbene were also formed. A kinetic analysis showed the reaction is first order in cluster and silane concentrations but zero order in alkyne concentration. The reaction is strongly inhibited by CO but is unaffected by mercury. A mechanism involving CO dissociation, silane oxidative addition, alkyne addition, a Si−C bond-forming step, and silylolefin dissociation is proposed with all transformations occurring at a ruthenium triangle. $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}TolC_2Tol)(\mu_3\text{-}H)(\mu\text{-}H)$, **2b**, was also found to be an effective catalyst for the hydrosilylation of $TolC_2Tol$ to (*E*)-Tol-(H)C_2(SiEt$_3$)Tol, TOF of 32 h^{-1}. $Ru_3(CO)_9(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)_2$ and $PtRu_2(CO)_8(\mu_3\text{-}PhC_2Ph)$-(dppe) are relatively poor catalysts, TOF = 3.9 and 2.3 h^{-1}, respectively. $[NBu_4][Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)]$, **3**, formed by deprotonation of **2a**, also exhibits good catalytic activity, but its catalysis is inhibited by mercury, which may be indicative of heterogeneous catalysis.

Introduction

Mixed-metal heterogeneous catalysts have attracted much attention because of their superior properties.[1] Mixed-metal cluster complexes have been shown to be good precursors to supported mixed-metal catalysts.[2] It is believed that the presence of different types of metals in the proximity of a catalytically active site can lead to a higher activity in certain cases.[3] This phenomenon is loosely defined as synergism.[3,4] Synergism may assume a variety of forms, but there are very few cases where the mechanisms of synergism are understood at the atomic and molecular level. It has been assumed that the studies of the catalytic properties of mixed-metal cluster complexes in solution may provide opportunities to characterize fully some forms of this mixed-metal synergism. However, there have been only a few reports where superior catalytic properties have been attributed to well-defined polynuclear mixed-metal cluster complexes.[5−9]

In recent studies, we have prepared a number of layer-segregated platinum−ruthenium and platinum−osmium high-nuclearity metal carbonyl cluster complexes which have well-defined arrangements of the metal atoms.[10,11] The platinum−ruthenium complex $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu\text{-}H)_3$, **1**, can be converted to the alkyne derivatives $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}RC_2R)(\mu_3\text{-}H)(\mu\text{-}H)$, **2a** (R = Ph) and **2b** (R = tolyl), where the alkyne ligand

(1) (a) Sinfelt, J. H., *Bimetallic Catalysts. Discoveries, Concepts and Applications*; Wiley: New York, 1983. (b) Sinfelt, J. H. Bifunctional Catalysis. *Adv. Chem. Eng.* **1964**, *5*, 37. (c) Sinfelt, J. H. *Sci. Am.* **1985**, *253*, 90. (d) Sinfelt, J. H., *Acc. Chem. Res.* **1977**, *10*, 15. (e) Sachtler, W. M. H. *J. Mol. Catal.* **1984**, *25*, 1. (f) Guczi, L. *J. Mol. Catal.* **1984**, *25*, 13. (g) Sachtler, W. M. H.; van Santen, R. A. *Adv. Catal.* **1977**, *26*, 69. (h) Ponec, *Adv. Catal.* **1983**, *32*, 149. (i) Biswas, J.; Bickle, G. M.; Gray, P. G.; Do, D. D.; Barbier, J. *Catal. Rev.-Sci. Eng.* **1988**, *30*, 161. (j) Diaz, G.; Garin, F.; Maire, G. *J. Catal.* **1983**, *82*, 13. (k) Goodman, D. W.; Houston, J. E. *Science* **1987**, *236*, 403. (l) Rodriguez, J. A. *Surf. Sci. Rep.* **1996**, *24*, 223. (m) Früberger, B.; Chen, J. G. *Catal. Lett.* **1997**, *45*, 85.

(2) (a) Braunstein, P.; Rosé, J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Elsevier: New York, 1995; Vol. 10, Chapter 7. (b) Braunstein, P.; Rosé, J. In *Catalysis by Di- and Polynuclear Metal Complexes*; Adams, R. D., Cotton F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 13.

(3) Ichikawa, M. *Adv. Catal.* **1992**, *38*, 283.

(4) (a) Dombek, B. D. *Organometallics* **1985**, *4*, 1707. (b) Ishii, Y.; Miyashita, M.; Kamita, K.; Hidai, M. *J. Am. Chem. Soc.* **1997**, *119*, 6448. (c) Fukuoka, F.; Ichikawa, M.; Hriljac, J. A.; Shriver, D. F. *Inorg. Chem.* **1987**, *26*, 3643.

(5) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. *J. Am. Chem. Soc.* **1994**, *116*, 9103.

(6) (a) Aubart, M. A.; Pignolet, L. H. *J. Am. Chem. Soc.* **1992**, *114*, 7901. (b) Aubart, M. A.; Koch, J. F. D.; Pignolet, L. H. *Inorg. Chem.* **1994**, *33*, 3852. (c) Kappen, T. G. M. M.; Bour, J. J.; Schlebos, P. P. J.; Roelofsen, A. M.; van der Linden, J. G. M.; Steggerda, J. J.; Aubart, M. A.; Krogstad, D. A.; Schoondergang, M. F. J.; Pignolet, L. H. *Inorg. Chem.* **1993**, *32*, 1074. (d) Pignolet, L. H. In *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 3.

(7) (a) Ojima, I.; Donovan, R. J.; Ingallina, P.; Clos, N.; Shay, W. R.; Eguchi, M.; Zeng, Q.; Korda, A. *J. Cluster Sci.* **1992**, *3*, 423. (b) Ojima, I.; Li, Z. In *Catalysis by Di- and Polynuclear Metal Complexes*; Adams, R. D., Cotton F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 9.

(8) Evans, J.; Jingxing, G. *J. Chem. Soc., Chem. Commun.* **1985**, 39.

