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130220-54-1; (Z,E)-CHPh=CPhCH=CHSiMe₃, 130220-55-2; (Z,E)-CHPh=CPhCH=CHPh, 87968-73-8; (Z,E),(E,Z)-CHPh=CPhCH=CH(CH₂)₄CH=CHCPh=CHPh, 130220-56-3; 3-hexyne, 928-49-4; (trimethylsilyl)acetylene, 1066-54-2; 3,3-dimethyl-1-butyne, 917-92-0; 2-butyne, 503-17-3; phenylacetylene, 536-74-3; 1,7-octadiyne, 871-84-1.

Supplementary Material Available: Full details of the structure solution and crystallographic details for (DIPP)₃Ta(PhC≡CPh) and (DIPP)₃Ta(CEt=CetCet=Cet) including tables of atomic positional and thermal parameters, bond distances and angles, and dihedral angles and ORTEP figures (26 pages); tables of observed and calculated structure factor amplitudes (48 pages). Ordering information is given on any current masthead page.

Indirect Cooperative Effects Leading to Synergism in Bimetallic Homogeneous Catalysts Containing Azolates as Bridging Ligands

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The binuclear compounds [H(CO)(PPh₃)₂Ru(μ-bim)Ir(COD)] (1) (bim = 2,2'-biimidazolate, COD = 1,5-cyclooctadiene) and [H(CO)(PPh₃)₂Ru(μ-pz)₂Ir(TFB)] (2) (pz = pyrazolate, TFB = tetrafluorobenzobarrelene) are more active catalysts for the hydrogenation of cyclohexene than the mononuclear parent compounds [RuH(Hbim)(CO)(PPh₃)₂], [Ir(Hbim)(COD)], [RuH(pz)(CO)(Hpz)(PPh₃)₂], and [Ir(TFB)(Hpz)₂BF₄]. In the presence of 1, the reaction rate is first order with respect to the concentration of 1 and cyclohexene, second order with respect to hydrogen pressure, and inversely proportional to the concentration of added phosphine. For the reaction catalyzed by 2, the experimental data are in accordance with a rate expression of the form $-d[\text{cyclohexene}]/dt = k[2][\text{cyclohexene}]P(\text{H}_2)$ [$P(\text{H}_2)$ = hydrogen pressure]. On the basis of the kinetic results and experimental evidence, the origin of the catalytic synergism is assigned to indirect cooperative effects between the metallic centers of the binuclear complexes. The kinetic investigation of the hydrogenation of cyclohexene catalyzed by [Ir(μ-pz)(TFB)]₂ (3) is also reported, suggesting that the full catalytic cycle involves binuclear species.

Introduction

Studies of multicomponent metal systems under homogeneous conditions have revealed the existence of catalytic activity enhancement when compared to that of the individual components;¹ this enhancement effect is known collectively as synergism,^{2,3} and it has played an important role in the development of homogeneous polymetallic catalysis.⁴ From a mechanistic point of view, the concept

of synergism has been applied to metal atoms either operating individually³ or, more rigorously, in concert⁵⁻⁸ in reaction sequences. A genuine bimetallic mechanism in which two metal centers act in concert has been postulated by Kalck's group, for the olefin hydroformylation catalyzed by compounds of the type *cis*-[Rh₂(μ-SBu^t)₂(CO)₂(PR₃)₂], on the basis of theoretical calculations and spectroscopic studies.⁵ Bimetallic catalytic pathways involving the concerted action of two metals have been also proposed for processes such as the hydration of acrylonitrile to acrylamide catalyzed by dinuclear palladium complexes,⁶ alkene hydroformylation catalyzed by compounds of the type [Ru₂(μ-OOCR)₂(CO)₄(PR₃)₂],⁷ or hydrogen transfer

(1) See for example: (a) Choukroun, R.; Gervais, D.; Kalck, P.; Senocq, F. *J. Organomet. Chem.* 1987, 335, C9. (b) Choukroun, R.; Iraqi, A.; Gervais, D.; Daran, J.; Jeannin, Y. *Organometallic* 1987, 6, 1197. (c) Dany, F.; Mutin, R.; Lucas, C.; Dufand, V.; Thivolle-Cazat, J.; Basset, J. M. *J. Mol. Catal.* 1989, 51, L15. (d) Mutin, R.; Lucas, C.; Thivolle-Cazat, J.; Dufand, V.; Dany, F.; Basset, J. M. *J. Chem. Soc., Chem. Commun.*, 1988, 896. (e) Senocq, F.; Randrianalimanana, C.; Thorez, A.; Kalck, P.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* 1988, 1376. (f) Senocq, F.; Randrianalimanana, C.; Thorez, A.; Kalck, P.; Choukroun, R.; Gervais, D. *J. Mol. Catal.* 1986, 35, 213. (g) Choukroun, R.; Gervais, D.; Jand, J.; Kalck, P.; Senocq, F. *Organometallics*, 1986, 5, 67. (h) Evans, J.; Jinxing, G. *J. Chem. Soc., Chem. Commun.* 1985, 39. (i) Choukroun, R.; Gervais, D.; Rifai, C. *Polyhedron*, 1989, 8, 1760. (j) Hidai, M.; Matsuzaka, H. *Polyhedron* 1988, 7, 2369. (k) Ojima, I.; Okabe, M.; Kato, K.; Kwon, H. B.; Horvath, I. T. *J. Am. Chem. Soc.* 1988, 110, 150.

(2) Adams, R. D. *Polyhedron* 1988, 7, 2251.

(3) Dombek, B. D. *Organometallics* 1985, 4, 1707.

