Homogeneous Hydrogenation of Diphenylacetylene Promoted by a Cationic Hydridoalkenyltriruthenium Cluster Complex. Kinetic Evidence for Cluster Catalysis

Javier A. Cabeza,* Ignacio del Río, José M. Fernández-Colinas, and Víctor Riera

Instituto de Química Organometálica "Enrique Moles", Facultad de Química, Universidad de Oviedo-CSIC, 33071 Oviedo, Spain

Received June 9, 1995[⊗]

Summary: The cationic cluster complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(\mu,\eta^1{:}\eta^2\text{-}PhC{=}CHPh)(CO)_8][BF_4]$ (**1**) *(Hampy = 2-amino-6-methylpyridine) promotes the homogeneous catalytic hydrogenation of diphenylacetylene to cis- and trans-stilbene under very mild conditions (333 K,* $P(H_2) < 1$ *atm). Reactivity, spectroscopic, and kinetic studies support a hydrogenation mechanism in which the catalytic intermediates are cationic trinuclear complexes.*

Introduction

This report describes the ability of a cationic hydridocarbonyltriruthenium cluster complex to promote the homogeneous catalytic hydrogenation of diphenylacetylene under very mild conditions. We carried out this study prompted by the fact that cationic carbonylmetal cluster complexes have never been used before as catalyst precursors in homogeneous catalysis.

On the other hand, there is currently a great interest about the nuclearity of the catalytic species operating in cluster-promoted catalytic reactions.[1−6] Although quite a few alkyne hydrogenation reactions have been found to be promoted by ruthenium carbonyl clusters,[3−6] the intermediacy of polynuclear catalytic species has been demonstrated only in a few instances.[4−6] The catalytic reaction we report here is a new example of alkyne hydrogenation under homogeneous conditions in which kinetic, chemical, and spectroscopic studies support a catalytic mechanism based on trinuclear cluster species.

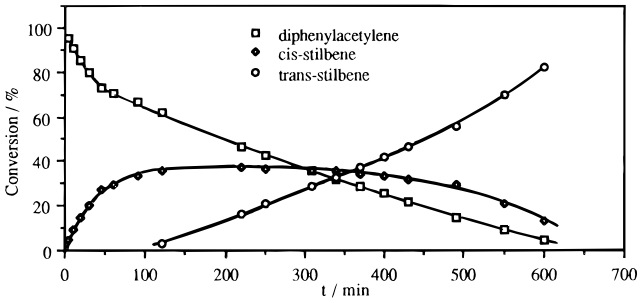
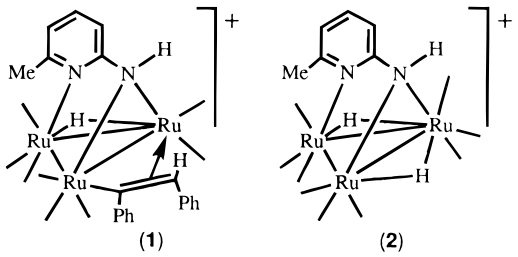


Figure 1. Evolution of the catalytic hydrogenation of diphenylacetylene promoted by complex **1** (1,2-dichloroethane, 333 K, $[\mathbf{1}] = 1.11 \times 10^{-3}$ M, $[Ph_2C_2] = 0.111$ M, $P(H_2) = 0.573$ atm).