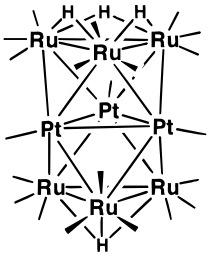
(9) Giordano, R.; Sappa, E. *J. Organomet. Chem.* **1993**, *448*, 157.

(10) (a) Adams, R. D.; Li, Z.; Wu, W. *Organometallics* **1992**, *11*, 4001. (b) Adams, R. D.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1991**, *30*, 3613. (c) Adams, R. D.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1992**, *31*, 2556. (d) Adams, R. D.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1991**, *30*, 2257.

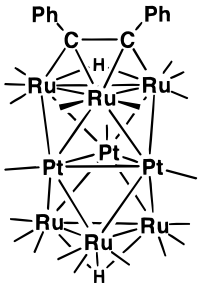
(11) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. H. *Organometallics* **1994**, *13*, 2357.

S0276-7333(98)00117-4 CCC: $15.00
Publication on Web 05/20/1998

is coordinated as a triply bridging ligand to one of the ruthenium triangles.[11]



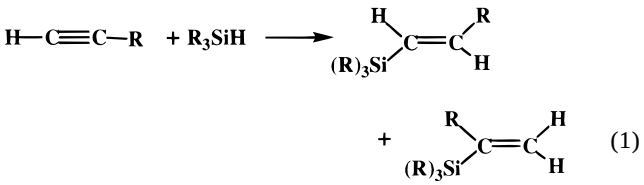
1



2a

Compound **2a** has been shown to be an effective catalyst for the hydrogenation of diarylalkynes to *cis*-diaryl olefins and is more active for this reaction than complexes derived from either of the metals by themselves.[5] It was speculated that the two different types of metal atoms in complex **2** both participate in the activation of the reagents and each plays a different role.[5]

We have now found that the compounds **2** are also effective catalysts for the hydrosilylation of diarylalkynes to *cis*-diarylsilylolefins. The hydrosilylation reaction has received considerable attention over the years, and the hydrosilylation of alkenes and alkynes has been studied extensively.[12] The hydrosilylation of alkynes provides the most convenient and direct route to vinylsilanes, which are important reagents in organic synthesis and as intermediates for cross-linked silicones, eq 1.[12e,f]



(1)

Several studies have described the use of metal carbonyl cluster complexes as catalyst precursors for hydrosilylation reactions,[13−15] but the hydrosilylation of alkynes by mixed-metal cluster complexes has been studied in only a few cases. Ojima and co-workers reported the hydrosilylation of 1-hexyne by rhodium−cobalt mixed-metal clusters, resulting in a mixture of α- and β-isomers (eq 1).[16] The use of rhodium−iron cluster anions to catalyze the hydrosilylation of phenylacetylene also produced a mixture of isomers.[17]

Experimental Section

General Procedures. All reactions were performed under a nitrogen atmosphere unless specified otherwise. The compounds $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$ (**2a**),[11] $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}TolC_2Tol)(\mu_3\text{-}H)(\mu\text{-}H)$ (**2b**),[5] $Ru_3(CO)_9(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)_2$,[9] $PtRu_2(CO)_8(\mu_3\text{-}PhC_2Ph)(dppe)$,[18] and Et_3SiD[19] were synthesized as described previously. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals, Inc., and used as received. Et_3SiH and $(EtO)_3SiH$ were purchased from Aldrich and vacuum distilled prior to use. Diphenylacetylene, PhC_2Ph, and ditolylacetylene, $TolC_2Tol$, were purchased from Aldrich and purified by column chromatography. $[NBu_4]OH$ (40 wt % in H_2O) was purchased from Aldrich and used as received. $CDCl_3$ solvent was purchased from Cambridge Isotope Laboratories and was distilled and deoxygenated prior to use. CH_2Cl_2 was distilled under nitrogen from P_2O_5 prior to use. C_6Me_6 purchased from Aldrich was used as an internal standard for all kinetic measurements. Reaction rates were obtained by measuring the consumption of diphenylacetylene as a function of time by following the reactions by ^1H NMR spectroscopy. Plots of the kinetic data were fitted using Cricket Graph version 1.3 of Cricket Software on a Macintosh LCIII computer.

General Procedures for the Kinetic Studies. All studies were conducted in clean 5 mm NMR tubes in $CDCl_3$ solvent and were followed by ^1H NMR spectroscopy. A selected amount of **2a** was dissolved in a known volume of $CDCl_3$ under nitrogen in a 10 mL Schlenk flask equipped with a stir bar. The solution was stirred to dissolve **2a** completely to create a solution of the required catalyst concentration. The appropriate amount of PhC_2Ph and approximately 1.5 mg of C_6Me_6 were placed in a clean, dry NMR tube. The tube was sealed with a rubber septum and evacuated and filled with nitrogen 5 times. A 0.7 mL volume of the catalyst solution was transferred to the sealed NMR tube via syringe. A measured amount of Et_3SiH was then added in a similar fashion. The tube was shaken to mix the reactants thoroughly and was then placed in a thermostated water bath at 303 K. All kinetic experiments were performed at least twice. Except for the Et_3SiH dependence measurements, all reaction rates were determined by measuring the disappearance of PhC_2Ph by the integration of the downfield phenyl multiplet at $\delta = 7.54-7.50$ ppm against the C_6Me_6 internal standard in a series of NMR spectra taken during the reaction. After the reaction was complete, the solvent and volatiles were removed by vacuum distillation and the residue was washed with hexane to remove C_6Me_6. The remaining solid was then separated by TLC, weighed, and verified by IR spectroscopy.

