Tricyclohexylphosphine- versus Triphenylphosphine-Substituted Derivatives of a Face-Bridged Triruthenium Carbonyl Cluster Complex. A Comparative Study of Their Synthesis, Structure, and Catalytic Activity in the Homogeneous Hydrogenation of Diphenylacetylene

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The face-bridged cluster complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) (Hampy = 2-amino-6-methylpyridine) react with tricyclohexylphosphine (PCy_3) to give the respective monosubstituted derivatives $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PCy_3)]$ (**3a**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_8(PCy_3)][BF_4]$ (**4a**). Protonation of **3a** with $HBF_4{\cdot}OEt_2$ affords **5a** (an isomer of **4a**); this complex can also be prepared by stirring **4a** in THF at reflux temperature. Complex **3a** is a catalytic precursor for the homogeneous hydrogenation of diphenylacetylene (80 °C, $P(H_2) < 1$ atm), but the reaction is very slow. The alkenyl-bridged compounds $[Ru_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(CO)_7(PCy_3)]$ (**6a**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(CO)_6(PCy_3)]$ (**7a**), which are intermediates in the catalytic hydrogenation reaction, have been prepared by the sequential reactions of complex **3a** with diphenylacetylene and hydrogen. All compounds have been characterized spectroscopically (IR, NMR). The structure of complex **6a** has been determined by X-ray diffraction methods: $C_{45}H_{51}N_2O_7PRu_3$, triclinic, space group $P\bar{1}$, $a = 11.568(7)$ Å, $b = 11.684(2)$ Å, $c = 18.958(11)$ Å, $\alpha = 81.34(3)°$, $\beta = 75.84(6)°$, $\gamma = 63.92(3)°$, $Z = 2$. All results obtained are compared to those previously determined for related cluster compounds containing PPh_3 instead of PCy_3.

Introduction

In a previous paper,[2] we reported that the face-bridged cluster complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (**1**) (Chart 1, Hampy = 2-amino-6-methylpyridine) reacts with 2 equiv of tricyclohexylphosphine (PCy_3) to give the asymmetrically disubstituted derivative $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PCy_3)_2]$ (Chart 2). Interestingly, the bis(triphenylphosphine)-substituted derivative $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PPh_3)_2]$ is symmetrical (Chart 2),[3] and we have demonstrated that electronic factors are responsible for this structural difference.[2] Although little explored, the reactivity of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PCy_3)_2]$[2] differs considerably from that of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(PPh_3)_2]$.[2-4]

All these facts prompted us to examine the structure and reactivity of the products formed in the reactions of complex **1** and of its protonated derivative $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**, Chart 1) with 1 equiv of tricyclohexylphosphine. This paper reports the results obtained, comparing them to those previously described for related reactions using triphenylphosphine.[5]

On the other hand, the complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PPh_3)]$, which is the product of the reaction of

Chart 1

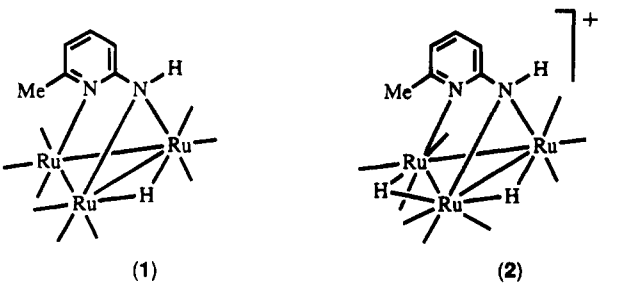
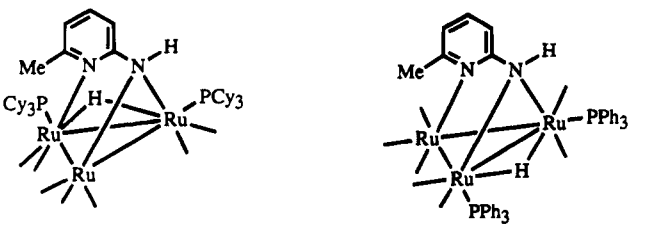


Chart 2



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(1) (a) Universidad de Oviedo. (b) CNRS.

(2) Cabeza, J. A.; Franco, R. J.; Llamazares, A.; Riera, V.; Pérez-Carreño, E.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 55.

(3) Andreu, P. L.; Cabeza, J. A.; Pellinghelli, A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* **1991**, *30*, 4616.

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

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

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complex **1** with 1 equiv of triphenylphosphine, promotes the homogeneous hydrogenation of diphenylacetylene, under very mild conditions (80 °C, $P(H_2)$ < 1 atm), following a catalytic mechanism which involves only trinuclear species.[6] Although many catalytic transformations of organic chemicals are now known to be promoted by carbonyl cluster complexes, the number of well-documented catalytic mechanisms involving polynuclear species is still low.[7] Moreover, it is known that appropriately chosen phosphine ligands may enhance the activity and selectivity of homogeneous catalysts.[8,9] In this context, this paper also reports the use of the tricyclohexylphosphine derivative $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PCy_3)]$ as a catalyst precursor for the homogeneous hydrogenation of diphenylacetylene, as well as some stoichiometric reactions relevant to the mechanism of this catalytic process.

Results and Discussion

Reactivity of Compounds 1 and 2. Complex **1** and its protonated derivative **2** (Chart 1) reacted instantaneously with 1 equiv of tricyclohexylphosphine, in THF at room temperature, to give the monosubstituted compounds $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PCy_3)]$ (**3a**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_8(PCy_3)][BF_4]$ (**4a**), respectively, in quantitative yields.

The ^1H NMR spectrum of **3a** shows the hydride resonance as a doublet with J_{P-H} = 8.9 Hz, indicative of a cis arrangement of the phosphine and hydride ligands.[3,5,10] This spectrum, as well as the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of this compound, is compatible with the structure depicted in Scheme 1 for this complex and also with a structure similar to that of the triphenylphosphine derivative **3b**, which is indeed the expected structure if one considers the strong cis-labilizing effect of the amide and hydride ligands.[3,5,10] However, the carbonyl stretching regions of the IR spectra of **3a** (Experimental Section) and **3b**[5] are considerably different, and although this spectral difference may be caused by the different basicity of the phosphine ligands, it might also be the consequence of different molecular structures. Moreover, when we prepared complex **3a** we were already aware of the different structures of the disubstituted derivatives $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_7(L)_2]$ (L = PCy_3, PPh_3; Chart 2).[2] These facts induced us to carry out a comparative ^1H NOE NMR spectroscopic study of compounds **3a** and **3b**. No single crystals of **3a** suitable for X-ray diffraction studies could be obtained.