Chart 1



Results and Discussion

The cationic hydridoalkenyl cluster complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(\mu,\eta^1{:}\eta^2\text{-}PhC{=}CHPh)(CO)_8][BF_4]$ (**1**; Hampy = 2-amino-6-methylpyridine) (Chart 1), which can be easily made by protonation of $[Ru_3(\mu_3\text{-}ampy)(\mu,\eta^1{:}\eta^2\text{-}PhC{=}CHPh)(CO)_8]$ with $HBF_4{\cdot}OEt_2$,[6] has been found to be a catalyst precursor for the homogeneous hydrogenation of diphenylacetylene under very mild conditions (turnover frequency 29.2 h^{-1}, in 1,2-dichloroethane, at 333 K, for $[\mathbf{1}] = 1.11 \times 10^{-3}$ M, $[Ph_2C_2] = 0.111$ M, and $P(H_2) = 0.573$ atm), giving a mixture of *cis*- and *trans*-stilbene (Figure 1). As normally observed in other hydrogenations of diphenylacetylene, *cis*-stilbene is the kinetic product since the *cis*- to *trans*-stilbene ratio decreases continuously as the hydrogenation of the alkyne progresses.[3−6] Hydrogenation of stilbene to 1,2-diphenylethane was not detected, even at high conversions. No activation period was observed. Compound **1** was the only metal complex observed in the catalytic solutions by IR spectroscopy.

* E-mail: jac@dwarf1.quimica.uniovi.es. Fax: int + 34.8.5103446.
⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) For relevant reviews on metal clusters in homogeneous catalysis, see: (a) 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. (b) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41. (c) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A. *Synlett* **1995**, 579. (d) Marko, L.; Vici-Orosz, A. In *Metal Clusters in Catalysis*; Knözinger, H., Gates, B. C., Guczi, L., Eds.; Elsevier: Amsterdam, The Netherlands, 1986; Chapter 5, p 89. (e) Whyman, R. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; John Wiley & Sons: New York, 1980; Chapter 8, p 545.

(2) See, for example: (a) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693, and references therein. (b) Laine, R. M. *J. Mol. Catal.* **1982**, *14*, 137.

(3) 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.; Bonnet, J.-J. *J. Am. Chem. Soc.* **1990**, *112*, 8607. (f) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *J. Mol. Catal.* **1992**, *71*, L7. (g) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *Organometallics* **1992**, *11*, 4355. (h) Cabeza, J. A.; Fernández-Colinas, J. M.; García-Granda, S.; Llamazares, A.; López-Ortiz, F.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 426.

(4) (a) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *Organometallics* **1993**, *12*, 4141. (b) Alvarez, S.; Briard, P.; Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; Mulla, F.; Ouahab, L.; Riera, V. *Organometallics* **1994**, *13*, 4360. (c) Cabeza, J. A.; Llamazares, A.; Riera, V.; Briard, P.; Ouahab, L. *J. Organomet. Chem.* **1994**, *480*, 205.

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

(6) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *Organometallics* **1994**, *13*, 4352; *Organometallics* **1995**, *14*, 3120.

0276-7333/96/2315-0449$12.00/0

Table 1. Kinetic Data for the Hydrogenation of Diphenylacetylene Promoted by Complex 1 in 1,2-Dichloroethane at 333 K

$P(H_2)$ (atm)	10^3[**1**] (M)	[Ph_2C_2] (M)	10^6(rate)[a]
0.205	1.11	0.111	0.31
0.331	1.11	0.111	0.48
0.468	1.11	0.111	0.63
0.573	1.11	0.111	0.80
0.965	1.11	0.111	1.41
1.178	1.11	0.111	1.52
0.573	0.55	0.111	0.37
0.573	0.83	0.111	0.50
0.573	1.66	0.111	0.95
0.573	2.22	0.111	1.08
0.573	1.11	0.028	0.63
0.573	1.11	0.056	0.75
0.573	1.11	0.224	1.10
0.573	1.11	0.337	0.90

[a] Rate, $-dV_c/dt$ (L s^{-1}), where V_c is the volume of consumed hydrogen corrected to that corresponding to 1 atm.