Kinetic Studies. Dependence of Reaction Rate upon Alkyne Concentration. A 5.0 mg amount of **2a** was dissolved in 5.0 mL of $CDCl_3$ (5.2×10^{-4} M in catalyst). A 0.7 mL volume of this solution (equivalent to 0.7 mg of catalyst (0.000363 mmol)) was transferred to a sealed NMR tube containing 6.5 mg of PhC_2Ph (0.0363 mmol) and a known amount of C_6Me_6, followed by 58 μL of Et_3SiH (0.363 mmol). The hydrosilylation reaction was monitored by ^1H NMR spectroscopy for 2h. After 1 h, 29% of the PhC_2Ph was converted to (*E*)-[(1,2-diphenyl)ethenyl]triethylsilane.[20] There

(12) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (c) *Comprehensive Handbook on Hydrosilylation*; Marciniec, B.; Ed.; Pergamon Press: Oxford, 1992. (d) Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1993**, *446*, 15. (e) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 25, pp 1479−1526. (f) Ojima, I.; Kogure, T. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1981**, *5*, 7−66. (g) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 9.1.

(13) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 7.

(14) (a) Ojima, I.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 2606 and references therein. (b) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38. (c) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332.

(15) (a) Ojima, I.; Fuchikami, T.; Yatake, M. *J. Organomet. Chem.* **1984**, *260*, 335. (b) Süss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231. (c) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonada, N. *J. Org. Chem.* **1986**, *51*, 3890. (d) Hilal, H.; Khalaf, S.; Jondi, W. *J. Organomet. Chem.* **1993**, *452*, 167.

(16) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127.

(17) Kopylova, L. I.; Pukhnarevich, V. B.; Gurevskaya, L. B.; Tsybenov, M. Ts.; Voronkov, M. G. *Zh. Obshch. Khim.* **1992**, *62*, 346.

(18) Adams, R. D.; Wu, W. *Organometallics* **1993**, *12*, 1248.

(19) West, R. *J. Am. Chem. Soc.* **1954**, *76*, 6012.

was no evidence for the formation of (*Z*)-[(1,2-diphenyl)ethenyl]-triethylsilane. After 2 h, the reaction was stopped and an NMR analysis showed that 60% of the PhC_2Ph was converted to (*E*)-[(1,2-diphenyl)ethenyl]triethylsilane. An additional 6% was converted to (*Z*)-stilbene. The observed rate constants (k_{obs}) were determined by measuring the consumption of PhC_2-Ph as a function of time. Recovery of the catalyst as previously described yielded 0.5 mg of **2a**.

Dependence upon Et_3SiH Concentration. A 5.0 mg amount of **2a** was dissolved in 5.0 mL of $CDCl_3$. A 0.7 mL volume of the catalyst solution (0.000363 mmol) was transferred to a sealed NMR tube containing 12.9 mg of PhC_2Ph (0.0724 mmol) and a known amount of C_6Me_6, followed by 2.9 μL of Et_3SiH (0.0182 mmol). The reaction was monitored by ^1H NMR spectroscopy for 6 h. The observed rate constants were determined by measuring the disappearance of Et_3SiH as a function of time.

Dependence upon Catalyst Concentration. The catalyst solution was prepared by dissolving an appropriate amount of **2a** in 5.0 mL of $CDCl_3$. A 0.7 mL volume of the catalyst solution was transferred to a sealed NMR tube containing 6.5 mg of PhC_2Ph (0.0363 mmol) and a known amount of C_6Me_6. A 58 μL amount of Et_3SiH (0.363 mmol) was then added via syringe. The reaction was carried out according to the procedures described above and monitored by ^1H NMR spectroscopy. The observed rate constants (k_{obs}) were determined by measuring the disappearance of PhC_2Ph as a function of time.

Effects of Added CO on Rate of Hydrosilylation of PhC_2Ph. A 5.0 mg amount of **2a** was dissolved in 5.0 mL of $CDCl_3$. A 0.7 mL volume of this solution was transferred to a sealed NMR tube containing 6.5 mg of PhC_2Ph and a measured amount of C_6Me_6. The sealed NMR tube was then subjected to a slow CO purge for 3 min, and then 58 μL of Et_3SiH was added via syringe. The reaction was carried out according to the procedures described above and monitored by ^1H NMR spectroscopy for 2 h. No reaction was observed after a period of 2 h, indicating complete inhibition of the catalysis by CO.

Temperature Dependence Measurements. A 5.0 mg amount of **2a** was dissolved in 5.0 mL of $CDCl_3$. A 0.7 mL volume of this solution was transferred to a sealed NMR tube containing 6.5 mg of PhC_2Ph and a known amount of C_6Me_6, followed by 58 μL of Et_3SiH. The hydrosilylation reactions were carried out at five different temperatures. The reactions were followed by ^1H NMR spectroscopy by heating the AM-300 spectrometer probe to the desired reaction temperature and placing the NMR tube in the heated probe for the duration of the reaction. The k_{obs} values were obtained by measuring the disappearance of PhC_2Ph as a function of time. The activation parameters, $\Delta H^{\ddagger} = 17(2)$ kcal/mol and $\Delta S^{\ddagger} = -18(5)$ eu, were determined from an average of two data sets. The indicated errors represent the difference between the values determined for the two independent sets of data.

Effect of Mercury on Catalytic Activity of 2a. A 5.0 mg amount of **2a** was dissolved in 5.0 mL of $CDCl_3$. A 0.7 mL volume of this solution was transferred to a sealed NMR tube containing 6.5 mg of PhC_2Ph and a known amount of C_6Me_6. Mercury (585 mg) was added to the NMR tube via syringe, followed by 58 μL of Et_3SiH. The hydrosilylation reaction was then performed under the standard conditions and monitored by ^1H NMR spectroscopy for 2 h. The k_{obs} for the reaction was, within experimental error, identical to the k_{obs} of the reactions without mercury, indicating there was no measurable inhibition of the catalysis by the mercury.