(4) (a) Bhaduri, S.; Sharma, K. *J. Chem. Soc., Chem. Commun.* 1988, 173. (b) Bianchini, C.; Meli, A.; Laschi, F.; Ramirez, J. A.; Zanello, P.; Vacca, A. *Inorg. Chem.* 1988, 27, 4429. (c) Okoroafor, M.; Shen, L.; Honeychuck, R. V.; Brubaker, C. H., Jr. *Organometallics* 1988, 7, 1297. (d) Gelmini, L.; Stephan, D. W. *Organometallics* 1988, 7, 849.

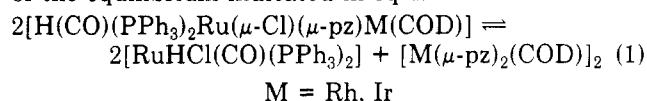
(5) (a) Dedieu, A.; Escaffre, P.; Frances, J. M.; Kalck, P.; Thorez, A. *Nouv. J. Chem.* 1986, 10, 631. (b) Kalck, P. *Polyhedron* 1988, 7, 2441. (6) McKenzie, C.; Robson, R. *J. Chem. Soc., Chem. Commun.* 1988, 112.

(7) Jenck, J.; Kalck, P.; Pinelli, E.; Siani, M.; Thorez, A. *J. Chem. Soc., Chem. Commun.* 1988, 1428.

(8) Jothimony, K.; Vancheesan, S. *J. Mol. Catal.* 1989, 52, 301.

from alcohols to ketones in the presence of $[\text{HfE}_3(\text{CO})_{11}]^{\cdot 8}$. These proposals have been postulated on the basis of two ideas: (i) the flexibility of M-L-M' bridges permits the transfer of an atom or ligand from one metal center to the other; (ii) an electronic cooperative effect can take place between metallic centers via orbital interactions with the bridging ligands. However, no kinetic investigation has been reported to prove the integrity of the catalysts during the reactions.

Interestingly, Maitlis has found kinetic evidence in favor of the total cleavage of the bridges between the metallic atoms of compound $[\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ (M = Rh, Ir) or $[\text{Ir}(\text{C}_5\text{Me}_5)\text{ClH}]_2$, which catalyze the hydrogenation of olefins.⁹ In this line, Sánchez-Delgado et al. have postulated on the basis of kinetic data that for the reactions catalyzed by simple metal carbonyl clusters the fragmentation of the clusters is a general phenomenon.¹⁰ In this context, we have recently studied the reduction of cyclohexanone by hydrogen transfer from 2-propanol catalyzed by the complexes $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-Cl})(\mu\text{-pz})\text{M}(\text{COD})]$ (M = Rh, Ir; pz = pyrazolate; COD = 1,5-cyclooctadiene); the kinetic results suggest the existence, under reaction conditions, of the equilibrium indicated in eq 1.¹¹



In a previous communication,¹² we reported that the binuclear complexes $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-bim})\text{M}(\text{COD})]$ (bim = 2,2'-biimidazolate; M = Rh, Ir) are more active as catalysts for the hydrogenation of cyclohexene than the mononuclear parent compounds $[\text{RuH}(\text{Hbim})(\text{CO})(\text{PPh}_3)_2]$ and $[\text{M}(\text{Hbim})(\text{COD})]$ (M = Rh, Ir), suggesting that the enhancement of catalytic activity was probably due to electronic communication between the nonadjacent metal centers through the biimidazolate ligand.¹³ As a continuation of this work, we describe now the results of a kinetic investigation of the hydrogenation of cyclohexene catalyzed by $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-bim})\text{Ir}(\text{COD})]$ (1) or by the related compounds $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TfB})]$ (2) (TfB = tetrafluorobenzobarrelene) and $[\text{Ir}(\mu\text{-pz})(\text{TfB})]_2$ (3).

Results and Discussion

Kinetics of the Hydrogenation of Cyclohexene. A simple rate law for a catalytic hydrogenation of cyclohexene is

$$-d[\text{cyclohexene}]/dt = -d[\text{H}_2]/dt = k_2[\text{cyclohexene}]^m[\text{cat}]^n[\text{H}_2]^q \quad (2)$$

Working at constant temperature and with a large excess of cyclohexene, this rate law is further simplified to

$$-d[\text{cyclohexene}]/dt = -d[\text{H}_2]/dt = k_{\text{obs}}[\text{catalyst}]^n(P(\text{H}_2))^q \quad (3)$$

(9) Maitlis, P. M. *Acc. Chem. Res.* 1978, 11, 301.

(10) Sánchez-Delgado, R. A.; Andriollo, A.; Puga, J.; Martin, G. *Inorg. Chem.* 1987, 26, 1867.

(11) García, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Organomet. Chem.* 1990, 388, 365.

(12) García, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Chem. Commun.* 1988, 793.

(13) Recent data on iridium azolate complexes offer clear evidence for electronic communication between the iridium centers via orbital interaction with bridging ligands. See: (a) Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* 1982, 104, 920. (b) Coleman, A. W.; Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* 1982, 104, 922. (c) Bushnell, G. W.; Fjeldsted, D. O. K.; Stobart, S. R.; Zaworotko, M. J. *Organometallics* 1985, 4, 1107. (d) Lichtenberger, D. L.; Copenhaver, A. S.; Gray, H. B.; Marshall, J. L.; Hopkins, M. D. *Inorg. Chem.* 1988, 27, 4488. (e) Brost, R. D.; Fjeldsted, D. O. K.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* 1989, 488.