Scheme 1

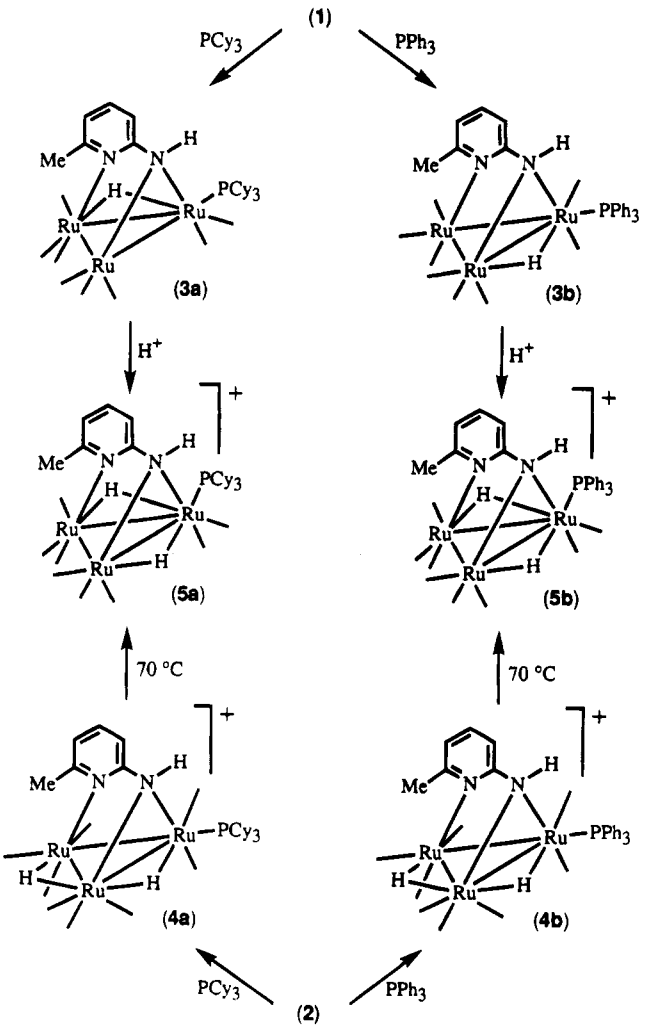


Figure 1 shows the ^1H NMR spectrum of **3a** and the NOE enhancements produced after presaturation at the frequencies of the hydride, amide, and methyl proton resonances. Interestingly, presaturation at the methyl frequency produces a positive enhancement of the hydride resonance (trace d), indicating that the methyl hydrogens and the hydride ligand are close to each other.[11] However, as expected, no enhancement of the hydride resonance of complex **3b** was observed after presaturation of its methyl resonance. These data strongly support the structure shown in Scheme 1 for complex **3a**.

The structure of the cationic dihydride derivative **4a** (Scheme 1) was established by comparing its IR and NMR spectra with those of complex **4b**. The hydride region of the ^1H NMR spectrum of **4a** is similar to that of **4b**[5] and consists of one triplet and one doublet of

(6) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *Organometallics* **1993**, *12*, 4141.

(7) For reviews on metal cluster complexes in homogeneous catalysis, see: (a) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693. (b) Gates, B. C. *Catalytic Chemistry*; John Wiley: New York, 1992; Chapter 2. (c) 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. (d) Markó, L.; Vici-Orosz, A. In *Metal Clusters in Catalysis*; Knözinger, H., Gates, B. C., Guczi, L., Eds.; Elsevier: Amsterdam, 1986; Chapter 5.

(8) See, for example: (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition-Metal Complexes*; Wiley: New York, 1992. (b) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: London, 1981. (c) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York, 1983.

(9) When coordinated to carbonyl cluster complexes, triarylphosphines undergo P—C and/or C—H bond activation reactions more easily than trialkylphosphines. Such ligand degradation reactions have often dissuaded researches from using cluster compounds containing phosphine ligands as homogeneous catalyst precursors. See, for example: (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171. (b) Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 5. (c) Minahan, D. M. A.; Hill, W. E.; McAuliffe, C. A. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2, Chapter 5.

(10) (a) Andreu, P. L.; Cabeza, J. A.; Riera, V. *Inorg. Chim. Acta* **1991**, *186*, 225. (b) Andreu, P. L.; Cabeza, J. A.; Cuyás, J. L.; Riera, V. *J. Organomet. Chem.* **1992**, *427*, 363.

(11) With few exceptions, ^1H NOE enhancements are normally observed when the distance between the corresponding hydrogen atoms is shorter than 4 Å. See, for example: Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989; Chapter 3.

