Molecular Clusters in Homogeneous Catalysis: Kinetic and Chemical Evidence for the Participation of Triruthenium Cluster Complexes in a Cluster-Promoted Catalytic Hydrogenation of Diphenylacetylene

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The cluster complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PPh_3)]$ (1) (Hampy = 2-amino-6-methylpyridine) promotes the selective homogeneous hydrogenation of diphenylacetylene to stilbene (353 K, $P(H_2) < 1$ atm). A kinetic study of the catalytic reaction, which is first order in cluster concentration, as well as the isolation and characterization of the compounds $[Ru_3(\mu_3\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-}Ph_2C_2H)(CO)_7(PPh_3)]$ (2) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-}Ph_2C_2H)(CO)_6(PPh_3)]$ (3), which are the products of the sequential reactions of 1 with diphenylacetylene and hydrogen, indicate that the catalytic species are trinuclear and that the rate determining step in the catalytic cycle is an isomerization reaction in complex 3 which favors the reductive coupling of the hydride and alkenyl ligands to give *cis*-stilbene. Complex 1 does not react with hydrogen under the conditions used in the catalytic runs.

Introduction

As pointed out recently by Gladfelter and Roesselet,[1] the determination of catalytic reaction mechanisms involving metal clusters is difficult, and no one should expect quick and easy answers. One of those expected answers is related to the nuclearity of the actual catalytic species of a particular process. In this context, as far as hydrogenation reactions with ruthenium cluster complexes as catalyst precursors are concerned, the presence of polynuclear catalytic species has been confirmed in very few instances;[1,2] in some cases, the precursor fragments under the catalytic conditions, giving rise to species of different nuclearity,[1,3] whereas in most cases, since very few kinetic studies have been carried out, the fate of the catalytic precursor is unknown.[1,4,5]

In previous works,[6,7] we have reported the catalytic activity of the cluster complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (Hampy = 2-amino-6-methylpyridine) and $[Ru_3(\mu\text{-H})(\mu,\eta^1{:}\eta^2\text{-}C_8H_{11}N_2)(CO)_9]$ ($C_8H_{12}N_2$ = 1,2-diamino-4,5-dimethylbenzene) in the homogeneous hydrogenation of alkynes. Although we have so far been unable to completely interpret the kinetic results in the former case, kinetic and chemical studies carried out with the latter complex showed that the catalytic species are actually mononuclear.[7]

We now describe the catalytic activity of the cluster complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PPh_3)]$[8] (1) (Chart I) in the homogeneous hydrogenation of diphenylacetylene to stilbene, together with chemical and kinetic studies which indicate the participation of trinuclear species in the catalytic process.

Results and Discussion

Kinetics of the Catalytic Hydrogenation of Diphenylacetylene Promoted by 1. Complex 1 is a catalyst precursor for the homogeneous hydrogenation of diphenylacetylene under mild conditions, rendering a mixture of *cis*- and *trans*-stilbene; *cis*-stilbene is the kinetic product since the *cis*- to *trans*-stilbene ratio decreases continuously as the hydrogenation of diphenylacetylene progresses. No hydrogenation of stilbene to 1,2-diphenylethane was observed. The reaction is rather slow (turnover frequency 10.9 h^{-1}, in toluene at 353 K and $P(H_2) = 0.663$ atm), but fast enough to allow kinetic studies.

Initial hydrogenation rates ($-dV_c/dt$) were obtained by measuring the hydrogen uptake as a function of time and correcting the volume of consumed hydrogen to that corresponding to 1 atm (V_c), as shown in Figure 1. In order to determine the rate dependence on each reagent, runs were carried out at different diphenylacetylene and cluster concentrations and at different hydrogen pressures (Table I). Plots of $\log(-dV_c/dt)$ vs $\log P(H_2)$ and $\log(-$

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(1) 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, p 329.