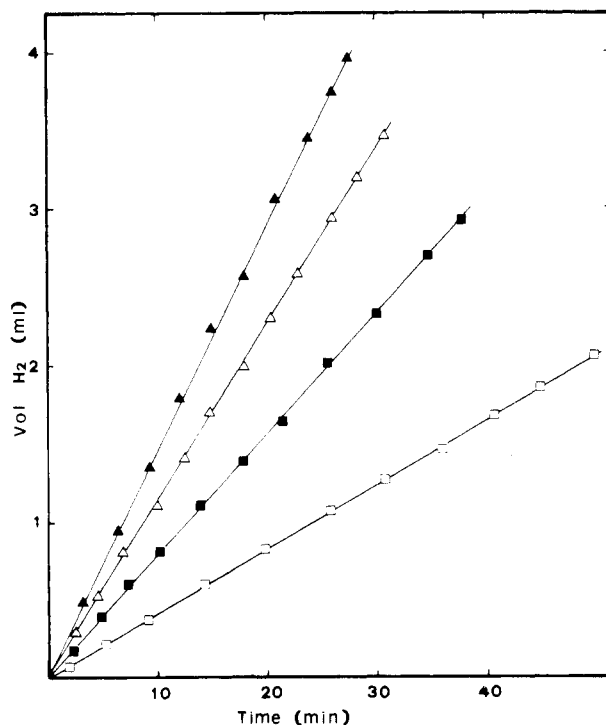


Figure 1. H_2 gas uptake plots for the $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-bim})\text{Ir}(\text{COD})]$ (1) catalyzed hydrogenation of cyclohexene to cyclohexane in 2-propanol/toluene (1:1) at 60 °C (1 atm of H_2 ; 1.61×10^{-3} M 1). [Cyclohexene]: (□) 0.10 M, (■) 0.20 M, (△) 0.31 M, (▲) 0.50 M.

Table I. Kinetic Data for the Hydrogenation of Cyclohexene to Cyclohexane Catalyzed by 1^a

$10^3[\text{RuIr}]$, M	$P(\text{H}_2)$, atm	[cyclohexene], M	$10^4[\text{PPh}_3]$, M	$10^7(-dV/dt)$, L s^{-1}
0.76	1.00	0.50		10.7
1.06	1.00	0.50		17.3
1.38	1.00	0.50		18.8
1.61	1.00	0.50		22.0
1.61	0.65	0.50		6.0
1.61	0.69	0.50		6.5
1.61	0.81	0.50		9.5
1.61	0.93	0.50		14.3
1.61	1.18	0.50		19.0
1.61	1.00	0.35		20.2
1.61	1.00	0.31		18.7
1.61	1.00	0.25		16.7
1.61	1.00	0.20		12.8
1.61	1.00	0.15		9.0
1.61	1.00	0.10		6.8
1.61	1.00	0.50	1.32	18.0
1.61	1.00	0.50	1.89	14.5
1.61	1.00	0.50	3.78	10.3
1.61	1.00	0.50	5.67	6.5

^a In 2-propanol/toluene (1:1) at 60 °C.

where $P(\text{H}_2)$ is hydrogen pressure.

The reactions were followed by measuring the hydrogen consumption as a function of time. The volume of H_2 corrected to 1 atm was converted to a pseudo-zero-order rate constant k_{obs} by

$$-(dV/dt)/RTV_{\text{sol}} = k_{\text{obs}}[\text{catalyst}]^n(P(\text{H}_2))^q \quad (4)$$

where $-dV/dt$ is the initial rate measured from gas uptake experiments, R is the molar gas constant, T is the temperature (K), and V_{sol} is the total volume (L) of the reacting solution.

1. Hydrogenation of Cyclohexene Catalyzed by 1. The binuclear complex 1 catalyzes the hydrogenation of cyclohexene in a 2-propanol/toluene (1:1) solution at 60

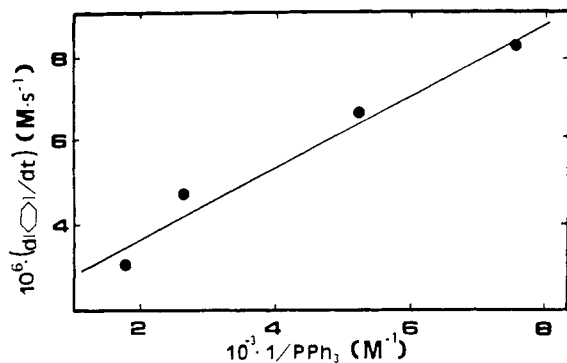


Figure 2. Plot of the rate of hydrogenation of cyclohexene to cyclohexane versus $[PPh_3]^{-1}$ catalyzed by $[H(CO)(PPh_3)_2Ru(\mu-bim)Ir(COD)]$ (**1**) in 2-propanol/toluene (1:1) at 60 °C (1 atm of H_2 ; 1.61×10^{-3} M (**1**); 0.5 M cyclohexene).

°C. No reduction of the organic substrate was observed in 2-propanol under N_2 , showing that hydrogen transfer from the solvent does not represent an important mechanistic pathway in the catalysis.

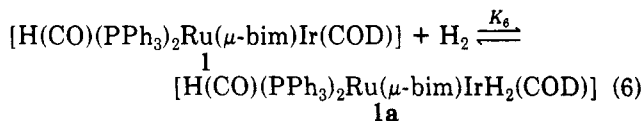
Initial hydrogenation rates were obtained from gas uptake experiments, as exemplified in Figure 1. In order to determine the rate dependence on the various reaction components, hydrogenation runs were performed at different **1** and cyclohexene concentrations and at different hydrogen pressures (Table I). Plots of $\log -(dV/dt)$ versus $\log [1]$ and $\log -(dV/dt)$ versus $\log P(H_2)$ yield straight lines of slope 0.9 and 2.3, respectively, suggesting that the reduction of cyclohexene is first order in catalyst concentration and second order in hydrogen pressure. Plots of $\log -(dV/dt)$ versus $\log [cyclohexene]$ yield a straight line of slope 0.8, indicating that for cyclohexene concentrations lower than ~ 0.5 M the reaction is, practically, first order in cyclohexene concentration ($m = 1$ in eq 2).

