

$\nu(\text{C-O-C}$  and  $\text{ClO}_4)$  1089 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{34}\text{ClO}_{10}\text{STl}$ : C, 37.21; H, 4.62. Found: C, 37.45; H, 4.64.

**(18-Crown-6)phenyl(4-bromo-2-thienyl)thallium(III) perchlorate (10)**, mp 223 °C dec, was isolated in 92% yield (0.743 g, 0.92 mmol) after recrystallization from 5 mL/100 mL  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ .  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.62 (s, 24 H, 18-crown-6), 7.64 (dd,  $J_{\text{TH}} = 547$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.56 (dt,  $J_{\text{TH}} = 183$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_3$ ), 7.41 (dt,  $J_{\text{TH}} = 66$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_4$ ), 7.34 (d,  $J_{\text{TH}} = 244$  Hz, 1 H,  $\text{H}_3$ ), 7.74 (d,  $J_{\text{TH}} = 160$  Hz, 1 H,  $\text{H}_5$ ). IR (Nujol):  $\nu(\text{C-O-C}$  and  $\text{ClO}_4)$  1086 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{31}\text{BrClO}_{10}\text{STl}$ : C, 32.73; H, 3.87. Found: C, 32.58; H, 3.99.

**(18-Crown-6)phenyl(4-formyl-2-thienyl)thallium(III) perchlorate (11)**, mp 295 °C dec, was isolated in 48% yield (0.363 g, 0.48 mmol) after silica gel column chromatography (20 mm i.d.  $\times$  150 mm, eluent 1/2  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ , Nakarai Tesque mesh 70-230) and recrystallization from 5 mL/100 mL  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ .  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.64 (s, 24 H, 18-crown-6), 7.70 (dd,  $J_{\text{TH}} = 544$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.59 (dt,  $J_{\text{TH}} = 182$  Hz,  $J_{\text{TH}} = 7.0$  Hz, 2 H,  $\text{H}_3$ ), 7.45 (dt,  $J_{\text{TH}} = 65$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_4$ ), 7.79 (d,  $J_{\text{TH}} = 258$  Hz, 1 H,  $\text{H}_3$ ), 8.65 (d,  $J_{\text{TH}} = 157$  Hz, 1 H,  $\text{H}_5$ ), 10.20 (d,  $J_{\text{TH}} = 66$  Hz, 1 H, CHO). IR (Nujol):  $\nu(\text{C=O})$  1680 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{32}\text{ClO}_{11}\text{STl}$ : C, 36.52; H, 4.26. Found: C, 36.24; H, 4.18.

**Preparation of (18-Crown-6)phenyl(2-furyl)thallium(III) Perchlorate (12)**. The reaction of 1 (0.745 g, 1.00 mmol) with furan (0.272 g, 8.00 mmol) was carried out at room temperature for 1 day. The complex 13 (0.477 g, 67%), mp >230 °C dec, was isolated after recrystallization from 5 mL/100 mL  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ .  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  3.67 (s, 24 H, 18-crown-6), 7.69 (dd,  $J_{\text{TH}} = 527$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_2$ ), 7.66 (dt,  $J_{\text{TH}} = 170$  Hz,  $J_{\text{HH}} = 7.0$  Hz, 2 H,  $\text{H}_3$ ), 7.42 (dt,  $J_{\text{TH}} = 64$  Hz,  $J_{\text{HH}} = 8.0$  Hz, 1 H,  $\text{H}_4$ ), 7.37 (d,  $J_{\text{TH}} = 200$  Hz, 1 H,  $\text{H}_3$ ), 6.90 (d,  $J_{\text{TH}} = 62$  Hz, 1 H,  $\text{H}_4$ ), 7.31 (d,  $J_{\text{TH}} = 38$  Hz, 1 H,  $\text{H}_5$ ). IR (Nujol):  $\nu(\text{C-O-C}$  and  $\text{ClO}_4)$  1080 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{32}\text{ClO}_{11}\text{Tl}$ : C, 37.10; H, 4.53. Found: C, 37.04; H, 4.59.