Hydrosilylation of $TolC_2Tol$ by 2b. A 4.1 mg amount of **2b** was dissolved in 4.0 mL of $CDCl_3$ (5.2×10^{-4} M in catalyst). A 0.7 mL volume of this solution (0.71 of mg catalyst (0.000363 mmol)) was transferred to a sealed NMR tube containing 7.5 mg of $TolC_2Tol$ (0.0363 mmol) and a known amount of C_6Me_6, followed by 58 μL of Et_3SiH (0.363 mmol). The reaction was performed using the standard procedures and monitored by ^1H NMR spectroscopy for 2 h. After 1 h, 32% of the $TolC_2Tol$ was converted to (*E*)-$Tol(H)C_2(SiEt_3)Tol$, a TOF of 32 h^{-1}. Recovery of the catalyst as previously described yielded 0.5 mg of **2b**.

Labeling Experiments. Hydrosilylation of $TolC_2Tol$ by 2a. A 32.0 mg amount of $TolC_2Tol$ (0.155 mmol) and a 10.0 mg amount of **2a** (0.00518 mmol) were dissolved in 10 mL of CH_2Cl_2 in a 25 mL three-neck flask. The sealed flask was placed in a thermostated water bath at 303 K and allowed to equilibrate for 10 min, after which 248 μL of Et_3SiH (1.55 mmol) was added via syringe. The reaction solution was stirred for 45 min. After stopping the reaction, the solvent was removed in vacuo. A ^1H NMR spectrum of the residue (including 2.4 mg of C_6Me_6 as an internal standard) showed that 20% (6 turnovers) of the $TolC_2Tol$ was reduced to (*E*)-$Tol(H)C_2(SiEt_3)Tol$. Separation of the metal complexes by TLC (hexane/CH_2Cl_2 (3/1)) yielded 1.7 mg of **2b** and 5.2 mg of **2a**.

Reaction of 2a with $TolC_2Tol$ in the Absence of Et_3SiH. A 5.0 mg amount of **2a** (0.00259 mmol) and a 16.0 mg amount of $TolC_2Tol$ (0.776 mmol) were dissolved in 5 mL of CH_2Cl_2 in a 25 mL three-neck flask. The sealed flask was placed in a thermostated water bath at 303 K for 45 min. The solvent was removed in vacuo, and the residue was separated by TLC (hexane/CH_2Cl_2 (3/1)), affording 4.0 mg of unreacted **2a** (80%). There was no evidence for the formation of **2b**.

Test for Kinetic Hydrogen Isotope Effect. Hydrosilylation using Et_3SiD. A 5.0 mg amount of **2a** was dissolved in 5.0 mL of $CDCl_3$. A 0.7 mL volume of this solution was transferred to a sealed NMR tube containing 6.5 mg of PhC_2Ph and a known amount of C_6Me_6, followed by 58 μL of Et_3SiD. The hydrosilylation reaction was carried out under the usual conditions and monitored by ^1H NMR spectroscopy for 2 h. The k_{obs} value was determined by measuring the disappearance of PhC_2Ph as a function of time. The kinetic isotope effect, $k_H/k_D = 1.2(1)$, was determined from an average of two sets of data. The indicated error represents the difference between the values for two independent sets of data.

Hydrogen Isotope Exchange between Two Different Silanes. A 5.0 mg amount of **2a** was dissolved in 5 mL of $CDCl_3$. A 1.0 mL volume of this solution (0.00052 mmol **2a**) was transferred to a sealed NMR tube containing 1.6 mg of C_6Me_6, followed by 8.4 μL of Et_3SiD (0.052 mmol, 100% d_1) and 9.6 μL of $(EtO)_3SiH$ (0.052 mmol). After shaking the tube to mix the reactants thoroughly, the tube was placed in a water bath at 303 K. The progress of the reaction was monitored by ^1H NMR spectroscopy. After 3 h, a 1/1.3 ratio of Et_3SiH/$(EtO)_3SiH$ was found, indicating hydrogen isotope exchange occurs between the two silanes.

Preparation of $[NBu_4][Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)]$, 3. A 10.0 mg amount of **2a** (0.00518 mmol) was dissolved in 15 mL of dichloromethane in a three-neck flask. A 3.5 μL amount of $[NBu_4]OH$ solution (0.0053 mmol) was added via syringe, and the solution was stirred at room temperature for 15 min. The solvent was removed in vacuo, and the residue was separated by TLC using a dichloromethane/hexane (2/1) solvent mixture. This yielded 2.8 mg of brown $[NBu_4][Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)]$, **3** (25%). Data for **3**: IR (ν(CO), cm^{-1}, CH_2Cl_2): 2077 (m), 2032 (br, s). ^1H NMR (δ, $CDCl_3$): 7.23−7.09 (m, Ph, 10H), 3.01 (m, NCH_2, 8H), 1.55 (m, NCH_2CH_2, 8H), 1.39 (m, $NCH_2CH_2CH_2$, 8H), 1.00 (t, CH_3, 12H), −18.60 (s, 1H).

Hydrosilylation Using 3 as the Catalyst. A 5.6 mg amount of **3** (0.0026 mmol) was dissolved in 5 mL of $CDCl_3$. A 0.7 mL volume of this solution was tested for catalytic activity toward hydrosilylation under conditions identical to **2a**. The reaction was monitored by ^1H NMR spectroscopy for 2 h. The observed rate constants were determined by measuring the

(20) (a) Brockmann, M.; Dieck. H.; Klaus, J. *J. Organomet. Chem.* **1986**, *301*, 209. (b) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1525.

Table 1. Turnover Frequencies (TOFs) of Hydrosilylation of Diphenylacetylene to (*E*)-[(1,2-Diphenyl)ethenyl]triethylsilane for Various Platinum and Ruthenium Complexes at 30 °C

compound	reaction time (h)	product: *E*-vinylsilane (turnover no.)	product: *Z*-stilbene (turnover no.)	TOF for *E*-vinylsilane
2a	2	60	6	30
3	2	68	3	34
3/Hg	1.7	23	0	14
$Ru_3(CO)_{12}$	2	0	0	0
$H_2Ru_3(CO)_9(PhC_2Ph)$	2	7.2	0	3.6
$PtRu_2(CO)_8(PhC_2Ph)(dppe)$	2	4.6	0	2.3

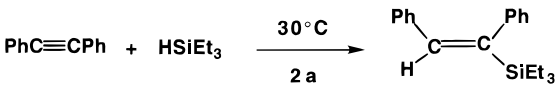
disappearance of PhC_2Ph as a function of time. The k_{obs} for the reactions were similar to those of **2a**.