The 1H NMR spectrum of the catalytic solution shows that complex **1** is the main species; this, together with the first-order dependence of the rate on the concentration of **1**, eliminates the possibility of **1** breaking down to mononuclear catalytically active species. Furthermore, it is interesting to mention that **1** was recovered unchanged after the catalytic reactions, indicating that the 1,5-cyclooctadiene ligand coordinated to the iridium atom is not hydrogenated, suggesting, therefore, that the ruthenium atom is the only active center.¹⁴ Because the ruthenium atom is the only active center and is coordinatively saturated, the coordination of cyclohexene implies the displacement of PPh_3 . In accordance with this, the rate of formation of cyclohexane was found to be inhibited by the addition of PPh_3 . The initial rate was found to be inversely proportional to the concentration of added phosphine (Figure 2), so the catalytic rate law can be written as

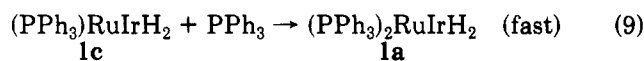
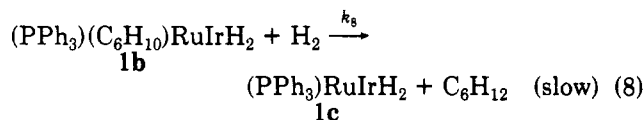
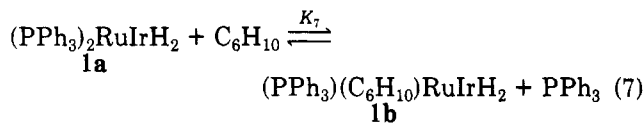
$$d[cyclohexane]/dt = -d[cyclohexene]/dt = k_5[cyclohexene][1](P(H_2))^2/[PPh_3] \quad (5)$$

The second-order dependence of the rate on the hydrogen pressure can only be rationalized if we assume that **1** is the catalyst precursor and, under catalytic conditions, it is in rapid equilibrium with active species **1a** formed by addition of molecular hydrogen on the iridium atom of **1**, according to eq 6.

The equilibrium shown in eq 6 is supported by the following facts: (i) When a solution of **1**, in toluene- d_8 , is exposed to hydrogen, the 1H NMR spectrum at -70 °C



shows the hydride resonance of the starting material together with two weak signals at -22.0 and -22.9 ppm that can be assigned to the nonequivalent hydride ligands coordinated to the iridium atom in **1a**; previously, it has been observed that the complex $[Ir_2(COD)_2(PNNP)]^+$ reacts, at low temperature, reversibly with hydrogen to give $[Ir(COD)(PNNP)IrH_2(COD)]^+$.¹⁵ (ii) Under catalytic conditions, the related compound $[H(CO)(PPh_3)_2Ru(\mu-bim)Ir(TFB)]$ decomposes to Ir^0 and other unidentified ruthenium products. The higher stability of **1** relative to $[H(CO)(PPh_3)_2Ru(\mu-bim)Ir(TFB)]$ can be assigned to the higher stability of the "IrH(COD)" unit toward the insertion of the hydride ligand in the olefinic bonds. In this line, it has been previously reported that in solution the hydride proton of the complex $[IrH(TFB)(AsPh_3)_2]$ attacks a double bond of the coordinated TFB ligand, while for the related 1,5-cyclooctadiene compound this attack is not observed.¹⁶ In light of these considerations, the following set of reactions could be consistent with the catalytic cycle



The rate of formation of cyclohexane follows the kinetic law

$$d[cyclohexane]/dt = k_8[1b]P(H_2) \quad (10)$$

Since $[1b] = K_7[1a][cyclohexene]/[PPh_3]$ and $[1a] = K_6[1]P(H_2)$, then $[1b] = K_6K_7[1][cyclohexene]P(H_2)/[PPh_3]$. Therefore

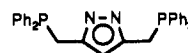
$$d[cyclohexane]/dt = k_8K_6K_7[1][cyclohexene](P(H_2))^2/[PPh_3] \quad (11)$$

The inspection of eq 11 shows that the rate of the catalytic reaction is directly proportional to $[1]$ and $[cyclohexene]$, second order with respect to hydrogen pressure, and inversely proportional to $[PPh_3]$, which agrees well with experimental data (see eq 5).

Hydrogenation Mechanism. On the basis of eq 11, we propose that the hydrogenation of cyclohexene catalyzed by **1** proceeds by the mechanism of Scheme I in which the reaction between **1b** and hydrogen is the rate-determining step.

Some more details of this cycle remain to be elucidated; the reaction of **1b** with hydrogen is likely to involve a series of elementary steps. One plausible sequence would be the

(15) (a) PNNP =



(b) Schenck, T. C.; Milne, C. R. C.; Sawyer, J. F.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2338.

(16) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1986**, *316*, 343.

(14) The hydrogenation of the coordinated 1,5-cyclooctadiene is a typical observation for active iridium 1,5-cyclooctadiene catalyst precursors. Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.

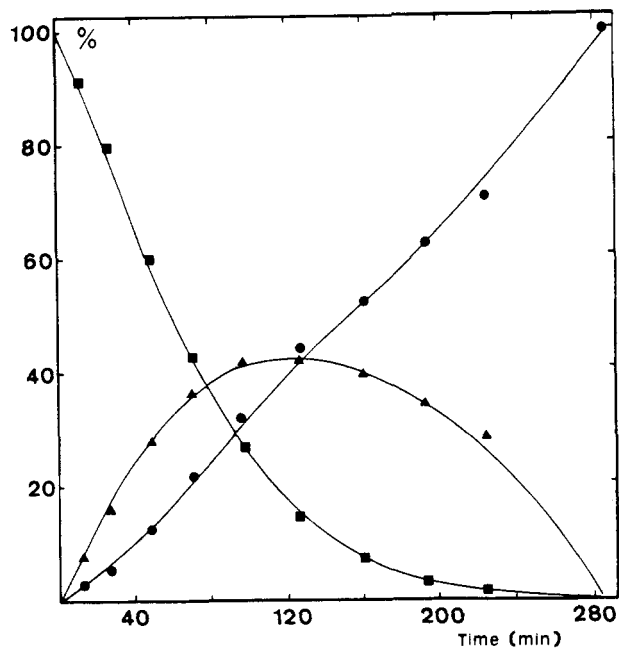


Figure 3. Hydrogenation of tetrafluorobenzobarrelene (TFB) catalyzed by $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TFB})]$ (**2**) in 2-propanol/toluene (1:1) at 60°C (1 atm of H_2 ; 1.25×10^{-3} M **2**; 0.156 M TFB). (■) TFB, (▲) H_2TFB , (●) H_4TFB .