(2) (a) Doi, Y.; Koshizuka, K.; Keii, T. *Inorg. Chem.* **1982**, *21*, 2732. (b) Doi, Y.; Tamura, S.; Koshizuka, K. *J. Mol. Catal.* **1983**, *19*, 213. (c) Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 2154. (d) Zuffa, J. L.; Blohm, M. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 552.

(3) See, for example: (a) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959. (b) Warren, B. K.; Dombek, B. D. *J. Catal.* **1983**, *79*, 334. (c) Mercer, G. D.; Shing-Shu, J.; Brauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 1967. (d) Sánchez-Delgado, R.; Andriollo, A.; Puga, J.; Martín, G. *Inorg. Chem.* **1987**, *26*, 1867.

(4) (a) Markó, L.; Vici-Orosz, A. In *Metal Clusters in Catalysis*; Knözinger, H., Gates, B. C., Guczi, L., Eds.; Elsevier: Amsterdam, 1986; Chapter 5, p 89. (b) Whyman, R. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; John Wiley & Sons: New York, 1980; Chapter 8, p 545.

(5) For the homogeneous hydrogenation of internal alkynes promoted by ruthenium carbonyl cluster complexes see, for example: (a) Castiglioni, M.; Giordano, R.; Sappa, E. *J. Organomet. Chem.* **1989**, *362*, 339. (b) Castiglioni, M.; Giordano, R.; Sappa, E. *J. Organomet. Chem.* **1991**, *407*, 377. (c) Michelin-Lausarot, P.; Vaglio, G. A.; Valle, M. *Inorg. Chim. Acta* **1977**, *25*, L107. (d) Michelin-Lausarot, P.; Vaglio, G. A.; Valle, M. *Inorg. Chim. Acta* **1979**, *36*, 213. (e) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimata, E. W.; Bonnett, J. J. *J. Am. Chem. Soc.* **1990**, *112*, 8607.

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(7) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *Organometallics* **1992**, *11*, 4355.

(8) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Bois, C.; Jeannin, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 3347.

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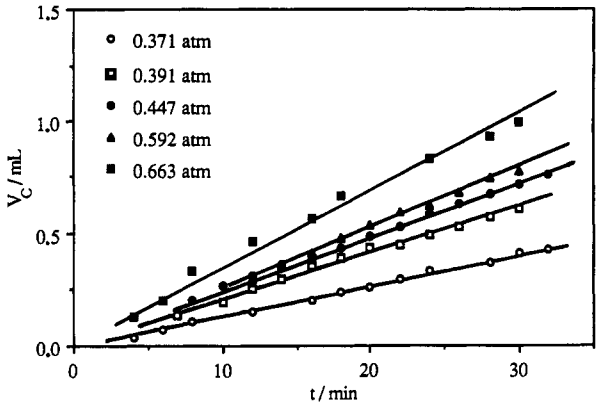
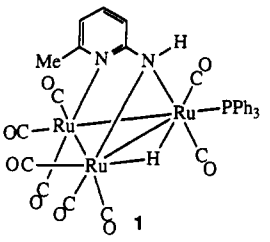
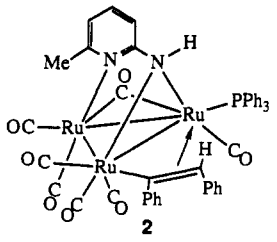


Figure 1. Hydrogen-uptake (corrected to 1 atm) plots, at different hydrogen pressures, for the hydrogenation of diphenylacetylene promoted by 1, in toluene at 353 K. [1] = 1.10×10^{-3} M; [Ph_2C_2] = 0.112 M.