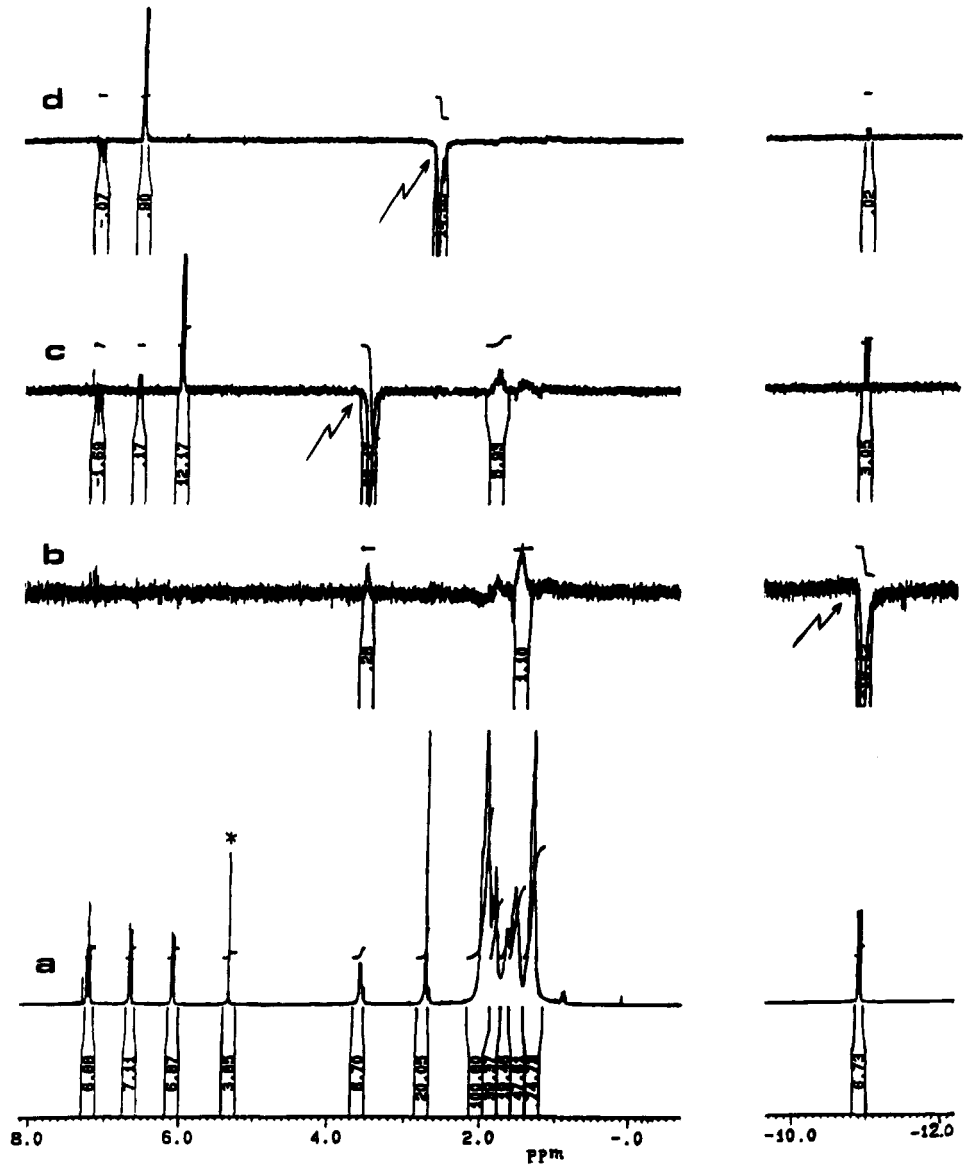


Figure 1. ^{1}H NMR spectrum (a) and difference ^{1}H NOE NMR spectra of complex **3a** after presaturation of the μ-hydride (b), NH (c), and Me (d) resonances ($CDCl_3$, 300 MHz). The peak marked with an asterisk is a solvent impurity (CH_2Cl_2).

doublets, with coupling constants ($J_{H-H'}$ = 3.3 Hz, J_{H-P} = 3.3 Hz, $J_{H'-P}$ = 12.6 Hz) which indicate that the phosphine ligand is cis to one hydride and far away from the other one. In spite of the different basicities of the PCy_3 and PPh_3 ligands, the carbonyl IR absorptions of **4a** and **4b** are nearly identical. All these data confirm that **4a** and **4b** are isostructural.

Complex **3a** could be easily protonated with $HBF_4{\cdot}OEt_2$ in dichloromethane to give the cationic dihydride $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PCy_3)][BF_4]$ (**5a**). The protonation is expected to take place at the basic, hydride-unbridged, Ru—Ru edge which contains the PCy_3 ligand; in fact, the ^{1}H NMR spectrum of **5a** suggests that the phosphine ligand is cis to one hydride (J_{H-P} = 11.6 Hz) and trans to the other ($J_{H'-P}$ = 32.4 Hz). The similarity of the IR and NMR spectroscopic data of **5a** with those of the triphenylphosphine derivative **5b**, which was previously characterized by X-ray diffraction methods,[5] indicates that both compounds are isostructural (Scheme 1). It should be noted that the transformation of **3b** into **5b** implies not only a protonation reaction but also a migration of the phosphine ligand from a position cis (in **3b**) to trans (in **5b**) to the hydride which spans the amido-bridged Ru—Ru edge. This ligand migration is not required for the transformation of **3a** into **5a**.

Complexes **4a** and **5a** are isomers, the latter being thermodynamically more stable, since the former could be transformed into the latter by stirring it in refluxing THF. However, no reaction was observed when the solution contained free tricyclohexylphosphine, suggesting that phosphine dissociation occurs in one of the reaction steps. It seems curious that the transformation of **4a** into **5a** is slower than that of **4b** into **5b**, although PCy_3 is more basic than PPh_3 and the higher basicity of the Ru—Ru—P edge was expected to be the driving force for the hydride migration. This suggests that, probably due to the different basicity of the phosphine ligands, the activation energy for PCy_3 dissociation in **4a** is higher than that for PPh_3 in **4b** and that the phosphine dissociation step occurs prior to the migration of the hydride ligand.

Catalytic Hydrogenation of Diphenylacetylene Promoted by Complex 3a and Related Stoichiometric Reactions. Complex **3a** was found to be a catalyst precursor for the homogeneous hydrogenation of diphenylacetylene to stilbene (cis and trans isomers)