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## Kinetic and Chemical Evidence for the Participation of Mononuclear Catalytic Species in the Homogeneous Hydrogenation of Diphenylacetylene Promoted by an Edge-Bridged Triruthenium Carbonyl Cluster Complex

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**Summary:** The edge-bridged cluster complex  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-C}_8\text{H}_{11}\text{N}_2)(\text{CO})_9]$  (1) ( $\text{C}_8\text{H}_{12}\text{N}_2 = 1,2\text{-diamino-4,5-dimethylbenzene}$ ) is a catalyst precursor for the selective homogeneous hydrogenation of diphenylacetylene to stilbene under very mild conditions. The binuclear ruthenium(I) alkenyl derivative  $[\text{Ru}_2(\mu\text{-C}_8\text{H}_{11}\text{N}_2)(\mu\text{-}\eta^1, \eta^2\text{-PhC=C(H)Ph})(\text{CO})_5]$  (2), which has been observed during the catalytic reaction, has been isolated from the reaction of 1 with diphenylacetylene; however, 2 does not react with hydrogen. These results, coupled to a kinetic study of the catalytic reaction, which follows the rate law  $-\text{d}[\text{H}_2]/\text{dt} = K[1](P(\text{H}_2))$ , where  $K = 9.18 \times 10^{-3} \text{ atm}^{-2} \text{ s}^{-1}$  at 333 K, suggest that the catalytic species is mononuclear.

### Introduction

There is great interest in the search for bi- or polynuclear complexes in which two or more metal centers are active in catalysis under homogeneous conditions.<sup>1</sup> However, this has been confirmed only in a few instances.<sup>1a</sup> In other cases, it is known that the original polynuclear framework fragments to give species of different nuclearity,<sup>2</sup> but in

most cases, the fate of the catalytic precursor is unknown.<sup>1</sup> The use of ligand-bridged polynuclear complexes has been claimed as a method for preventing cluster degradation,<sup>3</sup> but it has met only a limited success.<sup>4</sup> In this context, the knowledge of the reaction kinetics is essential to establish the nuclearity of the catalytic species and the reaction mechanisms.<sup>1a</sup>

We have been interested in the effectiveness of ligand-bridged triruthenium cluster complexes as homogeneous catalyst precursors in hydrogenation reactions.<sup>5,6</sup> Here we report the reactivity of diphenylacetylene and hydrogen with  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-C}_8\text{H}_{11}\text{N}_2)(\text{CO})_9]$  (1) ( $\text{C}_8\text{H}_{12}\text{N}_2 = 1,2\text{-diamino-4,5-dimethylbenzene}$ ), a cluster complex containing an edge-bridging N-donor ligand,<sup>7</sup> and its use as catalyst

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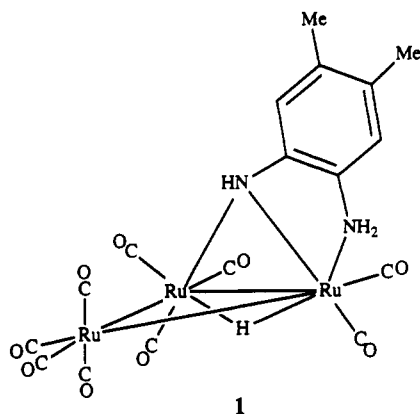
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precursor in the hydrogenation of diphenylacetylene.