In order to get some knowledge about the nature of the catalytic species involved in the hydrogenation process, the reactivity of complex **1** with hydrogen and diphenylacetylene was studied. Complex **1** reacted with hydrogen (1,2-dichloroethane, H_2 bubbled, 333 K, 1 h) to give *cis*- and *trans*-stilbene, the known[7] dihydride [$Ru_3(\mu$-H$)_2(\mu_3$-ampy$)(CO)_9$][BF_4] (**2**; Chart 1), and minor amounts of some unidentified decomposition products. This reactivity can be compared to that found for the neutral precursor [$Ru_3(\mu_3$-ampy$)(\mu,\eta^1{:}\eta^2$-PhC═CHPh$)(CO)_8$], which reacts with hydrogen to give a mixture of [$Ru_3(\mu$-H$)(\mu_3$-ampy$)(CO)_9$] and a hexanuclear hexahydrido derivative.[6] On the other hand, no reaction was observed between complex **1** and diphenylacetylene (1,2-dichloroethane, 333 K, 1 h); however, although the reactivity of [$Ru_3(\mu_3$-ampy$)(\mu,\eta^1{:}\eta^2$-PhC═CHPh$)(CO)_8$] with alkynes has not been reported, the related neutral complex [$Ru_3(\mu_3$-anpy$)(\mu,\eta^1{:}\eta^2$-PhC═CHPh$)(CO)_8$] (Hanpy = 2-anilinopyridine) reacts with alkynes and other unsaturated organic molecules to give insertion products.[8]

As kinetic measurements are essential in order to establish mechanisms of homogeneously catalyzed reactions, a kinetic study of the hydrogenation of diphenylacetylene mediated by complex **1** was carried out. Hydrogenation rates were obtained at 333 K by measuring the hydrogen uptake as a function of time. We used data corresponding to the first 30 min of each reaction in order to base the kinetic analysis on initial rates and to make sure that all data correspond to the hydrogenation reaction (no *cis*- to *trans*-stilbene isomerization is observed during this period, Figure 1) . The rate dependence on each reagent was determined by measuring the rates of several runs at different concentrations of that reagent with the concentrations of the other two reagents kept constant (Table 1). Plots of log(rate) *vs* log($P(H_2)$), log[**1**], and log[Ph_2C_2] afforded straight lines of slopes 0.80, 0.94, and 0.05, respectively (Figure 2), indicating that the catalytic reaction is first order in the concentration of **1**, first order in hydrogen pressure, and zero order in the concentration of diphenylacetylene. These data confirm that the incorporation of the substrate into the catalytic cycle should occur after the rate-limiting step, which should be the oxidative addition of hydrogen or a subsequent reaction. The first-order dependence in cluster concentration indicates that each trinuclear cluster **1** produces only one catalytic species (which may be itself).

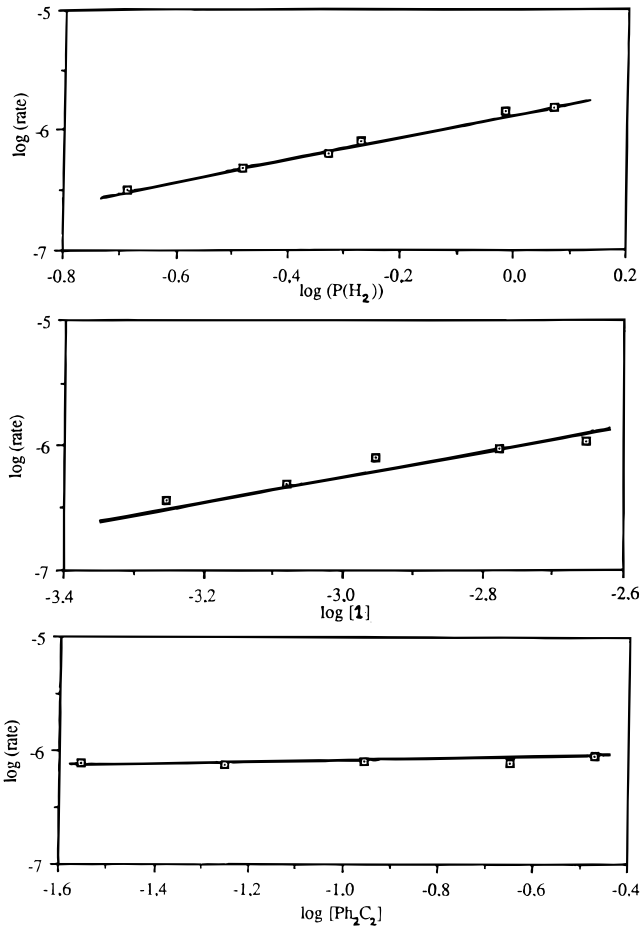


Figure 2. Partial reaction orders with respect to $P(H_2)$ (top), [**1**] (middle), and [Ph_2C_2] (bottom) for the hydrogenation of diphenylacetylene promoted by complex **1**.