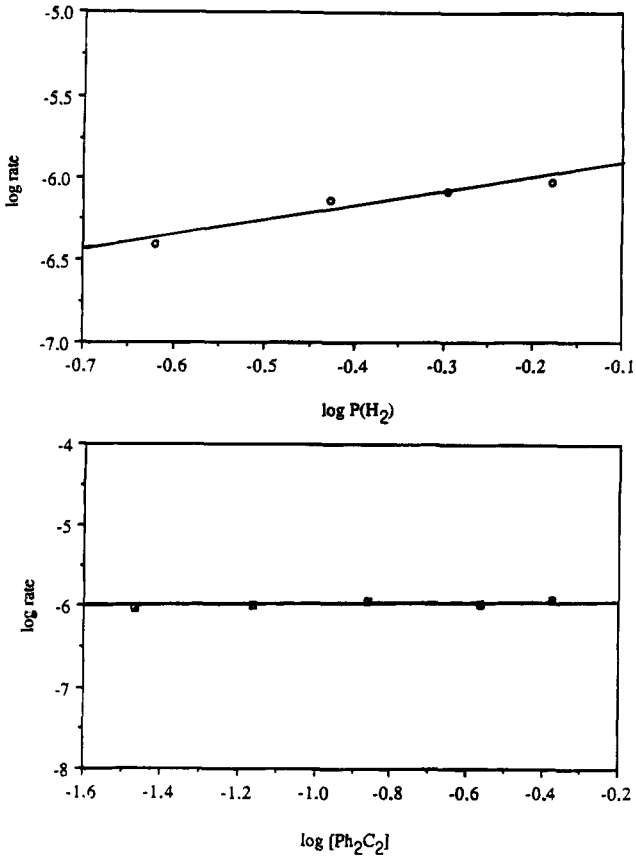


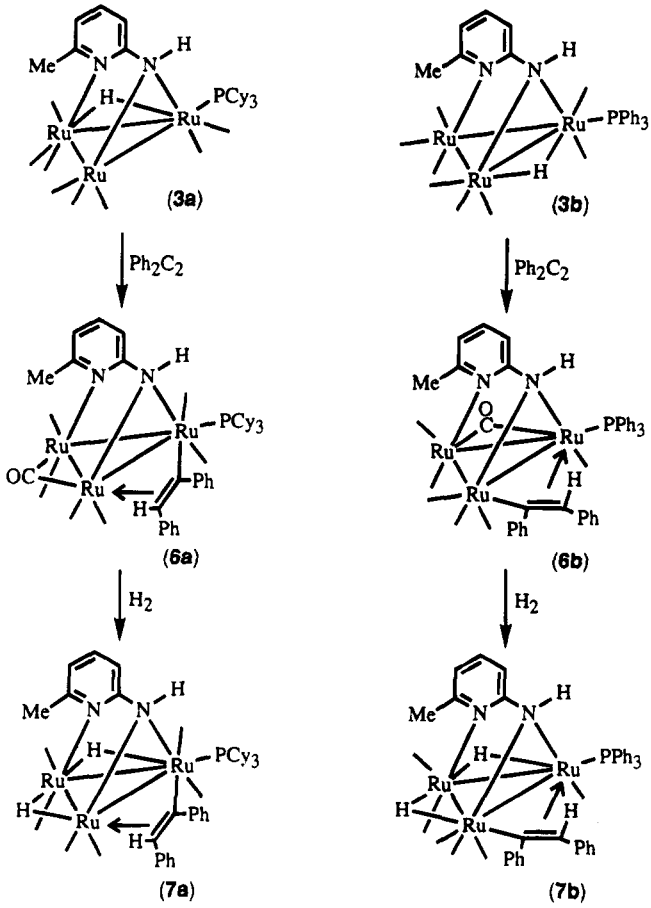
Figure 2. Kinetic plots for the catalytic hydrogenation of diphenylacetylene promoted by complex **3a** (toluene, 80 °C, [**3a**] = 1.02 × 10^{-3} mol L^{-1}, rate = liters of consumed hydrogen, corrected to 1 atm, per second) showing that the reaction is first order in hydrogen pressure (top plot, $[Ph_2C_2]$ = 0.273 mol L^{-1}, $P(H_2)$ = 0.240–0.663 atm) and zero order in substrate concentration (bottom plot, $[Ph_2C_2]$ = 0.034–0.421 mol L^{-1}, $P(H_2)$ = 0.663 atm).

under mild conditions, but the reaction is very slow (turnover frequency 8.6 h^{-1}, in toluene, at 80 °C, and $P(H_2)$ = 0.663 atm).[12] Under the same conditions, the triphenylphosphine complex **3b** is a better catalyst precursor than **3a** for the same hydrogenation reaction (turnover frequency 10.9 h^{-1}).[6]

Reaction rates were obtained by measuring the hydrogen consumption as a function of time. Unfortunately, due to the slow reaction rates and to the presence of activation periods (of variable duration depending on the concentration of **3a**) we could not carry out a detailed kinetic study of the hydrogenation reaction. Nevertheless, we managed to observe first-order kinetics in hydrogen pressure and zero-order kinetics in substrate concentration (Figure 2). The same reaction orders, as well as a first reaction order in catalyst precursor, but no activation periods, were observed when complex **3b** was used as promoter.[6]

(12) For the homogeneous hydrogenation of internal alkynes promoted by hydridoruthenium 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.; 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.

Scheme 2



In order to obtain knowledge about the mechanism of this catalytic process, the stoichiometric reactions of complex **3a** with hydrogen and diphenylacetylene were studied.

No reaction was observed when **3a** was treated with hydrogen under the conditions used in the catalytic runs. Therefore, in the catalytic reaction, complex **3a** should react first with diphenylacetylene and then with hydrogen.

The alkenyl derivative [$Ru_3(\mu_3$-ampy)(μ-PhC=CHPh)-$(CO)_7(PCy_3)$] (**6a**, Scheme 2) was found to be the only product of the reaction of complex **3a** with diphenylacetylene. Its spectroscopic data, although confirming the presence of all the ligands, were insufficient to precisely assign a structure to this cluster; therefore, an X-ray diffraction study was carried out (Figure 3, Table 1).

In complex **6a**, the alkenyl group spans the same Ru—Ru edge as the amido fragment of the ampy ligand, being σ-bonded to the ruthenium atom that supports the phosphine ligand, Ru(1), and π-bonded to the other ruthenium atom, Ru(3). A bridging carbonyl group spans the Ru(2)—Ru(3) edge. The structural parameters of the ampy and alkenyl groups are similar to those found in other triruthenium complexes containing these ligands.[13,14] Interestingly, the structure of **6a** is different from that of the triphenylphosphine complex **6b**, since the phosphine ligand of the latter is not attached to the ruthenium atom which is σ-bonded to the alkenyl group (Scheme 2).[13d]

The dihydride derivative [$Ru_3(\mu$-H)$_2(\mu_3$-ampy)(μ-PhC=CHPh)$(CO)_6(PCy_3)$] (**7a**, Scheme 2) was easily ob-

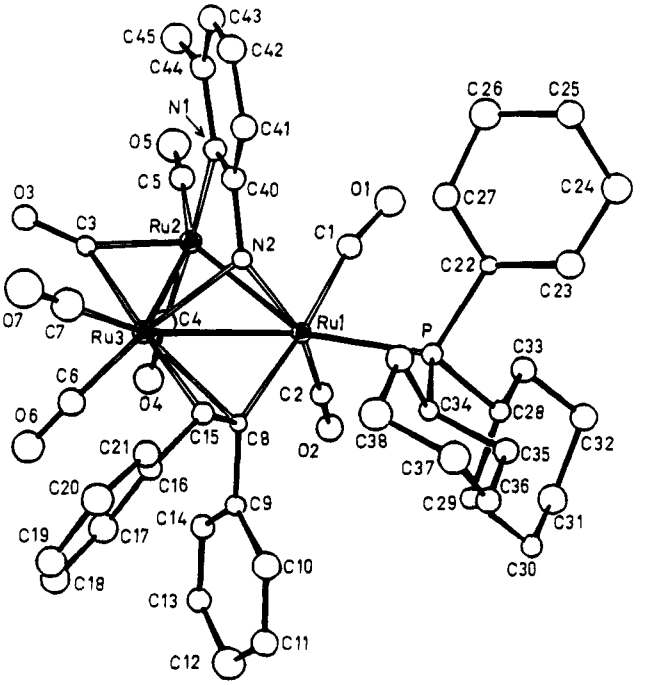


Figure 3. X-ray structure of $[Ru_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(CO)_7(PCy_3)]$ (**6a**).