insertion of cyclohexene into the hydride–ruthenium bond with formation of a 16e cyclohexyl–Ru species, which would allow H_2 to coordinate and protonate (if (H_2)) or reductively eliminate (if $(\text{H})_2$) with the cyclohexyl to give **1c**. The reaction of **1a** with cyclohexene to form **1b** is less clear-cut from an intimate mechanistic point of view, even though the relatively long distance observed for Ru–N bond trans to the hydride ligand in the related compound $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-bim})\text{Rh}(\text{COD})]$ (2.283 (5) Å)¹² suggests that this bond could be broken during the reaction.

The enhancement of catalytic activity of the mononuclear fragment $[\text{RuH}(\text{Hbim})(\text{CO})(\text{PPh}_3)_2]$ by bonding to “Ir(COD)” deserves further comment. Replacement of the acid proton of the $[\text{Hbim}]^-$ ligand in $[\text{RuH}(\text{Hbim})(\text{CO})(\text{PPh}_3)_2]$ by “Ir(COD)” produces a significant decrease in the electron density on the ruthenium atom as evidenced by the displacement of the ν_{CO} absorption toward higher frequencies.¹⁷ The addition of molecular hydrogen on the iridium atom must lead to a further decrease in the electron density on the ruthenium atom as previously observed for similar cases,^{15b} which agrees well with theoretical studies.^{5a} Interestingly, the most active catalysts for the reduction of organic unsaturated compounds are second- and third-row metal mononuclear complexes, such as, for example $[\text{Ir}(\text{COD})(\text{PR}_3)_2]^+$, $[\text{Ir}(\text{COD})\text{L}(\text{PR}_3)]^+$ (L = nitrogen donor ligand),^{14,18} $[\text{Rh}(\text{COD})(\text{PR}_3)_2]^+$,¹⁹ or $\text{OsHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$,²⁰ which show Lewis acid behavior.²¹

2. Hydrogenation of Cyclohexene Catalyzed by 2. Under the catalytic conditions mentioned above, the ac-

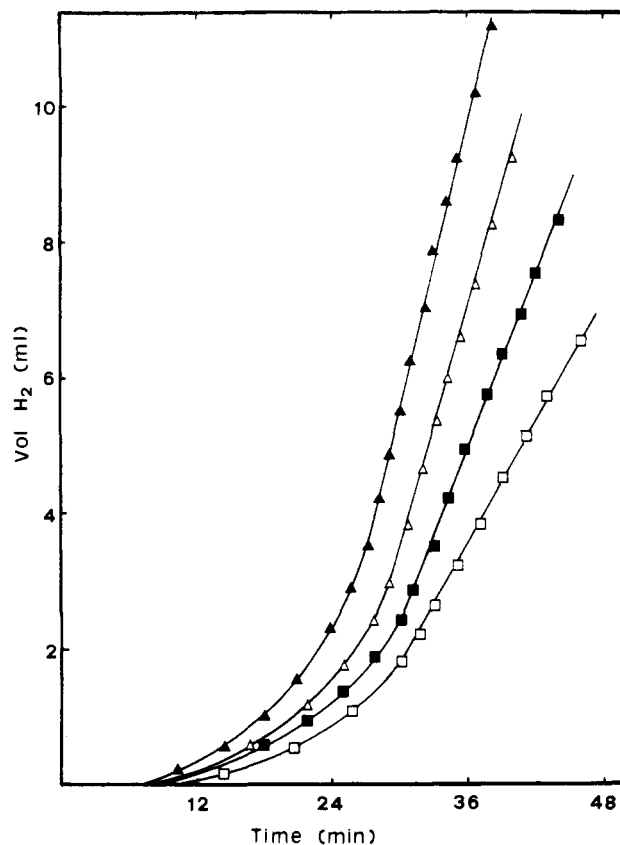


Figure 4. H_2 gas uptake plots for the $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TFB})]$ (**2**) catalyzed hydrogenation of cyclohexene to cyclohexane in 2-propanol/toluene (1:1) at 60°C . (1 atm of H_2 ; 0.97×10^{-3} M **2**). [Cyclohexene]: (□) 0.23 M, (●) 0.32 M, (▲) 0.39 M, (▲) 0.50 M.

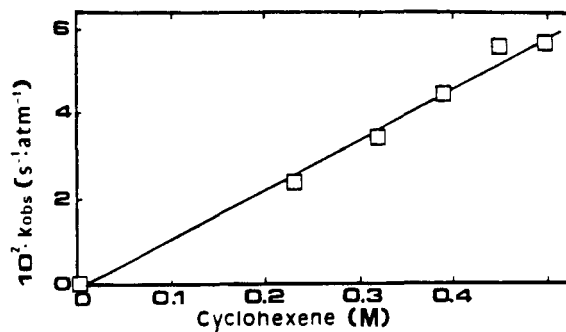


Figure 5. Rate constant for the hydrogenation of cyclohexene to cyclohexane catalyzed by $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TFB})]$ (**2**) in 2-propanol/toluene (1:1) at 60°C (1 atm of H_2 ; 0.97×10^{-3} M **2**).