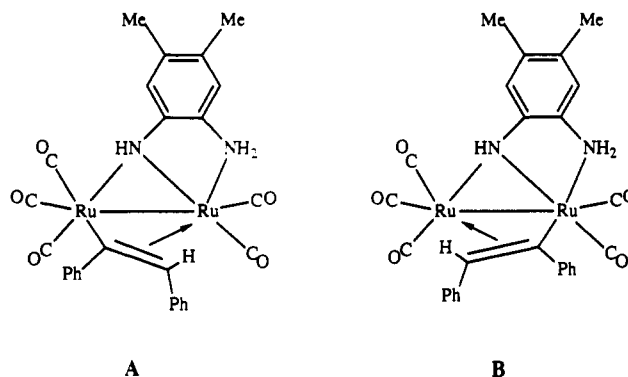


## Results and Discussion

**Reactivity of Complex 1 with Diphenylacetylene and Hydrogen.** The reactions of 1 with diphenylacetylene and hydrogen were investigated on a stoichiometric basis. With diphenylacetylene a mixture of products was observed from which only one, namely  $[\text{Ru}_2(\mu\text{-C}_8\text{H}_{11}\text{N}_2)(\mu\text{-}\eta^1, \eta^2\text{-PhC}=\text{C}(\text{H})\text{Ph})(\text{CO})_5]$  (2), could be isolated and characterized (vide infra). This complex partially decomposes on the chromatographic column and could only be obtained in 33% yield. A brown residue remained uneluted at the top of the column, and trace amounts of two other compounds, perhaps corresponding to decomposition products, were also eluted but could not be identified.<sup>8</sup> These results suggest that 1 reacts with diphenylacetylene to give a mixture of 2 and a mononuclear species which is retained in the chromatographic column. Similar reactions of the edge-bridged clusters  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-Cl})(\text{CO})_{10}]$  and  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-O}=\text{CR})(\text{CO})_{10}]$ , which involve the loss of one metal center upon treatment with alkynes or olefins to give binuclear complexes, have been reported.<sup>9</sup>

Compound 2 was characterized spectroscopically and by elemental analysis. Its IR spectrum showed five absorptions in the carbonyl region, and its <sup>1</sup>H NMR spectrum confirmed the absence of hydride ligands and the presence of the deprotonated form of the 1,2-diamino-4,5-dimethylbenzene and the diphenylalkenyl ligands. At -40 °C, its <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed, apart from the resonances of the organic ligands, five carbonyl resonances, at 204.6, 204.1, 201.1, 199.5, and 196.4 ppm; those at 204.6, 201.1, and 196.4 ppm broadened as the temperature was raised, being nearly unobservable at room temperature. These data indicate the existence of a fluxional process at room temperature and are consistent with a tripodal twist of a  $\text{Ru}(\text{CO})_3$  unit.<sup>10</sup> Therefore, we propose for complex 2 one of the two isomeric structures shown (A or B). Unfortunately, we were unable to grow single crystals suitable for an X-ray diffraction analysis.

No reaction was observed when complex 1 was treated with hydrogen (1 atm) in refluxing THF; even in refluxing toluene, the reaction was slow, giving an untractable mixture of products. This implies that in catalytic ex-



periments, which take place efficiently at 60 °C (vide infra), complex 1 reacts with diphenylacetylene and not with hydrogen, being transformed into 2 and a catalytic precursor which most likely is mononuclear. Complex 2 does not catalyze the hydrogenation of diphenylacetylene (1 atm, 60 °C).

**Hydrogenation of Diphenylacetylene Promoted by 1.** Figure 1 shows that complex 1 is an efficient catalyst precursor for the homogeneous hydrogenation of diphenylacetylene. The turnover frequency in toluene at 333 K and 0.838 atm of  $\text{H}_2$  was shown to be ca. 1.3 mol of converted diphenylacetylene per mol of 1 per min. *cis*-Stilbene is the kinetic product, but it is progressively isomerized into *trans*-stilbene while diphenylacetylene is being consumed; no hydrogenation of stilbene to ethylbenzene was observed.

A simple rate law for this catalytic reaction is

$$-d[\text{H}_2]/dt = k_1[1]^a[\text{Ph}_2\text{C}_2]^b(P(\text{H}_2))^c \quad (1)$$

With a large excess of diphenylacetylene, the rate law is simplified to

$$-d[\text{H}_2]/dt = k_2[1]^a(P(\text{H}_2))^c \quad (2)$$

Initial hydrogenation rates were obtained by measuring the hydrogen uptake as a function of time, as shown in Figure 2. From the ideal gas law it can be deduced that  $d[\text{H}_2]/dt = d(n/V_{\text{sol}})/dt = d(PV/dt)/RTV_{\text{sol}}$ ; therefore, at any working pressure and using a large excess of diphenylacetylene, correcting the volume of consumed  $\text{H}_2$  ( $V$ ) to that corresponding to 1 atm ( $V_c$ ) allows the use of eq 3, a rate law which is pseudo-zero order in hydrogen

$$-(dV_c/dt)/RTV_{\text{sol}} = K_{\text{obs}}[1]^a \quad (3)$$

pressure ( $P(\text{H}_2) = 1$ ), where  $-(dV_c/dt)$  is the initial rate measured from gas-uptake experiments,  $R$  is the molar gas constant,  $T$  is the temperature (K), and  $V_{\text{sol}}$  is the volume of the reaction solution.