Table 1. Selected Bond Lengths and Bond Angles in 6a

Bond Lengths (Å)			
Ru(1)–Ru(2)	2.8057(5)	Ru(1)–Ru(3)	2.7433(6)
Ru(2)–Ru(3)	2.7995(6)	Ru(1)–P	2.440(1)
Ru(1)–N(2)	2.193(6)	Ru(3)–N(2)	2.156(5)
Ru(2)–N(1)	2.243(6)	Ru(1)–C(1)	1.947(5)
Ru(1)–C(2)	1.859(8)	Ru(2)–C(3)	1.977(5)
Ru(2)–C(4)	1.819(8)	Ru(2)–C(5)	1.875(5)
Ru(3)–C(3)	2.217(4)	Ru(3)–C(6)	1.880(8)
Ru(3)–C(7)	1.937(8)	Ru(1)–C(8)	2.114(5)
Ru(3)–C(8)	2.268(5)	Ru(3)–C(15)	2.272(4)
C(8)–C(15)	1.397(9)		
Bond Angles (deg)			
Ru(1)–Ru(2)–Ru(3)	58.60(1)	Ru(1)–Ru(3)–Ru(2)	60.81(1)
Ru(2)–Ru(1)–Ru(3)	60.58(1)	Ru(2)–Ru(1)–P	152.53(4)
Ru(3)–Ru(1)–P	137.77(4)	C(8)–Ru(1)–Ru(3)	53.8(1)
C(8)–Ru(3)–Ru(1)	48.8(1)	C(8)–Ru(1)–Ru(2)	109.9(1)
C(8)–Ru(3)–Ru(2)	105.5(1)	C(15)–Ru(3)–Ru(1)	76.0(1)
C(15)–Ru(3)–Ru(2)	136.8(1)	C(8)–Ru(3)–C(15)	35.8(2)
Ru(1)–C(8)–Ru(3)	77.4(2)	C(15)–C(8)–Ru(1)	123.5(5)
C(15)–C(8)–Ru(3)	72.2(3)	C(8)–C(15)–Ru(3)	71.9(3)
Ru(2)–C(3)–O(3)	141.9(4)	Ru(3)–C(3)–O(3)	134.6(4)

tained when hydrogen was bubbled through a toluene solution of complex **6a** at 60 °C for 45 min. Small amounts of *cis*-stilbene (GC identification) and complex **3a** were also formed in this reaction. Longer reaction times or higher temperatures led to lower amounts of **7a** and more **3a** and stilbene. Complex **7a** was characterized by the presence of two hydride and six carbonyl resonances in its ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. These spectra also confirm the presence of the $\mu,\eta^1{:}\eta^2$-alkenyl group and all the other ligands, supporting the structure we propose for this complex in Scheme 2. Unfortunately, we were unable to grow single crystals of **7a** suitable for an X-ray diffraction study.

The following set of equations represents a possible mechanism for the catalytic hydrogenation of diphenylacetylene promoted by complex **3a**:

$$\mathbf{3a} + Ph_2C_2 \overset{K_1}{\rightleftharpoons} \mathbf{6a} + CO \quad (1)$$

$$\mathbf{6a} + H_2 \overset{K_2}{\rightleftharpoons} \mathbf{7a} + CO \quad (2)$$

$$\mathbf{7a} \overset{k_3}{\longrightarrow} \mathbf{7'a} \quad (3)$$

$$\mathbf{7'a} \xrightarrow{\text{fast}} [Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_6(PCy_3)] + Ph_2C_2H_2 \quad (4)$$

$$[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_6(PCy_3)] + Ph_2C_2 + H_2 \xrightarrow{\text{fast}} \mathbf{7a} \quad (5)$$

This mechanism is similar to that previously proposed for the hydrogenation of diphenylacetylene promoted by complex **3b**.[6] The fact that **7a** has been isolated suggests that its transformation should be slow. However, the coupling of a hydride with the alkenyl ligand in **7a** cannot be possible in one elemental reaction because the alkenyl α-carbon is not cis to any of the hydrides; therefore, complex **7a** should undergo an isomerization reaction, prior to the reductive elimination of *cis*-stilbene, which would place a hydride and the alkenyl α-carbon in a cis arrangement (**7'a**). This isomerization reaction (k_3) is expected to be the rate-determining step of the catalytic process. The release of stilbene from **7'a** should be fast, giving a very unsaturated species, $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_6(PCy_3)]$, which would rapidly add diphenylacetylene and hydrogen to give **7a**, thus closing the catalytic cycle. This mechanism is supported by the results of the above mentioned stoichiometric reactions and also by the available kinetic data.[6]

The fact that **3a** gives slower reaction rates than **3b** seems to be related to the higher basicity of PCy_3 as compared to that of the PPh_3 ligand. A basic ancillary ligand increases the electron density of the metal atoms, enhancing the retrodonating component of the metal–CO bond; but, as eqs 1 and 2 involve the release of carbon monoxide from the corresponding cluster complexes, the transformation of complex **3b** into **7b** should, therefore, be easier than that of complex **3a** into **7a**. In other words, the values of K_1 and K_2 for the **3a**-promoted reaction should be smaller than those for the **3b**-promoted reaction. Unfortunately, we do not know how much k_3 is influenced by the basicity of the phosphine ligand.