Chart I





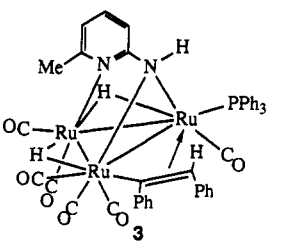


Table I. Kinetic Data for the Hydrogenation of Diphenylacetyene Promoted by 1 in Toluene at 353 K

$P(H_2)$/atm	10^3[1]/M	[Ph_2C_2]/M	$10^7(-dV_c/dt)$/L s^{-1}
0.371	1.10	0.112	2.31
0.391	1.10	0.112	3.36
0.447	1.10	0.112	3.81
0.592	1.10	0.112	4.44
0.663	1.10	0.112	5.42
0.663	0.55	0.112	2.88
0.663	0.84	0.112	3.83
0.663	1.67	0.112	7.38
0.663	2.20	0.112	9.62
0.663	1.10	0.011	3.41
0.663	1.10	0.028	3.89
0.663	1.10	0.042	4.42
0.663	1.10	0.056	4.56
0.663	1.10	0.084	4.74
0.663	1.10	0.168	5.17
0.663	1.10	0.252	4.58
0.663	1.10	0.337	5.09

dV_c/dt) vs log [1] afforded straight lines of slopes 1.14 and 0.88, respectively (Figure 2), indicating that the hydrogenation reaction is first order in hydrogen pressure and first order in the concentration of added 1. The dependence of the initial rate of hydrogen consumption on substrate concentration (Figure 3) is more complicated: it is close to zero order at high concentrations of diphenylacetylene, but at low concentrations the rate is slower, indicating a positive reaction order; disappointingly, at such low concentrations of diphenylacetylene the rates were too slow to allow the determination of the partial reaction order with respect to the concentration of the alkyne. Although we were unable to determine the rate dependence on the CO pressure, it is clear that it is negative, since small volumes (2–5 mL) of carbon monoxide injected into the reacting solutions produced a very strong reduction of the rate.

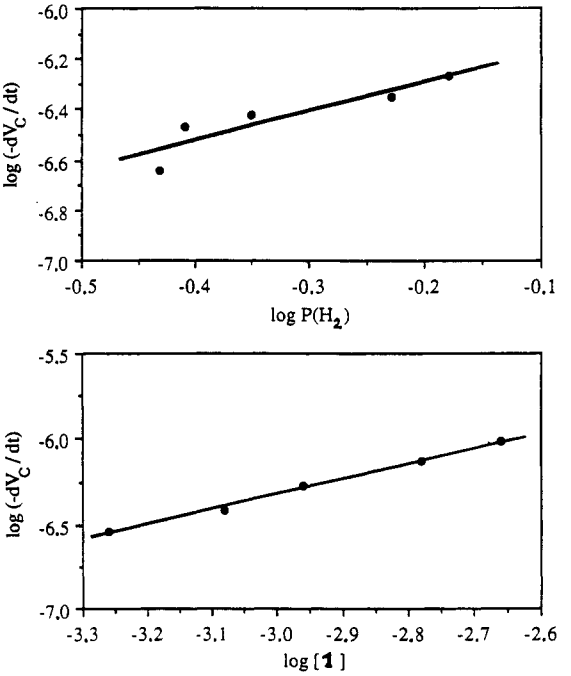


Figure 2. Partial reaction orders with respect to $P(H_2)$ (top) and [1] (bottom) for the hydrogenation of diphenylacetylene promoted by 1, in toluene at 353 K.

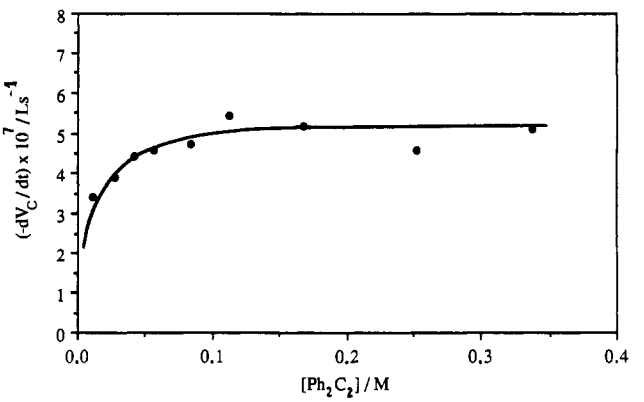


Figure 3. Plot of the reaction rate dependence on substrate concentration for the hydrogenation of diphenylacetylene promoted by 1, in toluene at 353 K.