Effect of Mercury on Catalytic Activity of 3. A 5.6 mg amount of **3** was dissolved in 5 mL of $CDCl_3$. The hydrosilylation reaction was carried out under standard conditions using 0.7 mL of the above solution in the presence of mercury metal (approximately 120 mg). The k_{obs} for the reaction was considerably less than the k_{obs} of the reaction without mercury, see Table 1 for results.

Catalytic Activity of Related Complexes. The catalytic activities of several other related platinum and ruthenium compounds toward hydrosilylation of PhC_2Ph were tested under conditions identical to those of **2a**. These results are listed in Table 1.

Results

The hydrosilylation of diphenylacetylene with triethylsilane is catalyzed by **2a** to yield (*E*)-[(1,2-diphenyl)-ethenyl]triethylsilane with high selectivity in $CDCl_3$ at 30 °C, eq 2. At 30 °C under the conditions of PhC_2Ph



(2)

(5.2×10^{-2} M) to **2a** (5.2×10^{-4} M) ratio of 100/1, 29 equiv of (*E*)-vinylsilane was formed in the first hour, corresponding to a turnover frequency (TOF, mol of product/(mol of catalyst·h)) of 29 h^{-1}. After 2 h, 60% of the PhC_2Ph was converted to (*E*)-diphenylvinyltriethylsilane. A small amount (6% yield) of (*Z*)-stilbene was observed. After the 2 h period, the presence of **2a** was verified by IR spectroscopy and **2a** was recovered in the amount of 70% by TLC. No other metal complexes were observed.

The dependence of the rate of hydrosilylation on the alkyne concentration was monitored by following the disappearance of PhC_2Ph (5.2×10^{-2} M) in the presence of excess Et_3SiH (0.52 M) at a 5.2×10^{-4} M concentration of **2a**. A plot ([PhC_2Ph] vs time) of these results is shown in Figure 1. The dependence on alkyne was unequivocally zero order.

The dependence of the rate of hydrosilylation on the silane concentration was determined by monitoring the disappearance of Et_3SiH (2.6×10^{-2} M) in the presence of excess PhC_2Ph (0.1 M) at a 5.2×10^{-4} M concentration of **2a**. A plot ($\ln([Et_3SiH]/[Et_3SiH]_o)$ vs time) of these results is shown in Figure 2. In this case, there is a first order dependence of the rate of hydrosilylation on the silane concentration.

A plot of the rate of hydrosilylation of PhC_2Ph as a function of the concentration of **2a** in the range ($0.26-1.3) \times 10^{-3}$ M is shown in Figure 3. This establishes a first-order dependence on the cluster concentration.

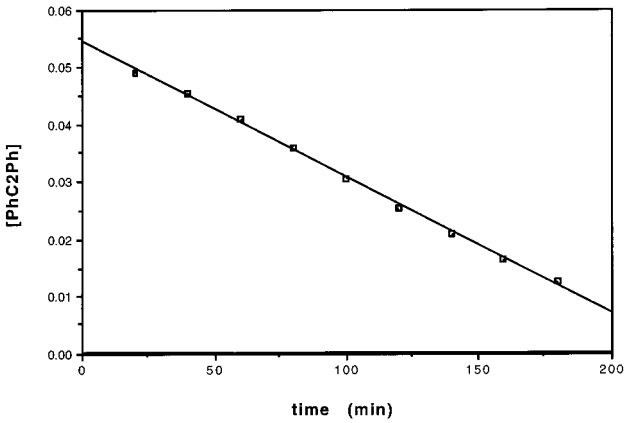


Figure 1. Plot of [PhC_2Ph] as a function of time for reaction 2.

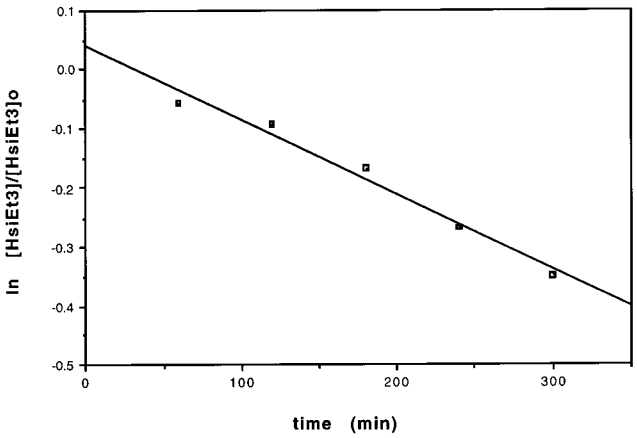


Figure 2. Plot of $\ln[HSiEt_3]/[HSiEt_3]o$ as a function of time for reaction 2.

As a result, these combined measurements have been used to establish the empirical rate equation given in eq 3. It was found that the hydrosilylation reaction was

$$\text{rate} = -\text{d}[PhC_2Ph]/\text{d}t = k_{obs}[\mathbf{2a}][\text{silane}] \quad (3)$$

inhibited by CO. After 2 h, under 1 atm of CO, there was no evidence for hydrosilylation of any of the PhC_2Ph.