In order to determine the rate dependence on the various reaction components, hydrogenation runs were carried out at different cluster and substrate concentrations and at different hydrogen pressures (Table I). Plots of  $\log(-dV_c/dt)$  vs  $\log[1]$ ,  $\log(-dV_c/dt)$  vs  $\log P(\text{H}_2)$ , and  $\log(-dV_c/dt)$  vs  $\log[\text{Ph}_2\text{C}_2]$  yielded straight lines of slopes 0.90, 1.03, and -0.05, respectively (Figure 3), indicating that the reaction is first-order in cluster concentration and in hydrogen pressure and zero-order in diphenylacetylene concentration ( $a = 1$ ,  $b = 0$ , and  $c = 1$  in eq 1). Therefore, the catalytic rate law is

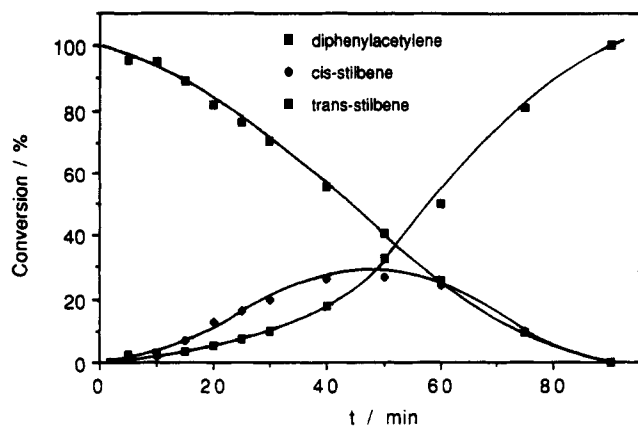
$$-d[\text{H}_2]/dt = k_3[1](P(\text{H}_2)) \quad (4)$$

Consequently,  $K_{\text{obs}} = K_3(P(\text{H}_2))$ . Since the values of  $K_{\text{obs}}$  (Table I) can be easily obtained from eq 3, a plot of  $K_{\text{obs}}$  vs  $P(\text{H}_2)$  afforded a value for  $K_3$  of  $9.18 \times 10^{-3} \text{ atm}^{-2} \text{ s}^{-1}$  at 333 K.

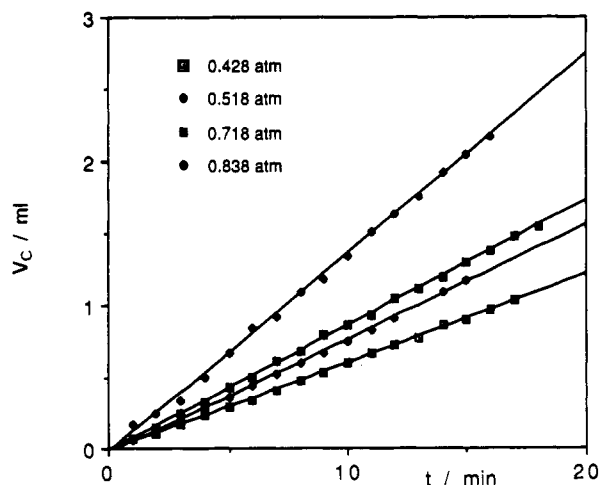
(8) The <sup>1</sup>H NMR spectra of these two products showed the presence of the  $\text{C}_8\text{H}_{11}\text{N}_2$  ligand. IR: orange product (THF), 2062 s, 2028 s, 2011 vs, 1992 s, 1973 m, 1941 w  $\text{cm}^{-1}$ ; yellow product (THF), 2063 w, 2037 m, 2022 m, 1999 vs, 1949 m, 1929 m  $\text{cm}^{-1}$ .

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**Figure 1.** Evolution of the hydrogenation of diphenylacetylene promoted by 1, in toluene at 333 K:  $[1] = 1.10 \times 10^{-3}$  M;  $[\text{Ph}_2\text{C}_2] = 0.112$  M;  $P(\text{H}_2) = 0.838$  atm.