tivity of the mononuclear compounds $[\text{RuH}(\text{pz})(\text{CO})(\text{H}_2\text{pz})(\text{PPh}_3)_2]$ and $[\text{Ir}(\text{TFB})(\text{H}_2\text{pz})_2]\text{BF}_4$ is rather poor; thus, after 24 h, the conversion is no more than 4%. However, the 2-propanol/toluene (1:1) solutions of the binuclear complex $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TFB})]$ (**2**) catalyze the hydrogenation of cyclohexene to cyclohexane at rates of about 1 order of magnitude faster than those observed for **1**. The reaction shows an induction period that disappears by treatment of the solution of **2** with hydrogen, for 1 h at 60°C . This induction period is most likely related to the reduction of the diolefin coordinated to the iridium atom. Thus, we have observed that **2** also catalyzes the hydrogenation of tetrafluorobenzobarrelene (Figure 3). Furthermore, the ^1H NMR spectrum ($\text{C}_6\text{D}_6/\text{CD}_3\text{OD}$ (1:1)) of **2** under hydrogen atmosphere contains the signals of **2** together with those of the hy-

(17) $\Delta\nu_{\text{CO}} = \nu_1 - \nu_{[\text{RuH}(\text{Hbim})(\text{CO})(\text{PPh}_3)_2]} = 1930 - 1915 = 15 \text{ cm}^{-1}$.

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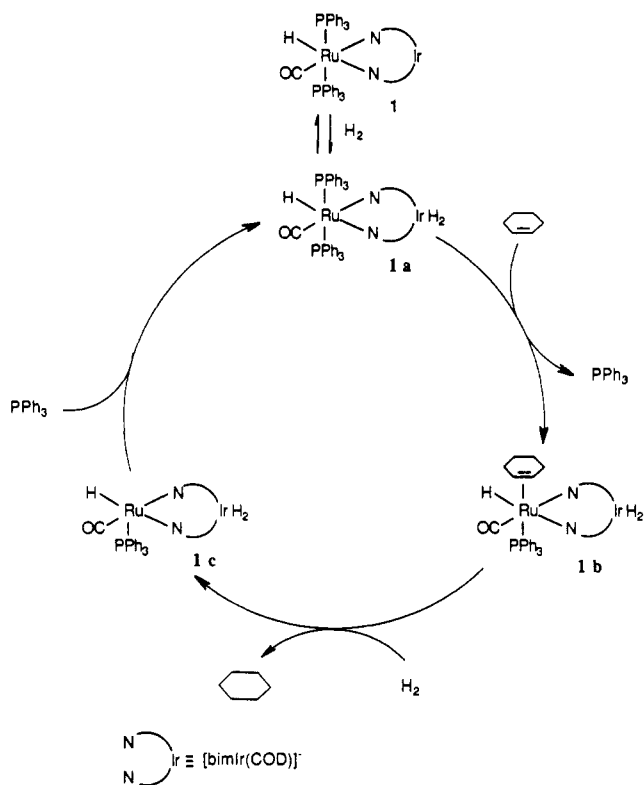
(21) (a) Crabtree, R. H.; Quirk, J. M. *J. Organomet. Chem.* **1980**, *199*, 99. (b) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem.* **1988**, *100*, 1621; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563.

Table II. Kinetic Data for the Hydrogenation of Cyclohexene to Cyclohexane Catalyzed by 2^c

$10^3[\text{Ru-Ir}]$, M	$P(\text{H}_2)$, atm	[cyclohexene], M	$10^6(-dV/dt)^b$, L s ⁻¹	10^2k_{obs} , s ⁻¹ atm ⁻¹	k_{12}^c , M ⁻¹ s ⁻¹ atm ⁻¹
0.26	1.00	0.45	3.1	5.46	0.12
0.45	1.00	0.45	5.6	5.73	0.13
0.64	1.00	0.45	6.6	4.72	0.11
0.97	1.00	0.45	11.7	5.51	0.13
1.25	1.00	0.45	18.3	6.70	0.15
1.52	1.00	0.45	19.3	5.80	0.13
1.95	1.00	0.45	28.3	6.64	0.15
0.97	0.58	0.45	6.0	4.89	0.11
0.97	0.72	0.45	8.8	5.74	0.13
0.97	0.82	0.45	9.4	5.38	0.12
0.97	1.00	0.23	5.1	2.37	0.10
0.97	1.00	0.32	7.2	3.40	0.11
0.97	1.00	0.39	9.3	4.39	0.11
0.97	1.00	0.50	11.9	5.59	0.11

^aIn 2-propanol/toluene (1:1) at 60 °C. ^bThe rate of absorption of H₂ was measured after the induction period (25–30 min). ^c $k_{12\text{mean}} = 0.12 \text{ M}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$.

Scheme I. Catalytic Cycle for the Hydrogenation of Cyclohexene Catalyzed by 1



hydrogenation of the tetrafluorobenzobarrelene (H₂TFB and H₄TFB) and a high-field signal at $\delta -10.53$ ppm as a triplet with a P–H coupling constant of 21 Hz that can be assigned to the species $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{IrS}_x]$ (**2a**) (S = CD₃OD). These observations suggest that the iridium center plays a fundamental role.