In conclusion, although the catalytic results reported herein are far from being of practical importance, the present work adds a new example to the very few in which the participation of cluster complexes in a homogeneous catalytic reaction has been established[7] and helps to shed light on the effect that phosphine ligands

(13) For X-ray diffraction structures of triruthenium cluster complexes containing the μ_3-ampy ligand, see, for example: (a) References 3–5. (b) Cabeza, J. A.; Llamazares, A.; Riera, V.; Triki, S.; Ouahab, L. *Organometallics* **1992**, *11*, 3334. (c) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 157. (d) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973. (e) Andreu, P. L.; Cabeza, J. A.; Llamazares, A.; Riera, V.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1991**, *420*, 431. (f) Andreu, P. L.; Cabeza, J. A.; Llamazares, A.; Riera, V.; García-Granda, S.; Van der Maelen, J. F. *J. Organomet. Chem.* **1992**, *434*, 123.

(14) For examples of bridging alkenyl ligands in carbonyl cluster complexes, see: Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimata, E. W.; Bonnet, J.-J. *Organometallics* **1992**, *11*, 1351 and references therein.

Table 2. Crystallographic and Refinement Data for 6a

formula	$C_{45}H_{51}N_2O_7PRu_3$
fw	1066.10
cryst syst	triclinic
space group	$P\bar{1}$
a, *b*, *c*, Å	11.568(7), 11.684(2), 18.958(11)
α, β, γ, deg	81.34(3), 75.84(6), 63.92(3)
V, Å³	2229(2)
Z	2
F(000)	1076
D_{calcd}, g/cm³	1.588
μ, cm⁻¹	10.687
cryst size, mm	0.90 × 0.25 × 0.25
radiation (λ, Å)	Mo Kα (0.710 73)
diffractometer	Enraf-Nonius CAD4
monochromator	graphite
temp, K	293(2)
scan method	$\theta-2\theta$
h, *k*, *l* ranges	0−6, −12 to +13, −21 to +22
2θ limits, deg	2−50
no. of meads reflns	5171
no. of unique rflns	4317
$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.041
no. of reflns with $I > 4\sigma(I)$	4035
no. of variables	514
$R(F)^a$	0.0397
$R_w(F)^b$	0.0618
GOF[c]	1.679
Δ/σ	0.00
max, min $\Delta\rho$, e/Å³	0.894, −0.255

[a] $R(F) = \Sigma[||F_o| - |F_c||]/\Sigma|F_o|$. [b] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 4F_o^2/[\sigma^2(I) + (0.07F_o^2)^2]$. [c] Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2}$.

have on the catalytic properties of metal complexes[8] and, in particular, of the much less studied metal clusters.[7]

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. Unless otherwise stated, the reactions were carried out under nitrogen at room temperature, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by qualitative TLC (silica gel). Compounds **1**[15] and **2**[5] were prepared as described previously. All other reagents were purchased from Aldrich. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. NMR spectra were run at 23 °C with Bruker AC-200 and AC-300 instruments, using $SiMe_4$ (internal, ^1H and ^{13}C) or 85% aqueous H_3PO_4 (external, ^{31}P) as the standard ($\delta = 0$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. GC analyses were carried out at 175 °C 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; quantification was achieved with a PE-Nelson 1020 integrator.

$[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_8(PCy_3)]$ (3a). Tricyclohexylphosphine (212 mg, 0.754 mmol) was added to a solution of complex **1** (500 mg, 0.754 mmol) in THF (20 mL). The color changed from orange to red-orange. The solvent was removed under reduced pressure and the residue washed with hexane (2 × 2 mL) to give complex **3a** as an orange solid (620 mg, 90%). Anal. Calcd for $C_{32}H_{41}N_2O_8PRu_3$: C, 41.97; H, 4.51; N, 3.06. Found: C, 42.05; H, 4.73; N, 2.95. IR, ν(CO) (THF): 2055 (s), 2014 (vs), 1983 (s), 1975 (sh), 1953 (m), 1938 (w), 1928 (w) cm⁻¹. ^1H NMR (CD_2Cl_2): δ 7.19 (t, J = 7.7 Hz, 1 H), 6.60 (d, J = 7.7 Hz, 1 H), 6.04 (d, J = 7.7 Hz, 1 H), 3.53 (d, J = 5.2 Hz, 1 H, NH), 2.59 (s, 3 H, Me), 1.9−1.1 (m, PCy_3 protons), −11.02 (d, J = 8.9 Hz, 1 H, μ-H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 43.0 (s) ppm. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2): 207.8 (s, 1 C), 204.3 (s, 2 C), 203.5 (s, 1 C), 203.4 (d, J = 13 Hz, 1 C), 201.8 (s), 199.2 (d, J = 5 Hz, 1 C), 189.2 (s, 1 C) (8 CO ligands) ppm; 178.7, 161.2, 138.3, 119.4, 108.5, 29.8 (all singlets, ampy carbon atoms) ppm.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-H Atoms of 6a