Reactions of Cluster 1 with Diphenylacetylene and Hydrogen. In order to get some knowledge about the nature of the metallic species involved in the catalytic process, the reactions of the catalytic precursor 1 with diphenylacetylene and hydrogen were studied.

As recently reported,[9] complex 1 reacts easily with diphenylacetylene to afford the trinuclear $\mu,\eta^1{:}\eta^2$-alkenyl derivative [$Ru_3(\mu_3$-ampy)$(\mu,\eta^1{:}\eta^2$-$Ph_2C_2H)(CO)_7(PPh_3)$] (2) (Chart I), presumably via CO elimination, coordination of the alkyne, and subsequent alkyne insertion into the hydride–metal bond.

No reaction was observed when complex 1 was treated with hydrogen under the conditions used in the catalytic

(9) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973.

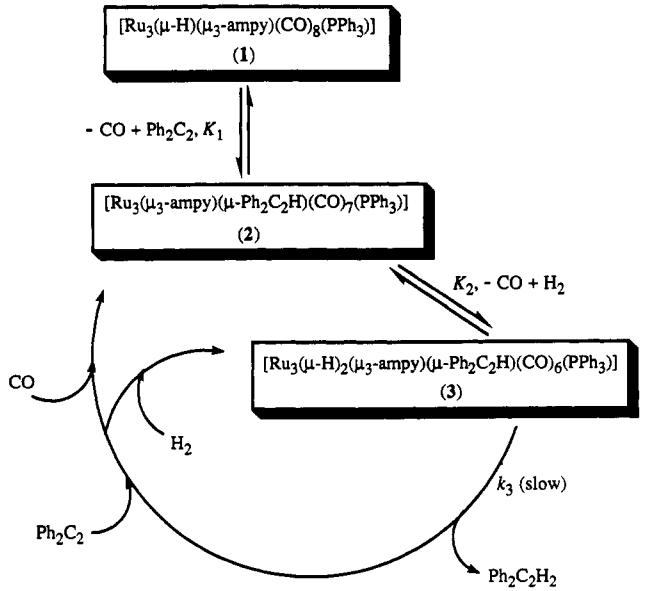


Figure 4. Proposed mechanism for the hydrogenation of diphenylacetylene promoted by complex 1.

runs. Therefore, it seems reasonable that, under hydrogen, complex 1 reacts first with diphenylacetylene (to give 2) and then with hydrogen.

The reaction of 2 with hydrogen (NMR tube, toluene-d_8, 353 K, H_2 bubbled) gave a mixture of at least four complexes, in which cluster 1 was the major component (as shown by the ^1H and ^{31}P NMR spectra of the reaction mixture). The reaction was also carried out in the presence of diphenylacetylene (10:1 Ph_2C_2:2 mole ratio), under the same conditions. In this case, before the complete hydrogenation of the diphenylacetylene (as observed by GC), a mixture of 1, 2, and a new complex (3), in an approximate 2:1:4 ratio, was observed by ^{31}P NMR spectroscopy, while a mixture of at least six different complexes, with cluster 1 as the major component, was observed when all the alkyne was hydrogenated.