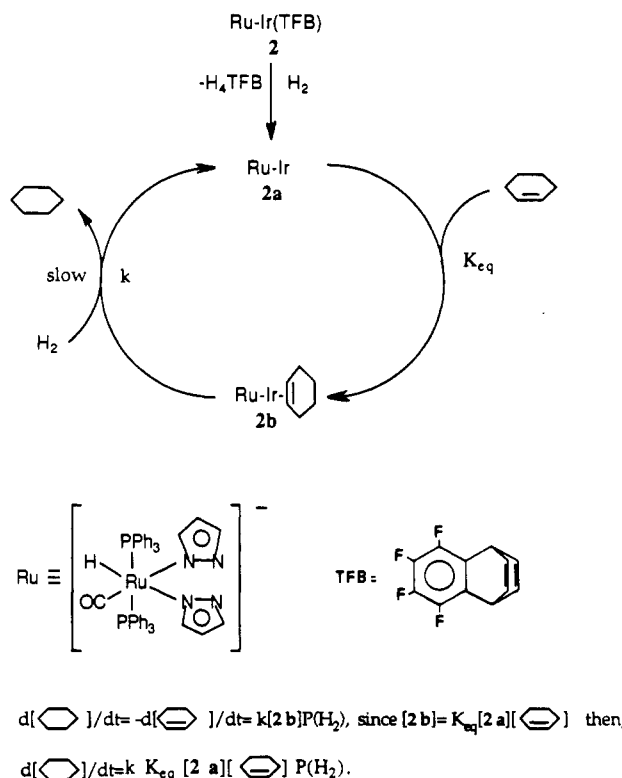
In order to determine the nuclearity of the catalytic species, the kinetics of the reaction was studied. Typical gas uptake measurements are shown in Figure 4. Following a kinetic analysis analogous to that described above for **1**, we deduce from the data collected in Table II and Figure 5 that the rate law for the hydrogenation of cyclohexene catalyzed by **2** is

$$-d[\text{cyclohexene}]/dt = k_{12}[\mathbf{2}][\text{cyclohexene}]P(\text{H}_2) \quad (12)$$

with a value of k_{12} of $0.12 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$ at 60 °C.

Equation 12 is consistent with the mechanism shown in Scheme II. This mechanism is a standard unsaturated mechanism,^{22a} and for example, it has been previously

Scheme II. Catalytic Cycle for the Hydrogenation of Cyclohexene Catalyzed by 2



proposed for the hydrogenation of olefins catalyzed by the mononuclear complex $[\text{Rh}(\text{diphos})\text{S}_x]^+_{22b-d}$

The significant modification of catalytic activity of the mononuclear iridium fragment by bonding to the "RuH(CO)(PPh₃)₂" unit merits further comment. The replacement of the acid protons of the pyrazole ligands in the mononuclear iridium complex by the ruthenium unit produces a decrease of electron-donor capacity of the pyrazole toward the iridium atom and a flow of the electron density from the iridium atom to the ruthenium one, as evidenced by the reduction of ν_{CO} of 13 cm⁻¹ in **2** compared with $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$. This reduction of electron density on the iridium atom is, most probably, responsible for its activation for catalysis, mainly in terms

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Table III. Kinetic Data for the Hydrogenation of Cyclohexene to Cyclohexane Catalyzed by 3^a

$10^3[\text{Ir-Ir}]$ M	$P(\text{H}_2)$ atm	[cyclohexene], M	$10^6(-dV/dt)^b$ L s ⁻¹	$10^2k_{14}^b$ s ⁻¹ atm ⁻²
0.37	1.00	0.46	6.7	8.3
0.64	1.00	0.46	7.8	5.6
0.84	1.00	0.46	14.5	7.9
1.06	1.00	0.46	16.4	7.1
1.25	1.00	0.46	16.6	6.1
1.41	1.00	0.46	23.3	7.5
0.84	0.65	0.46	6.4	8.2
0.84	0.66	0.46	6.9	8.1
0.84	0.76	0.46	10.3	9.7
0.84	0.85	0.46	12.7	9.6
0.84	1.00	0.14	9.5	5.2
0.84	1.00	0.21	9.6	5.2
0.84	1.00	0.33	10.3	5.6
0.84	1.00	0.60	13.2	7.2

^a In 2-propanol/toluene (3:1) at 60 °C. ^b $k_{14 \text{ mean}} = 7.3 \times 10^{-2} \text{ s}^{-1} \text{ atm}^{-2}$.

of the addition of hydrogen. Thus, it is known from other studies that the hydrogen addition process on mononuclear iridium-diolefin compounds is inhibited by relatively electron-donor ligands but occurs with relatively electron-accepting ligands.^{21a}

The ruthenium atom in **2a** could be active but does not contribute very significantly to the overall reaction. In this context, it is noteworthy that, as we have above mentioned, **2** catalyzes the reactions at rates about 1 order of magnitude faster than those observed for **1**.

3. Hydrogenation of Cyclohexene Catalyzed by 3. The kinetic results obtained for the hydrogenation of cyclohexene catalyzed by **1** and **2** show clear evidence in favor of an electronic cooperative effect between the metallic centers. However, the rigid biimidazolate ligand in **1** or the arrangement of the ligands in **2** does not favor a transfer of ligands from one metal center to the other. The higher flexibility of the pyrazolate bridges in complexes of the type $[\text{M}(\mu\text{-pz})\text{L}_2]_2$ (**3**) ($\text{M} = \text{Rh}, \text{Ir}$)²³ could permit this ligand transfer between the metals of the bimetallic compounds. This prompted us to investigate the hydrogenation of cyclohexene catalyzed by the complexes $[\text{Ir}(\mu\text{-pz})(\text{diolefin})]_2$ (diolefin = TFB (**3**), COD (**4**)).²⁴

The 2-propanol/toluene (3:1) solutions of **4** catalyze the hydrogenation of cyclohexene to cyclohexane at rates about twice as fast as those observed for **3**. The reactions shown an induction period that disappears when the solutions of **3** or **4** are treated with molecular hydrogen for 1 h at 60 °C before cyclohexene is added. In contrast to **2**, the catalyst was recovered unchanged after the catalytic reactions, indicating that the diolefins coordinated to iridium atoms are not hydrogenated during the reaction. On the other hand, it is known that the compound $[\text{Ir}(\mu\text{-pz})$