atom	*x/a*	*y/b*	*z/c*	B_{eq} (Å²)[a]
Ru(1)	0.07069(5)	0.14053(3)	0.27685(2)	2.14(1)
Ru(2)	−0.13505(5)	0.37699(4)	0.31824(2)	2.57(1)
Ru(3)	−0.04538(5)	0.31315(4)	0.17218(2)	2.56(1)
P	0.1879(2)	−0.0904(1)	0.29357(7)	2.53(5)
O(1)	−0.0611(5)	0.1267(4)	0.4392(2)	4.6(2)
O(2)	0.2493(5)	0.2081(4)	0.3358(2)	4.3(1)
O(3)	−0.2975(4)	0.5643(4)	0.2175(2)	4.0(1)
O(4)	0.0551(5)	0.4971(4)	0.2945(3)	6.0(2)
O(5)	−0.2749(5)	0.5475(4)	0.4465(2)	5.9(2)
O(6)	0.0546(5)	0.5121(4)	0.1051(3)	5.5(2)
O(7)	−0.2134(6)	0.3821(6)	0.0588(3)	8.2(2)
N(1)	−0.2711(5)	0.2865(4)	0.3195(2)	2.6(1)
N(2)	−0.0947(5)	0.1616(4)	0.2311(2)	2.0(1)
C(1)	−0.0215(6)	0.1446(5)	0.3779(3)	2.8(2)
C(2)	0.1885(6)	0.1764(4)	0.3106(3)	2.7(2)
C(3)	−0.2109(6)	0.4730(5)	0.2332(3)	2.3(2)
C(4)	−0.0203(7)	0.4497(5)	0.3053(3)	3.7(2)
C(5)	−0.2286(7)	0.4788(5)	0.3986(3)	3.2(2)
C(6)	0.0173(7)	0.4368(5)	0.1303(3)	4.6(2)
C(7)	−0.1507(8)	0.3558(6)	0.0988(3)	5.3(2)
C(8)	0.1592(6)	0.1535(4)	0.1661(3)	1.8(2)
C(9)	0.2870(6)	0.1671(5)	0.1461(3)	2.1(2)
C(10)	0.3984(7)	0.0728(5)	0.1046(3)	3.4(2)
C(11)	0.5175(7)	0.0808(6)	0.0830(3)	4.3(2)
C(12)	0.5316(7)	0.1815(7)	0.1017(4)	4.6(2)
C(13)	0.4267(7)	0.2761(6)	0.1434(4)	3.6(2)
C(14)	0.3098(6)	0.2685(5)	0.1636(3)	3.4(2)
C(15)	0.1097(6)	0.1428(5)	0.1085(3)	2.6(2)
C(16)	0.1514(6)	0.1632(5)	0.0278(3)	3.4(2)
C(17)	0.2101(7)	0.2405(5)	−0.0054(3)	3.4(2)
C(18)	0.2410(8)	0.2592(7)	−0.0809(4)	5.7(2)
C(19)	0.2106(7)	0.1990(7)	−0.1249(3)	5.2(2)
C(20)	0.1490(7)	0.1229(7)	−0.0942(3)	5.1(2)
C(21)	0.1184(7)	0.1038(6)	−0.0177(3)	3.9(2)
C(22)	0.0853(6)	−0.1588(5)	0.3593(3)	2.6(2)
C(23)	0.1440(7)	−0.3048(5)	0.3755(4)	4.3(2)
C(24)	0.0543(8)	−0.3387(6)	0.4409(4)	5.7(3)
C(25)	−0.0888(8)	−0.2862(7)	0.4347(4)	5.7(3)
C(26)	−0.1398(8)	−0.1448(7)	0.4162(4)	5.8(3)
C(27)	−0.0563(7)	−0.1140(6)	0.3479(4)	3.8(2)
C(28)	0.3339(6)	−0.1443(4)	0.3364(3)	2.6(1)[b]
C(29)	0.4442(7)	−0.1085(5)	0.2905(3)	3.4(2)
C(30)	0.5602(7)	−0.1597(6)	0.3281(4)	4.6(1)[b]
C(31)	0.5212(8)	−0.1164(7)	0.4055(4)	5.4(3)
C(32)	0.4121(7)	−0.1542(7)	0.4506(3)	4.5(2)
C(33)	0.2921(7)	−0.1011(6)	0.4160(3)	3.7(2)
C(34)	0.2595(6)	−0.1784(5)	0.2077(3)	2.9(2)
C(35)	0.3723(7)	−0.3135(5)	0.2090(4)	4.0(2)
C(36)	0.4274(8)	−0.3610(6)	0.1326(4)	5.2(2)
C(37)	0.3280(8)	−0.3602(6)	0.0952(4)	6.2(3)
C(38)	0.2154(8)	−0.2307(6)	0.0960(4)	6.3(2)
C(39)	0.1533(7)	−0.1843(5)	0.1743(3)	3.7(2)
C(40)	−0.2209(6)	0.1948(5)	0.2702(3)	2.7(2)
C(41)	−0.2955(7)	0.1359(5)	0.2596(3)	3.5(2)
C(42)	−0.4249(7)	0.1722(6)	0.2955(4)	3.9(2)
C(43)	−0.4769(7)	0.2680(6)	0.3456(4)	4.2(2)
C(44)	−0.3969(6)	0.3245(5)	0.3548(3)	3.0(2)
C(45)	−0.4598(7)	0.4316(6)	0.4063(4)	5.2(2)

[a] $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$. [b] B_{iso} (Å²).

$[Ru_3(\mu\text{-H})_2(\mu_3\text{-ampy})(CO)_8(PCy_3)][BF_4]$ (Isomer 4a). Tricyclohexylphosphine (22.2 mg, 0.079 mmol) was added to a solution of complex **2** (50 mg, 0.075 mmol) in THF (5 mL). The color changed from yellow to orange. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2 × 2 mL) to give complex **4a** as an orange solid (35 mg, 51%). Anal. Calcd for $C_{32}H_{42}BF_4N_2O_8PRu_3$: C, 38.29; H, 4.22; N, 2.79. Found: C, 38.41; H, 4.53; N, 2.65. IR, ν(CO) (THF): 2132 (m), 2079 (vs), 2048 (m), 2022 (m), 2003 (s), 1951 (m) cm⁻¹. ^1H NMR (CD_2Cl_2): 7.52 (t, J = 7.7 Hz, 1 H), 7.21

(15) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2201.

(d, J = 7.7 Hz, 1 H), 6.85 (d, J = 7.7 Hz, 1 H), 3.77 (s, br, 1 H, NH), 2.71 (s, 3 H, Me), 2.1–0.9 (m, PCy_3 protons), −12.88 (t, J = 3.3 Hz, 1 H, μ-H), −14.27 (dd, J = 12.6 and 3.3 Hz, 1 H, μ-H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 31.4 (s) ppm.

[$Ru_3(\mu$-H)$_2(\mu_3$-ampy)(CO)$_8$(PCy_3)][BF_4] (Isomer 5a). An excess of HBF_4·OEt_2 (ca. 0.2 mL) was added to a dichloromethane solution (10 mL) of complex **3a** (60 mg, 0.065 mmol). The color changed from orange to yellow. The solvent was removed under reduced pressure and the oily residue washed with diethyl ether (2 × 5 mL) to give complex **5a** as a yellow solid (63 mg, 95%). Anal. Calcd for $C_{32}H_{42}BF_4N_2O_8PRu_3$: C, 38.29; H, 4.22; N, 2.79. Found: C, 38.35; H, 4.60; N, 2.58. IR, ν(CO) (THF): 2100 (s), 2067 (vs), 2027 (w), 2017 (m), 2005 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): 7.52 (t, J = 7.7 Hz, 1 H), 7.04 (d, J = 7.7 Hz, 1 H), 6.88 (d, J = 7.7 Hz, 1 H), 5.98 (s, br, 1 H, NH), 2.62 (s, 3 H, Me), 2.2–1.1 (m, PCy_3 protons), −12.62 (d, J = 32.4 Hz, 1 H, μ-H), −13.93 (d, J = 11.6 Hz, 1 H, μ-H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 53.0 (s) ppm.