We managed to isolate complex 3, though in low yield, through a chromatographic separation of the mixture obtained from the reaction of complex 2 with hydrogen in the presence of diphenylacetylene. We have been unable to grow single crystals of 3 suitable for an X-ray diffraction study; nevertheless, its spectroscopic data strongly support the structure proposed in Chart I. Thus, the ^1H NMR spectrum shows two hydride resonances as doublets, with small J_{H-P} coupling constants, suggesting that one hydride is approximately cis to the phosphorus atom (J_{H-P} = 5.5 Hz), while the other one is further away from the phosphine ligand (J_{H-P} = 2.5 Hz).[8,10] The fact that the alkenyl–CH proton is coupled to phosphorus (J_{H-P} = 3.8 Hz) indicates that the CH fragment of the alkenyl ligand is bound to the same Ru atom as the phosphine ligand. The number of CO ligands in 3 was obtained from the $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample, which shows six CO resonances, two of which are coupled to phosphorus, corresponding to the axial carbonyl attached to the same Ru atom as the phosphine ligand (203.9 ppm, $^2J_{C-P}$ = 7.9 Hz) and to the equatorial carbonyl which forms part of the nearly linear P–Ru–Ru–CO arrangement (195.5 ppm, $^3J_{C-P}$ = 12.0 Hz).[8] It is also interesting to note that in the proton-coupled ^{13}C NMR spectrum of 3, only one carbonyl resonance is clearly split (197.7 ppm, doublet, J_{C-H} = 12.1 Hz) with respect to the proton-decoupled spectrum, indicating that the complex contains only one CO ligand approximately trans to a hydride ligand.[8,11]

Mechanistic Aspects of the Homogeneous Hydrogenation of Diphenylacetylene Promoted by 1. A reaction pathway for the homogeneous hydrogenation of diphenylacetylene promoted by 1 is proposed in Figure 4. This mechanism implies the engagement of only trinuclear species in the catalytic cycle. This is supported by the fact that the reaction is first order in cluster concentration[1,2] and by the fact that we have not identified any species different from the trinuclear ones in our catalytic experiments. This may be due to the presence of the face-bridging ligand ampy, which strongly binds the three metal atoms.[12]

The proposed mechanism involves the reaction of the precursor 1 with diphenylacetylene to give 2 (K_1), which subsequently reacts with hydrogen to give 3 (K_2). The fact that complex 3 is the major species observed by NMR spectroscopy in the catalytic solution implies that the transformation of 3 should be the rate determining step of the catalytic process. However, the coupling of a hydride with the alkenyl ligand in 3 to give stilbene cannot be possible in only one elemental reaction, because the α-carbon atom of the alkenyl ligand in 3 is not cis to any of the hydrides; therefore, the rate determining step (k_3) has to be an isomerization reaction which would place a hydride and the alkenyl α-carbon atom in a cis arrangement, prior to the reductive elimination of stilbene.

It is expected that the release of stilbene from the corresponding isomer of complex 3 would give a very unsaturated species which will rapidly undergo decomposition in the event that no diphenylacetylene is present in solution. This explains the high number of species observed by NMR spectroscopy when the reaction of 2 with hydrogen was carried out in the absence of diphenylacetylene (or, in a catalytic reaction, when the alkyne has been consumed). However, in the presence of diphenylacetylene, this unsaturated species would rapidly add diphenylacetylene and hydrogen (or CO) to close the catalytic cycle.

A kinetic analysis of the proposed mechanism gives the following rate law:[13]

$$\nu = -d[Ph_2C_2]/dt = \frac{K_2k_3[Ru_3]_T P(H_2)}{P(CO) + \{P(CO)^2/K_1[Ph_2C_2]\} + K_2P(H_2)}$$

where $[Ru_3]_T$ is the total concentration of triruthenium clusters in solution and is equal to the initial concentration of added catalyst precursor 1. At high Ph_2C_2 concentrations it can be assumed that $\{P(CO)^2/K_1[Ph_2C_2]\} \ll \{P(CO) + K_2P(H_2)\}$; therefore, the rate law can be simplified to

(10) (a) Andreu, P. L.; Cabeza, J. A.; Pellinghelli, M. A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* **1991**, *30*, 4611. (b) Andreu, P. L.; Cabeza, J. A.; Cuyás, J. L.; Riera, V. *J. Organomet. Chem.* **1992**, *427*, 363.

(11) See, for example: Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 157.