The effect of temperature was investigated in the temperature range 293−313 K. This yielded the activation parameters $\Delta H^{\ddagger} = 17(2)$ kcal/mol and $\Delta S^{\ddagger} = -18(5)$ eu from an average of two data sets. This enthalpy of activation is significantly lower than that found for the hydrogenation of PhC_2Ph by **2a**, $\Delta H^{\ddagger} = 24.9$ kcal/mol and $\Delta S^{\ddagger} = 1.4$ eu.[5]

The hydrosilylation reaction was also performed using Et_3SiD to try to detect the presence of a kinetic

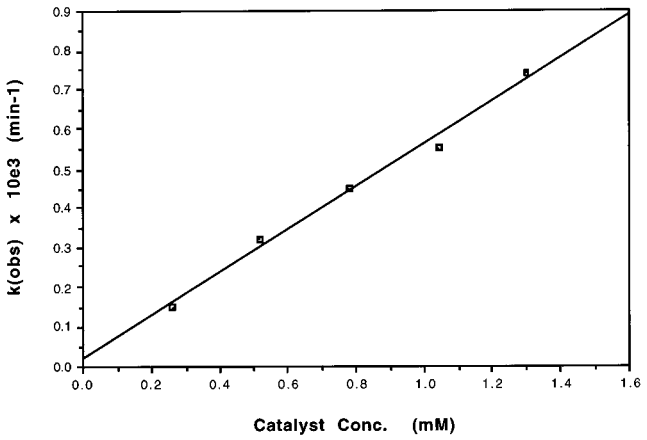


Figure 3. Plot of the rate of disappearance of diphenylacetylene as a function of the concentration of **2a**.

hydrogen isotope effect. A small kinetic isotope effect, k_H/k_D, of 1.2(1) was observed.

As a test for homogeneity, the reaction was also conducted in the presence of mercury. No detectable change in the catalytic activity of **2a** was observed in the presence of mercury.

The hydrosilylation of $TolC_2Tol$ by **2b** yields (*E*)-$Tol(H)C_2(SiEt_3)Tol$ with a TOF of 32 h^{-1} (based on the amount of product formed in the first 1 h). Since the catalyst **A** contains an alkyne ligand, we also performed catalytic hydrosilylation of $TolC_2Tol$ by using **2a** in order to test for incorporation of alkyne substrate into the catalyst during the course of catalysis. First it was verified that **2a** does not react with $TolC_2Tol$ under the catalytic conditions in the absence of silane, thus any incorporation of $TolC_2Tol$ in the cluster in the course of catalysis could be reasonably attributed to the participation of the cluster complex in the catalysis. To strengthen this conclusion still further, we stopped the catalysis in the very early stages, that is after only 6 turnovers of $TolC_2Tol$ to (*E*)-$Tol(H)C_2(SiEt_3)Tol$. Most significantly, an examination of the recovered cluster complex showed that approximately 30% of the cluster **2a** had been converted to the ditolylacetylene complex **2b**.

It was found that **2a** reacts with $[Bu_4N]OH$ to yield the deprotonated cluster $[NBu_4][Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)]$, **3**, in 25% yield after chromatographic workup. Compound **3** has not yet been characterized by single-crystal X-ray diffraction analysis, and its formulation is based on the similarities of its spectroscopic properties to the previously characterized anions $[Pt(PMe_3)_3H][Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu\text{-}H)_2]$, **4**,[21] and $[NBu_4][Pt_3Ru_6(CO)_{21}(\mu_3\text{-}HgI)(\mu_3\text{-}H)_2]$, **5**.[22] The IR spectrum of **3** shows a dominant absorption at 2032 cm^{-1}, reduced from 2065 cm^{-1} for **2a**. This shift to lower frequency indicates greater back-bonding to the CO ligands and is consistent with the formation of a negatively charged cluster species. The ^1H NMR spectrum of **3** at room temperature shows the presence of the phenyl resonances for the coordinated diphenylacetylene ligand, a singlet for one hydride ligand at δ −18.60, and the appropriate signals for one NBu_4 cation. All evidence is consistent with the formulation of **3** as $[NBu_4][Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)]$.

Compound **3** was also tested for it ability to produce the catalytic hydrosilylation of PhC_2Ph. Indeed, compound **3** showed similar rates of activity for the hydrosilylation of PhC_2Ph under the conditions similar to those used for **2a**. However, when the hydrosilylation reaction using **3** was conducted in the presence of mercury metal, the rate of the reaction decreased significantly, suggesting that heterogeneous species may be responsible for some if not all of the observed catalytic activity. Examination of the catalytic reaction solutions by infrared spectroscopy at the end of the reaction period showed only the presence of compound **3**, indicating that the observed catalytic activity of **3** was not due to the presence of **2a** that might have been formed by a protonation of **3**.

For comparison, the catalytic activity of several related complexes, $Ru_3(CO)_{12}$, $Ru_3(CO)_9(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)_2$,[9] and $PtRu_2(CO)_8(\mu_3\text{-}PhC_2Ph)(dppe)$,[18] were also tested. The TOFs for the formation of (*E*)-vinylsilane by these compounds were 0, 3.9, and 2.3 h^{-1}, respectively. See Table 1 for additional details.

Discussion

The most difficult question to answer in studies of catalysis by cluster complexes is, how does one establish that the catalysis is not being produced by mononuclear fragments or by heterogeneous species including colloids generated in situ.[23] This is especially appropriate in this case because platinum catalysts are the most effective of the hydrosilylation catalysts.[12] Lewis et al. have reported that Karstedt's catalyst is an effective catalyst for the addition of $HSi(OEt)_3$ to PhC_2Ph to yield *E*-$Ph(H)C_2(Ph)Si(OEt)_3$ at rates that appear to be significantly faster than those of **2a** (turnover frequencies were not calculated in this study).[24a] Karstedt's catalyst may be one of the few truly homogeneous platinum-containing hydrosilylation catalysts.[24] Lewis et al. have demonstrated that the catalysts generated from typical mononuclear platinum precursors, such as $Pt(COD)_2$, $Pt(COD)Cl_2$, and $PtCl_4$, are actually colloidal in form in their active states, and the presence of mercury leads "to complete poisoning of the catalysts" in these cases.[25] The absence of mercury inhibition in the catalysis by **2a**, thus appears to rule out not only colloidal platinum, but also probably many of the mononuclear species from which colloids are formed.