Isomerization of Complex 4a into 5a. A solution of complex **4a** (50 mg, 0.050 mmol) in THF (10 mL) was stirred at reflux temperature for 2 h. The solvent was removed under reduced pressure and the residue analyzed by $^{31}P\{^1H\}$ NMR, showing the presence of complexes **4a** and **5a** in a ca. 1:1 ratio.

[$Ru_3(\mu_3$-ampy)(μ-PhC=CHPh)(CO)$_7$(PCy_3)] (6a). A solution of complex **3a** (150 mg, 0.164 mmol) and diphenylacetylene (30 mg, 0.164 mmol) in THF (10 mL) was stirred at reflux temperature for 2.5 h. The color changed from orange to deep red. The solvent was removed under reduced pressure and the residue washed with hexane (2 × 5 mL) to give complex **6a** as a red solid (120 mg, 70%). Anal. Calcd for $C_{45}H_{51}N_2O_7PRu_3$: C, 50.70; H, 4.82; N, 2.63. Found: C, 50.75; H, 4.93; N, 2.55. IR, ν(CO) (THF): 2031 (s), 2015 (w), 1997 (vs), 1967 (m), 1924 (s), 1906 (w), 1792 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): 7.9–6.4 (complex mixture of signals, aromatic protons), 3.62 (s, 1 H, alkenyl =CH), 3.13 (s, br, 1 H, NH), 2.84 (s, 3 H, Me), 2.1–0.7 (m, PCy_3 protons) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 35.1 (s) ppm. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2): 237.4 (s, 1 C), 207.4 (d, J = 7.8 Hz, 1 C), 206.8 (d, J = 2.5 Hz, 1 C), 206.3 (s, 1 C), 205.5 (d, J = 7.3 Hz, 1 C), 204.9 (d, J = 3 Hz, 1 C), 201.8 (s, 1 C), 194.7 (d, J = 11 Hz, 1 C) (7 CO ligands + alkenyl *C*=CH) ppm; 174.0, 161.5, 138.5, 118.9, 112.7, 31.4 (all singlets, ampy carbon atoms) ppm; 81.2 (s, alkenyl C=*C*H) ppm.

[$Ru_3(\mu$-H)$_2(\mu_3$-ampy)(μ-PhC=CHPh)(CO)$_6$(PCy_3)] (7a). Hydrogen was bubbled for 45 min through a toluene solution (10 mL) of complex **6a** (160 mg, 0.149 mmol) thermostated at 60 °C. At this point, a qualitative TLC analysis of the solution indicated the presence of **3a**, **6a**, and **7a**. The solution was concentrated under reduced pressure to ca. 2 mL and introduced into a chromatography column packed with neutral alumina (3 × 10 cm, activity IV). Elution with 1:5 toluene–hexane afforded a yellow band containing a small amount of complex **3a** (IR identification). Further elution with 1:1 toluene–hexane afforded two bands: orange and red. The red band contained complex **6a** (IR identification). The solution obtained from the orange band was evaporated to dryness and the residue washed with hexane (2 mL) to give complex **7a** as an orange solid (25 mg, 16%). Anal. Calcd for $C_{44}H_{53}N_2O_6PRu_3$: C, 50.81; H, 5.14; N, 2.69. Found: C, 51.05; H, 5.21; N, 2.56. IR, ν(CO) (THF): 2028 (vs), 2002 (vs), 1959 (vs), 1944 (m), 1907 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): 8.1–6.7 (complex mixture of signals, aromatic protons), 3.62 (d, J = 3.2 Hz, 1 H, alkenyl =CH), 2.90 (s, br, 1 H, NH), 2.88 (s, 3 H, Me), 2.2–0.8 (m, PCy_3 protons), −8.90 (d, J = 4.7 Hz, 1 H, μ-H), −11.44 (d, J = 2.5 Hz, 1 H, μ-H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 35.4 (s) ppm. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2): 211.6 (d, J = 7.8 Hz, 1 C), 207.0 (s, 1 C), 205.5 (s, 1 C), 205.2 (d, J = 5.7 Hz, 1 C), 203.8 (s, 1 C), 197.6 (d, J = 4.1 Hz, 1 C), 196.1 (d, J = 11.5 Hz, 1 C) (6 CO ligands + alkenyl *C*=CH) ppm; 174.7, 161.2, 138.1, 118.4, 112.9, 31.9 (all singlets, ampy carbon atoms) ppm; 78.4 (s, alkenyl C=*C*H) ppm.

Catalytic Hydrogenation of Diphenylacetylene. The instrumentation and general procedures for the catalytic hydrogenation of diphenylacetylene have been described previously.[6] The reactions were carried out in toluene at 80 °C, with [**3a**], [Ph_2C_2], and $P(H_2)$ in the ranges (0.7–5.5) × 10^{-3} mol L^{-1}, 0.034–0.421 mol L^{-1}, and 0.24–0.66 atm, respectively. The evolution of the catalytic reactions was followed by GC. Reaction rates were obtained by measuring the hydrogen consumption as a function of time.

Crystal Structure of Complex 6a. A red crystal of **6a**, obtained at −20 °C in the interphase of a pentane layer placed on a solution of the complex in toluene, was used for the X-ray diffraction study. A selection of crystal and refinement data is given in Table 2. The cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with 15 ≤ 2θ ≤21°. Three standard reflections measured every hour revealed no intensity fluctuations. The data were corrected for Lorentz and polarization effects. No absorption correction was applied.

The structure was solved by direct methods and successive Fourier difference syntheses and was refined by full matrix least squares. After refinement of the positional and anisotropic (β_{ij}) thermal parameters for the non-hydrogen atoms, the positions of the hydrogen atoms were calculated (C–H = 0.95 Å, B = 4 Å^2) and included as a fixed contribution to F_c. Scattering factors and corrections for anomalous dispersion were taken from ref 16. All calculations were performed on a MicroVax 3100 computer using the Enraf-Nonius MoLen program package.[17]

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Supplementary Material Available: Tables of H-atom coordinates, bond distances, bond angles, and anisotropic thermal parameters for **6a** (5 pages). Ordering information is given on any current masthead page.

OM9404341

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