(12) Reactions of hydrido cluster complexes containing face-bridging ligands different from ampy with alkynes also afford trinuclear derivatives;[12a] however, reactions of alkynes or olefins with the edge-bridged clusters $[Ru_3(\mu\text{-}H)(\mu,\eta^1{:}\eta^2\text{-}C_8H_{11}N_2)(CO)_8]$[7] and $[Ru_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ (X = Cl, O=CR)[12b-d] involve the loss of one metal center to give binuclear complexes: (a) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimata, E. W.; Bonnet, J. J. *Organometallics* **1992**, *11*, 1351. (b) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4646. (c) Boag, N. M.; Sieber, W. J.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1988**, *355*, 385. (d) Xue, Z.; Sieber, W. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1991**, *112*, 1825 and ref therein.

$$\nu = -d[Ph_2C_2]/dt = \frac{K_2k_3[Ru_3]_TP(H_2)}{P(CO) + K_2P(H_2)}$$

At low hydrogen pressures, it can be further simplified to

$$\nu = -d[Ph_2C_2]/dt = K_2k_3[Ru_3]_TP(H_2)P(CO)^{-1}$$

a rate law that is zero order in Ph_2C_2 concentration and that agrees well with our experimental kinetic data obtained for $P(H_2) < 1$ atm and concentrations of Ph_2C_2 between 0.112 and 0.337 M.

At very low concentrations of Ph_2C_2, it can be assumed that $\{P(CO)^2/K_1[Ph_2C_2]\} \gg \{P(CO) + K_2P(H_2)\}$; consequently, the rate law can be expressed as

$$\nu = -d[Ph_2C_2]/dt = K_1K_2k_3[Ru_3]_TP(H_2)[Ph_2C_2]P(CO)^{-2}$$

a rate law that is first order in the concentration of Ph_2C_2, as also suggested by our experimental data.

Finally, considering the possibility of phosphine dissociation, we have not observed any compound containing none or two PPh_3 ligands at any stage of the catalytic reactions. Unfortunately, the rate dependence on the concentration of added PPh_3 cannot be measured, since complex **1** reacts readily with PPh_3 to give $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PPh_3)_2]$,[10a] a compound that is nearly inactive as a catalyst precursor for the hydrogenation of diphenylacetylene.[14] Furthermore, we have also measured the kinetics of the hydrogenation of diphenylacetylene promoted by $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ and, in this case, the reaction is one-third order in cluster concentration. All these data suggest that phosphine dissociation does not take place when complex **1** is used as catalyst precursor for the hydrogenation of diphenylacetylene.

In conclusion, the present work presents a mechanism for the hydrogenation of diphenylacetylene promoted by complex **1** which involves only trinuclear cluster complexes, being one of the very few examples in which cluster catalysis has been supported by both the results of chemical reactions and kinetic data.[1]

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Compounds **1**[8] and **2**[9] were prepared as described previously. A ^{13}CO-enriched sample of compound **3** was prepared from ^{13}CO-enriched $[Ru_3(CO)_{12}]$.[15] All other reagents (reagent grade) were used as received from commercial suppliers. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were run at 23 °C with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P) as standards ($\delta = 0$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. Analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 8600 gas chromatograph, equipped with a 12-m AQ2 capillary column (i.d. 0.22 mm) and a flame ionization detector, at 160 °C; quantification was achieved with a PE-Nelson 1020 integrator.