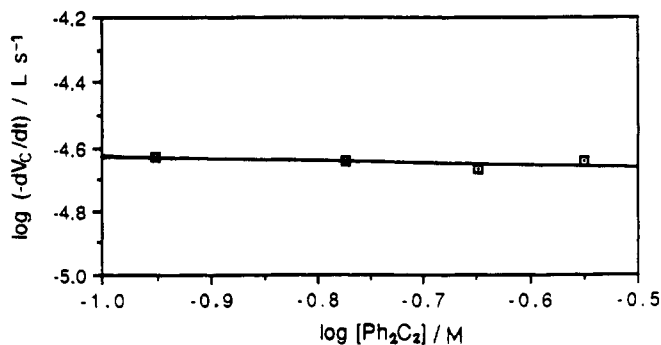
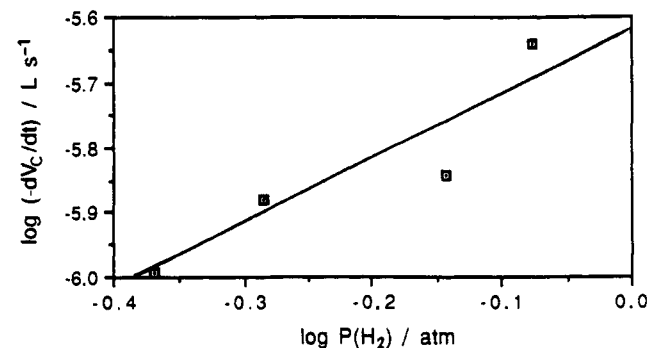
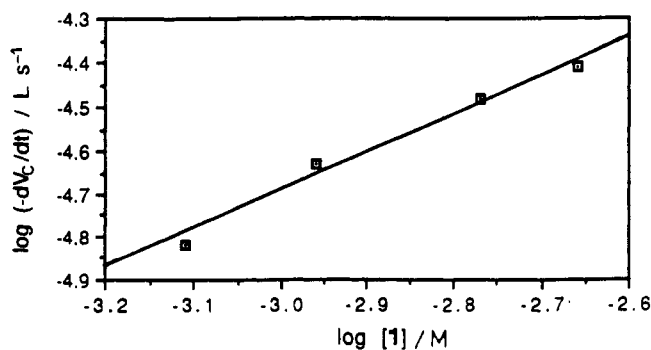
**Figure 2.** Gas-uptake (corrected to 1 atm) plots at different hydrogen pressures for the hydrogenation of diphenylacetylene promoted by 1, in toluene at 333 K:  $[1] = 1.10 \times 10^{-3}$  M;  $[\text{Ph}_2\text{C}_2] = 0.112$  M.

**Table I. Kinetic Data for the Hydrogenation of Diphenylacetylene Promoted by 1**

$T$ , K	$P(\text{H}_2)$ , atm	$10^3[1]$ , M	$[\text{Ph}_2\text{C}_2]$ , M	$10^6(-dV_c/dt)$ , L s $^{-1}$	$10^2K_{\text{obs}}$ , atm $^{-1}$ s $^{-1}$
333	0.428	1.10	0.112	0.10	0.33
	0.518	1.10	0.112	0.13	0.43
	0.718	1.10	0.112	0.14	0.47
	0.838	1.10	0.112	0.23	0.77
353	0.663	0.78	0.112	1.53	6.78
	0.663	1.10	0.112	2.36	7.41
	0.663	1.70	0.112	3.35	6.81
	0.663	2.20	0.112	3.87	6.08
	0.663	1.10	0.168	2.27	7.13
	0.663	1.10	0.225	2.12	6.66
	0.663	1.10	0.281	2.31	7.25

When the catalytic reactions were monitored by IR spectroscopy, complex 2 was observed from the beginning to the end of the reaction. However, in subsequent experiments, we proved that 2 does not react with hydrogen (1 atm, toluene, 110 °C), and therefore, it cannot be the catalytic species.