Figure 3 shows a possible mechanism for this hydrogenation reaction. It involves the decoordination of the olefinic moiety of the alkenyl ligand to give an unsaturated intermediate (**A**, K_1) which oxidatively adds hydrogen (k_2, rate-limiting step) to give a trihydrido intermediate (**B**); a fast reductive elimination of *cis*-stilbene from **B** would lead to an unsaturated dihydrido species which would rapidly add diphenylacetylene regenerating complex **1**. A kinetic analysis of this mechanism renders the rate law

$$v = -d[Ph_2C_2]/dt = K_1k_2[\mathbf{1}][H_2]$$

which is in excellent agreement with the experimental kinetic data. The fact that **1** is the only carbonyl complex observed by IR spectroscopy during the catalytic runs also supports this mechanism because the equilibrium constant K_1 should have a very small value (species **A** has never been observed in solutions of complex **1**), and if k_2 is the slowest step, all the other intermediates in the catalytic cycle should have very short lives. Furthermore, this mechanism would also explain the formation of the cationic dihydride [$Ru_3(\mu$-H$)_2(\mu_3$-ampy$)(CO)_9$][BF_4] (**2**) and some other decomposition products in the reaction of complex **1** with hydro-

(7) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Bois, C.; Jeannin, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 3347.
(8) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673.

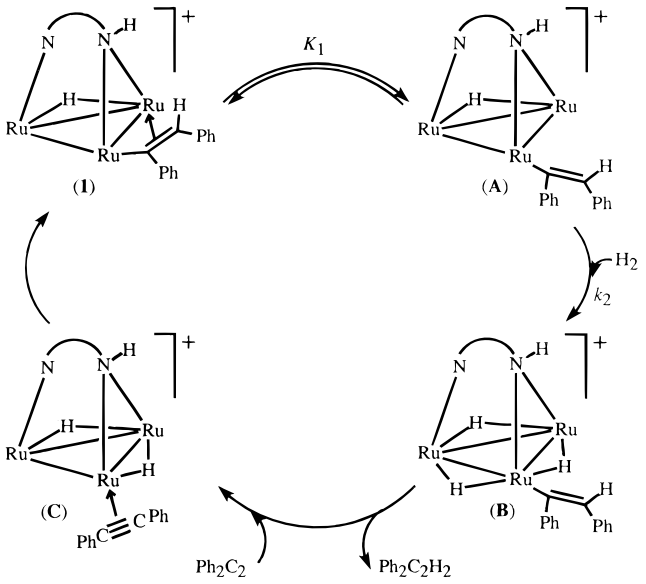


Figure 3. Proposed mechanism for the hydrogenation of diphenylacetylene promoted by complex **1**. All cluster compounds contain eight CO ligands.

gen, since in the absence of diphenylacetylene, the intermediate formed after the reductive elimination of stilbene from **B** should be an unstable coordinatively unsaturated dihydrido compound which only contains eight CO ligands.