Preparation of Complex 3. Hydrogen was bubbled through a boiling THF solution (10 mL) of complex **2** (161 mg, 0.154 mmol) and diphenylacetylene (25 mg, 0.139 mmol) for 35 min. The solvent was removed under reduced pressure and the residue dissolved in toluene (1.5 mL). The resulting solution was chromatographed under nitrogen on a neutral alumina column (10 × 2 cm, activity IV). Compounds **1** and **2** were obtained from the first (eluant: hexane–dichloromethane 5:1) and third (eluant: dichloromethane) bands. The second band, eluted with hexane–dichloromethane 2:1, was worked up to afford complex **3** as an orange solid (17 mg, 11%). Anal. Calcd for $C_{44}H_{35}N_2O_6PRu_3$: C, 51.71; H, 3.45; N, 2.74. Found: C, 51.85; H, 3.64; N, 2.58. IR, ν(CO) (THF): 2029 (s), 2004 (vs), 1978 (w), 1961 (s), 1942 (w), 1924 (vw) cm^{-1}. ^1H NMR (C_6D_6), δ (ppm): phenyl protons, 7.8–6.5 (m); ampy protons, 6.47 (t, J_{H-H} = 7.7 Hz), 6.27 (s, br, NH), 5.95 (d, J_{H-H} = 7.7 Hz), 5.55 (d, J_{H-H} = 7.7 Hz), 2.59 (s, Me); alkenyl C*H*, 2.87 (d, J_{H-P} = 3.8 Hz); hydride ligands, −8.28 (d, J_{H-P} = 5.5 Hz), −10.74 (d, J_{H-P} = 2.5 Hz). Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, sample enriched in ^{13}CO): δ 210.2 (s), 205.6 (s), 203.9 (d, J_{C-P} = 7.9 Hz), 202.9 (s), 197.7 (s), 195.5 (d, J_{C-P} = 12.0 Hz) (6 CO ligands), 174.6 (s), 161.2 (s), 138.7 (s), 118.6 (s), 111.9 (s), 31.7 (s) (ampy carbon atoms), 88.8 (s) (alkenyl *C*H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 43.2 (s) ppm.

Kinetic Studies. The evolution of the catalytic reactions was followed by gas chromatography. Reaction rates were obtained by measuring the hydrogen consumption as a function of time in a conventional gas buret.

The appropriate amounts of **1** and diphenylacetylene (Table I) were placed in a two-necked 25-mL flask with one neck connected to the gas buret, which in turn was connected to a vacuum line. The flask was closed by a silicone septum and the system evacuated and filled with hydrogen five times. Degassed toluene (10 mL) was then introduced into the flask and the required pressure adjusted in the gas buret. The flask was immersed in a bath thermostated at 353 K and shaken during the run at 600 min^{-1} with a Selecta shaker. An equilibration time of 10 min was allowed before acquiring any data. The working partial pressure of hydrogen was determined by subtracting the toluene vapor pressure at each temperature from the measured total pressure. Plots of the kinetic data were fitted using conventional regression programs.

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(13) According to the proposed mechanism, since the volume of consumed hydrogen is directly related to the disappearance of Ph_2C_2, the rate law is given by

$$\nu = -d[Ph_2C_2]/dt = k_3[3] = K_2k_3[2]P(H_2)P(CO)^{-1}$$

But, as $[Ru_3]_T = [1] + [2] + [3]$ and [1] and [3] can be expressed as a function of [2] through the equilibrium constants K_1 and K_2, respectively, $[Ru_3]_T = \{[2]P(CO)/K_1[Ph_2C_2]\} + [2] + \{K_2[2]P(H_2)/P(CO)\}$; therefore,

$$[2] = \frac{[Ru_3]_T}{1 + \{P(CO)/K_1[Ph_2C_2]\} + K_2P(H_2)/P(CO)}$$

and

$$\nu = -d[Ph_2C_2]/dt = \frac{K_2k_3[Ru_3]_TP(H_2)}{P(CO) + \{P(CO)^2/K_1[Ph_2C_2]\} + K_2P(H_2)}$$

(14) Briard, P.; Cabeza, J. A.; Llamazares, A.; Ouahab, L.; Riera, V. *Organometallics* **1993**, *12*, 1006.

(15) Andreu, P. L.; Cabeza, J. A.; Miguel, D.; Riera, V.; Villa, M. A.; García-Granda, S. *J. Chem. Soc., Dalton Trans.* **1991**, 533.