Although with all data reported above it is not possible to propose a mechanism for the catalytic reaction, it is clear that the addition of hydrogen to the catalyst is the slow step of the catalytic cycle and that the addition of diphenylacetylene is subsequent to the addition of hydrogen. With respect to the nuclearity of the catalyst, all the data suggest that it is a mononuclear species: (a) the trinuclear



**Figure 3.** Partial reaction orders with respect to  $[1]$  (top),  $P(\text{H}_2)$  (middle), and  $[\text{Ph}_2\text{C}_2]$  (bottom) for the hydrogenation of diphenylacetylene promoted by 1, in toluene.

complex 1 reacts with diphenylacetylene to give the binuclear complex 2 and a presumably mononuclear species, (b) 1 and 2 do not react with hydrogen under the conditions used in the catalytic runs, and (c) the catalytic reaction is first-order in the concentration of added 1 and this concentration should be equal to that of the mononuclear species that arises from the reaction of 1 with diphenylacetylene.

In conclusion, this work demonstrates that the trinuclear complex 1 is an efficient catalyst precursor for the selective homogeneous hydrogenation of diphenylacetylene under very mild conditions and presents data which suggest that the actual catalytic species is mononuclear,<sup>11</sup> contributing to shed light about the fate of edge-bridged trinuclear cluster complexes when used as homogeneous catalyst precursors.

### Experimental Section

Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or  $\text{CaH}_2$  (dichloromethane) and distilled under nitrogen prior to use. Noncatalytic reactions were carried out under

(11) In most published works in which carbonyl clusters are used as homogeneous catalyst precursors, the lack of kinetic studies prevents the determination of the nuclearity of the catalytic species.<sup>1</sup>

nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). Compound 1 was prepared as described previously;<sup>7</sup> <sup>13</sup>C-enriched 1 was made from <sup>13</sup>C-enriched [Ru<sub>3</sub>(CO)<sub>12</sub>].<sup>10</sup> Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF<sub>2</sub> cells. <sup>1</sup>H and <sup>13</sup>C NMR spectra were run with Bruker AC-200 and AC-300 instruments, using internal SiMe<sub>4</sub> as standard (δ = 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.

**Reaction of Compound 1 with Diphenylacetylene.** A THF (10 mL) solution of complex 1 (103 mg, 0.156 mmol) and diphenylacetylene (56 mg, 0.312 mmol) was stirred at reflux temperature for 35 min. The solvent was removed under reduced pressure and the residue dissolved in toluene (1 mL). The resulting solution was chromatographed on a neutral alumina column (10 × 3 cm, activity IV). Orange and yellow bands were eluted with 4:1 and 2:1 hexane-dichloromethane, respectively, but they only contained trace amounts of compounds which could not be identified.<sup>8</sup> Dichloromethane eluted a pale-yellow fraction, while a brown residue remained uneluted at the top of the column. The pale-yellow fraction was evaporated to dryness to give, after crystallization from dichloromethane-hexane, [Ru<sub>2</sub>(μ-C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>)(μ-η<sup>1</sup>,η<sup>2</sup>-PhC=C(H)Ph)(CO)<sub>5</sub>] (2) as an off-white solid (35 mg, 33% based on Ru). Anal. Found: C, 49.53; H, 3.62; N, 4.43. Calcd for C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>Ru<sub>2</sub>: C, 49.39; H, 3.38; N, 4.27. ν(CO) (*n*-pentane): 2052 m, 2006 s, 1992 m, 1959 m, 1939 m, cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz, 23 °C): 7.8–6.7 (m, phenyl protons), 6.29 (s, 1H), 6.06 (s, 1H) 3.73 (s, 1H, alkenyl CH), 3.08 (AB spin system, 2H, NH<sub>2</sub>), 2.47 (s, 1H, NH), 1.85 (s, 3H, Me), 1.80 (s, 3H, Me) ppm. Selected <sup>13</sup>C{<sup>1</sup>H} NMR data (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz, -40 °C, sample enriched in <sup>13</sup>C): 204.6, 204.1, 201.1, 199.5, 196.4, (5 CO ligands), 80.2 (alkenyl CH), 19.6, 19.1 (2 Me), ppm.