The possibilities that the catalysis would be promoted by the cationic dihydride **2** (which is formed from **1** and hydrogen) or by the neutral compound $[Ru_3(\mu_3\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_8]$ (which would arise from deprotonation of complex **1**) can be ruled out because, under similar catalytic conditions, the former complex gives very slow rates (turnover frequency 5.7 h^{-1}), while the latter is more efficient than complex **1** (turnover frequency 38.8 h^{-1}).[6] Moreover, the rates obtained using **1** as catalyst precursor are not affected by the addition of $HBF_4{\cdot}OEt_2$ to the catalytic solutions, supporting the nonexistence of a deprotonation step in the catalytic process, since complex **1** is quantitatively formed when $[Ru_3(\mu_3\text{-ampy})(\mu,\eta^1{:}\eta^2\text{-PhC=CHPh})(CO)_8]$ is treated with $HBF_4{\cdot}OEt_2$.[6]

Although the addition of a small volume of CO into the catalytic system produced a strong reduction of the hydrogenation rate, this does not necessarily imply the existence of a CO dissociation step in the catalytic cycle, since CO is an excellent ligand which may compete for the vacant coordination sites with the other reagents; in fact, it is known that complex **1** reacts with CO (1 atm, 293 K) to give $[Ru_3(\mu\text{-ampy})(CO)_{10}][BF_4]$.[9] More probably, the vacant site needed for the addition of hydrogen arises from decoordination of the alkene fragment of complex **1**. Such a ligand-based bridge-opening activation step has been previously postulated as that responsible for the high reactivity of carbonyl clusters containing $\mu,\eta^1{:}\eta^2$-alkenyl ligands.[6]

In conclusion, this work reports the first homogeneous catalytic reaction mediated by a cationic carbonyl cluster complex and presents data which support a mechanism in which only trinuclear cationic species are involved.

Experimental Section

General Data. Compound **1** was prepared as described previously.[6] 1,2-Dichloroethane (Aldrich) was dried over calcium hydride and distilled under nitrogen prior to use. Diphenylacetylene and *cis*- and *trans*-stilbene were used as received from Aldrich. Hydrogen (99.995%) was purchased from SEO. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using a 0.1-mm CaF_2 cell. ^1H NMR spectra were run at 23 °C on a Bruker AC-300 instrument, using $SiMe_4$ as internal standard.

Catalytic Hydrogenation of Diphenylacetylene. The appropriate amounts of complex **1** and diphenylacetylene (Table 1) were placed in a two-necked 25-mL flask with one neck connected to a gas buret, which in turn was connected to a vacuum line. The flask was closed by a septum and the system evacuated and filled with hydrogen five times. Degassed 1,2-dichloroethane (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 333 K and shaken during the run at 600 shakes min^{-1} with a Selecta shaker. An equilibration time of 2 min was allowed before acquiring any data. The working partial pressure of hydrogen was determined by substracting the solvent vapor pressure at 333 K from the measured total pressure. Reaction rates were obtained by measuring the hydrogen consumption in the gas buret as a function of time. Plots of the kinetic data were fitted using conventional regression programs. The data given in Figure 1 were obtained by monitoring the catalytic reaction by GC, using a Perkin-Elmer 8600 gas chromatograph, with an oven temperature of 250 °C, equipped with a 30-m Supelcowax-10 capillary column (i.d. 0.25 mm) and a flame ionization detector; quantification was achieved with a PE-Nelson 1020 integrator.

Reaction of Complex 1 with Hydrogen. A 50-mg amount of complex **1** and 10 mL of 1,2-dichloroethane were placed under nitrogen in a two-necked flask equipped with a hydrogen inlet and a reflux condenser stoppered with a silicone oil bubbler. Hydrogen was then bubbled through the solution while it was kept at 60 °C for 1 h. The solvent was removed in a vacuum line, and the residue was analyzed by GC and by ^1H NMR spectroscopy. The gas chromatogram showed *cis*- and *trans*-stilbene. The ^1H NMR spectrum ($CDCl_3$) showed the presence of $[Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-ampy})(CO)_9][BF_4]$[7] accompanied by small amounts of other hydrido derivatives.

Acknowledgment. Financial support of this work by the DGICYT (Grant PB92-1007) and the University of Oviedo (Grant DF94-222-3) is gratefully acknowledged.

OM950444H

(9) Cabeza, J. A.; del Río, I.; Llamazares, A.; Riera, V.; García-Granda, S.; Van der Maelen, J. F. *Inorg. Chem.* **1995**, *34*, 1620.