We have also performed tests on a few selected low-nuclearity complexes or precursors to other low-nuclearity species that could be derived from **2a**, e.g., $Ru_3(CO)_{12}$, $H_2Ru_3(CO)_9(\mu_3\text{-}PhC_2Ph)$, and $PtRu_2(CO)_8(\mu_3\text{-}PhC_2Ph)(dppe)$. $Ru_3(CO)_{12}$ is catalytically inactive at 30

(21) Adams, R. D.; Barnard, T. S.; Li, Z.; Zhang, L. *Chem. Ber.* **1997**, *130*, 729.

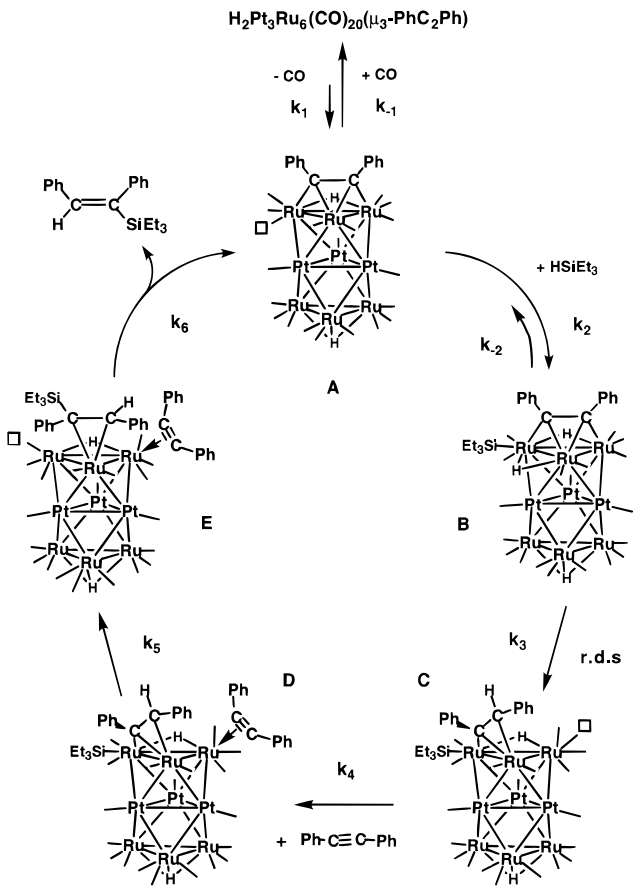
(22) Adams, R. D.; Barnard, T. S.; Cortopassi, J. E.; Zhang, L. *Organometallics* **1996**, *15*, 2664.

(23) (a) Laine, R. M.; Rosenberg, E. in *Catalysis by Di- and Polynuclear Metal Complexes*; Adams, R. D., Cotton F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 1. (b) Laine, R. M. *J. Mol. Catal.* **1982**, *14*, 137. (c) Hilal, H.; Jondi, W.; Khalf, S.; Abu-Halawa, R. *J. Organomet. Chem.* **1993**, *452*, 161. (d) Sanchez-Delgado, R. A.; Andriollo, A.; Puga, J.; Martin, G. *Inorg. Chem.* **1987**, *26*, 1867. (e) Castiglioni, M.; Giordano, R.; Sappa, E. *J. Organomet. Chem.* **1989**, *362*, 399.

(24) (a) Lewis, L. N.; Sy, K. G.; Donahue, P. E. *J. Organomet. Chem.* **1992**, *427*, 165. (b) Lappert, M. F.; Scott, F. P. A. *J. Organomet. Chem.* **1995**, *492*, C11. (c) Lewis, L. N.; Colborn, R. E.; Grade, H.; Bryant, G. L., Jr.; Sumpter, C. A.; Scott, R. A. *Organometallics* **1995**, *14*, 2202.

(25) (a) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. (b) Lewis, L. N.; Lewis, N. *Chem. Mater.* **1989**, *1*, 106.

Scheme 1



°C. The other two complexes each showed a low level of catalytic activity for hydrosilylation of PhC_2Ph to (*E*)-$Ph(H)C_2(SiEt_3)Ph$, but the activity of each is far below that of **2a**. It is clear that these clusters and any species that might be derived from them under the catalysis conditions are not responsible for the catalysis exhibited by **2a**.

The strongest evidence to support the claim that **2a** functions as an intact cluster catalyst is derived from the kinetic and labeling studies. The empirically derived rate eq 3 was established, and the linear dependence on the concentration of compound **2a** is indicative of a process which does not involve fragmentation of the cluster.[23] However, the strongest link between **2a** and the catalysis is the incorporation of the tolylC_2tolyl into the cluster in the course of the catalysis and the absence of its incorporation in the absence of catalysis, that is tolylC_2tolyl is incorporated into the cluster only during the process of catalysis.

The other kinetic results provide additional valuable mechanistic information. Particularly, there is no dependence of the reaction rate on the concentration of alkyne, but there is a first-order dependence on the concentration of silane. There is also a strong inhibition of the reaction in the presence of CO at 1 atm of pressure.

On the basis of this information, the mechanism based on a homogeneous process involving the intact cluster **2a** shown in Scheme 1 is proposed. This mechanism is a slight modification of the one proposed for the hydrogenation of diphenylacetylene by **2a**.[5] Inhibition by CO is consistent with an initial CO dissociation step to give the species **A**, which is the true catalyst. This is expected since compound **2a** is electronically saturated.[11] The ligand dissociation will provide a "vacant" site to which the first reagent can be added.[5] Because of the dependence on silane concentration and absence of dependence on alkyne concentration, we propose that the silane activation occurs at or before the rate-determining step, step k_2, and also precedes the alkyne addition. In fact, the alkyne addition, step k_3, must occur after the rate-determining step.