**Reaction of Compound 1 with Hydrogen.** Hydrogen was bubbled through a solution of complex 1 in refluxing THF (20

mL) for 2.2 h. Since no reaction was observed by IR spectroscopy, the solvent was removed under reduced pressure, toluene (15 mL) added, and hydrogen bubbled through the resulting solution at reflux temperature (110 °C) for 2.5 h. After removal of the toluene, CD<sub>2</sub>Cl<sub>2</sub> (1 mL) was added to give an insoluble residue and a solution whose <sup>1</sup>H NMR spectrum showed it to be a mixture of compounds with no peaks in the hydride region.

**Catalytic Hydrogenation Reactions.** The evolution of the catalytic reactions (Figure 1) 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 were placed in a two-necked 25-mL flask with one neck connected to the gas buret, which was in turn 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 thermostated bath and shaken during the run at 600 min<sup>-1</sup> 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 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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**Registry No.** 1, 126751-75-5; Ru, 7440-18-8; diphenylacetylene, 501-65-5; *cis*-stilbene, 645-49-8; 4,5-dimethyl-1,2-benzenediamine, 3171-45-7.

OM920289W

## Preference of Carbonyl Ligands over Isocyanide Ligands in Nucleophile-Induced Coupling with Alkylidyne Ligands

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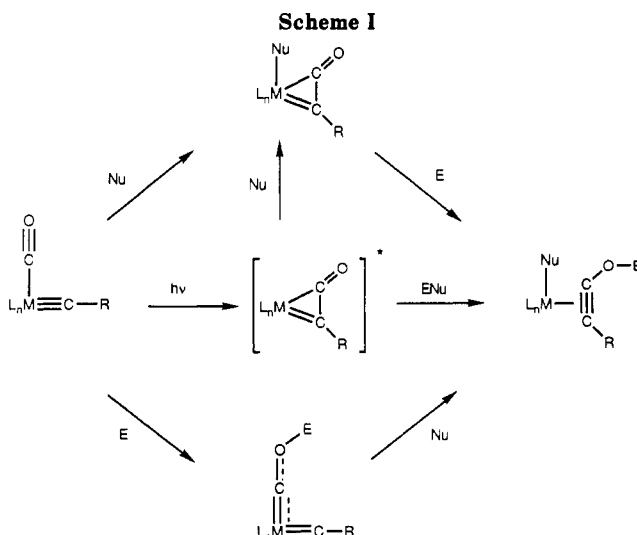
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**Summary:** W(CPh)Cl(CNCMe<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub> was prepared by reaction of W(CPh)Cl(CO)<sub>2</sub>(py)<sub>2</sub> with CNCMe<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. W(CPh)I(CNCMe<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub> was prepared by sequential reaction of W(CPh)Cl(CO)<sub>2</sub>(py)<sub>2</sub> with NaI in THF and with CNCMe<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>. Reaction of W(CPh)Cl(CNCMe<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub> with pyrrole-2-carboxaldehyde methylimine in the presence of KOH in THF gives the ketenyl complex K[W(C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>)<sub>2</sub>(PhCCO)(CO)]. Reaction of W(CPh)I(CNCMe<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub> with NaS<sub>2</sub>CNET<sub>2</sub> in THF gives a mixture of products, of which Na[W(PhCCO)(S<sub>2</sub>CNET<sub>2</sub>)<sub>2</sub>(CO)] is the main product. Reaction of W(CPh)Cl(CNCMe<sub>3</sub>)<sub>2</sub>(CO)(PMe<sub>3</sub>)<sub>2</sub> with NaS<sub>2</sub>CNET<sub>2</sub> in THF leads to the formation of [W(PhCCO)(S<sub>2</sub>CNET<sub>2</sub>)<sub>2</sub>(CO)(PMe<sub>3</sub>)<sub>2</sub>] and [W(CPh)(S<sub>2</sub>CNET<sub>2</sub>)(CO)(PMe<sub>3</sub>)<sub>2</sub>] as the main products.

### Introduction

In a recent review article<sup>1</sup> we distinguished three fundamentally different types of alkylidyne-carbonyl cou-



pling;<sup>2</sup> nucleophile-, electrophile-, and light-induced (Scheme I). Nucleophile-induced coupling (upper path-

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