Since there are nine metal atoms in complex **2a**, the question of the site of silane addition becomes an important one. Cabeza and co-workers have recently shown that when the silyl group and an alkenyl group are coordinated to different metal atoms in triruthenium cluster complexes, then catalytic hydrosilylation does not occur, presumably because the formation of the C−Si bond by reductive elimination is more difficult.[26] On the other hand, when alkenyl and silyl ligands are coordinated to the same metal atom, as found in the osmium complex $Os_3(CO)_{10}(\mu\text{-}HC_2(H)Bu^t)[Si(OMe)_3]$, then Si−C reductive elimination to yield a vinylsilane can occur.[27] For this reason, we propose that the site of Si−H addition is one of the ruthenium atoms of the Ru_3 triangle that contains the alkyne ligand, and this leads to the intermediate **B** in the catalytic cycle. Presumably, the CO ligand that was dissociated was eliminated from the same site, see intermediate **A**, but this is not required. Two of the three ruthenium atoms containing the PhC_2Ph ligand in **2a** contain three CO ligands while the third has only two.[11] It seems most probable that the CO dissociation will occur from one of the two ruthenium atoms containing three CO ligands since these CO ligands should have less π-back-bonding than those on the ruthenium atom that contains only two CO ligands. The silane activation step is shown with reversibility, k_{-2}, since hydrogen−deuterium exchange was observed to occur when Et_3SiD and $(EtO)_3SiH$ were combined in the presence of **2a**.

The next step in the catalytic cycle is proposed to be the rate-determining step, rds, k_3. It involves transfer of one of the hydride ligands to the PhC_2Ph ligand. The presence of an observable, albiet small, kinetic hydrogen isotope effect is consistent with this step. This will lead to the formation of a σ,π-diphenylvinyl ligand and some form of "unsaturation", possibly as a "vacant" site on one of the ruthenium atoms in intermediate **C**. It is expected that the diphenylvinyl ligand will have cis-positioned phenyl groups, as was observed in the formation of the compound $Pt_3Ru_6(CO)_{21}[\mu\text{-}PhC_2(H)Ph](\mu\text{-}H)$, **6**, upon the addition of CO to **2a**.[11] The next step is probably the addition of PhC_2Ph, presumably at the "vacant" site in **C**, to yield an electronically saturated complex **D**, step k_4. This must be fast kinetically since no PhC_2Ph dependence was observed in the reaction. We have shown previously that **2a** will react with PhC_2Ph in the absence of Et_3SiH or H_2 to yield $Pt_3Ru_6(CO)_{14}(\mu_3\text{-}PhC_2Ph)_3$,[5] but none of this compound was detected in any of these reactions. Reductive elimination to form the Si−C bond could yield a silylolefin

(26) Cabeza, J. A.; Garcia-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973.
(27) Adams, R. D.; Cortopassi, J. E.; Pompeo, M. P. *Organometallics* **1992**, *11*, 1.

complex such as **E**, step k_5. This may also result in unsaturation, but the PhC_2Ph ligand may fill this void in short order by converting to a triply bridging four-electron donor.[28] Indeed, the PhC_2Ph ligand may even promote the Si−C reduction elimination. Dissociation of the silylolefin would then close the cycle with regeneration of the intermediate **A**. In this analysis, all of the catalysis occurs at only one of the two Ru_3 triangles, but this is not a requirement. In fact, in our analysis of the catalytic hydrogenation of PhC_2Ph by **2a**, we invoked the involvement of both Ru_3 triangles.

A competing hydrogen transfer at step k_5 could explain the formation of the small amounts of *cis*-stilbene. Competing formation of hydrogenated alkynes has been observed in other alkyne−hydrosilylation reactions.[29]

Since we had observed in previous studies that the hydride-containing layer-segregated clusters could be deprotonated,[21,22] we felt it was necessary to test the possible deprotonated forms of **2a** for catalytic activity. Accordingly, we prepared the monoanion $[Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu\text{-}H)]$ by treatment of **2a** with $[NBu_4]OH$. Surprisingly, the salt of this anion, **3**, performs catalytic hydrosilylation of PhC_2Ph to $(E)\text{-}Ph(H)C_2(SiEt_3)Ph$ at rates which are similar to those of **2a**. However, there is one important difference in the catalytic activity, the catalysis by **3** was found to be strongly inhibited by the presence of metallic mercury. Therefore, it is suspected that the catalysis by **3** involves a catalytic species different from that generated by **2a**, that is the catalysis by **3** may involve a heterogeneous species[21] or possibly some molecular species that reacts readily with mercury metal. The nature of the catalyst formed in the solutions of **3** has not yet been determined. Suffice to say at this point, it does not appear to be the same species that is involved in the catalysis by the solutions of **2a**.

The combination of results in this study provides strong evidence that the high-nuclearity layer-segregated cluster complexes **2a** and **2b** are effective catalyst precursors for the highly selective catalytic hydrosilylation of diphenylacetylene to (*E*)-[(1,2-diphenyl)ethenyl]-triethylsilane. The true catalyst is actually the decarbonylated species, **A**. Although most (perhaps all) of the transformations occur at the ruthenium atoms, it is believed that the unusually high activity is due in part to some form of synergistic enhancement by the platinum simply because this high activity is not observed in the absence of platinum. The precise nature of this synergism remains to be established. Further studies to try to establish the role that each metal plays in this catalytic hydrosilylation reaction are in progress.

Acknowledgment. This research was supported by the National Science Foundation, Grant No. CHE-9422001.

OM980117K

(28) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(29) (a) Fernandez, M. J.; Oro, L. A. *J. Mol. Catal.* **1988**, *45*, 7. (b) Fernandez, M. J.; Esteruelas, M. A.; Jiménez, M. S.; Oro, L. A. *Organometallics* **1986**, *5*, 1519.