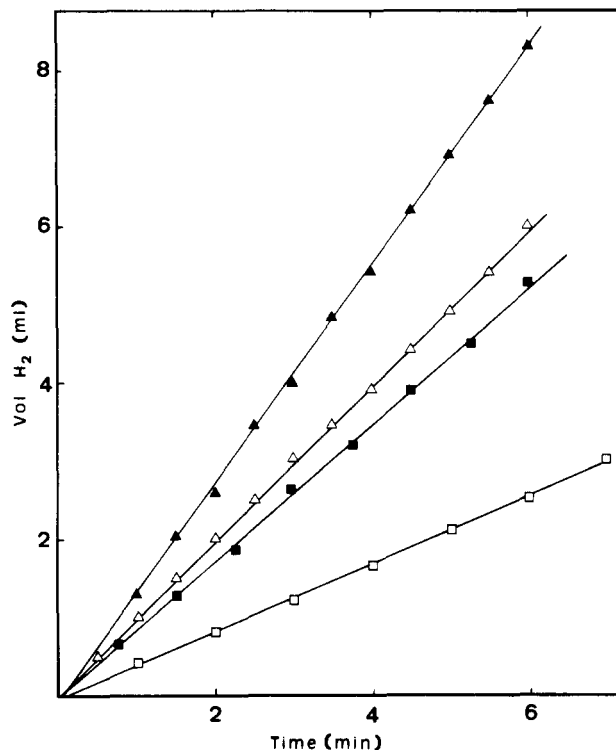
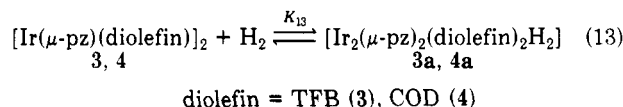


Figure 6. H₂ gas uptake plots for the $[\text{Ir}(\mu\text{-pz})(\text{TFB})_2]_2$ (**3**)-catalyzed hydrogenation of cyclohexene to cyclohexane in 2-propanol/toluene (3:1) at 60 °C (1 atm of H₂; 0.46 M cyclohexene). [**3**]: (□) $0.64 \times 10^{-3} \text{ M}$; (■) $0.84 \times 10^{-3} \text{ M}$; (Δ) $1.06 \times 10^{-3} \text{ M}$; (▲) $1.41 \times 10^{-3} \text{ M}$.

(CO)(PPh₃)₂ reacts with molecular hydrogen to give the iridium(II) dimer $[\text{Ir}(\mu\text{-pz})(\text{CO})(\text{PPh}_3)\text{H}]_2$.^{13a} Thus, it is likely that during the induction period related diiridium species of the formula $[\text{Ir}_2(\mu\text{-pz})_2(\text{diolefin})_2\text{H}_2]$ could be formed. Possibly an equilibrium as shown in eq 13 is reached.



In order to determine the possible mechanism of the catalytic reaction, kinetic measurements were performed on solutions of **3** pretreated with hydrogen for 1 h at 60 °C. Typical gas uptake measurements are shown in Figure 6. Following a kinetic analysis analogous to that described for **1**, it can be deduced from the data collected in Table III that the rate law for the hydrogenation of cyclohexene is

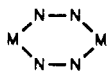
$$d[\text{cyclohexane}]/dt = -d[\text{cyclohexene}]/dt = k_{14}[\mathbf{3}](P(\text{H}_2))^2 \quad (14)$$

with a value of k_{14} of $(7.0 \pm 0.7) \times 10^{-2} \text{ s}^{-1} \text{ atm}^{-2}$ at 60 °C.²⁵

Equation 14 shows that the rate is directly proportional to $[\mathbf{3}]$, independent of [cyclohexene], and second order with respect to hydrogen pressure. At low temperature, **3** is not soluble enough to carry out a careful spectroscopic study of the catalytic solution, while at room temperature, the ¹H NMR spectrum shows the signals assigned to compound **3**. This together with the first-order dependence of the rate on the concentration of **3** proves that the full catalytic cycle involves binuclear species. Indeed, the no

(25) Plots of $\log(-dV/dt)$ versus $\log[\text{cyclohexene}]$ yield a straight line of slope 0.2, suggesting that for concentrations of cyclohexene lower than 0.6 M the reaction is, practically, zero order in cyclohexene concentration.

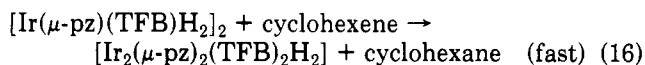
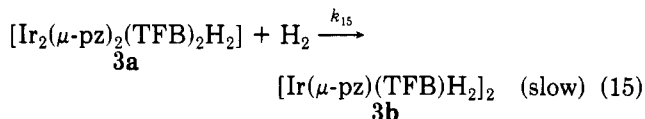
(23) Previous studies on μ -pyrazolate dirhodium complexes have demonstrated the good stability and the flexibility of the six-membered



cyclic core since the metal-metal distances range from 2.62 to 3.57 Å. (a) Usón, R.; Oro, L. A.; Ciriano, M. A.; Pinillos, M. T.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* 1981, 205, 247. (b) Usón, R.; Oro, L. A.; Ciriano, M. A.; Carmona, D.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* 1981, 206, C14. (c) Oro, L. A.; Pinillos, M. T.; Royo, M.; Pastor, E. *J. Chem. Res.* 1984, 206. (d) Beveridge, K. A.; Bushnell, G. W.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *Organometallics* 1983, 2, 1447 and references therein.

(24) It has previously reported that the complex $[\text{Ir}(\mu\text{-3,5-Me}_2\text{pz})(\text{CO})_2]_2$ catalyzes the hydrogenation of cyclohexene to cyclohexane. Nussbaum, S.; Retting, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* 1985, 63, 692.

dependence of the rate on the concentration of cyclohexene indicates that the olefin is not involved in the rate-determining step of the catalytic cycle or in a previous step to this. Therefore, the reaction of the catalyst with molecular hydrogen must be the initial step of the catalytic cycle. Furthermore, the second-order dependence of the rate on the hydrogen pressure implies that the catalyst is formed by reaction of **3** with hydrogen (eq 13). In light of these considerations, the following set of reactions could be consistent with the catalytic cycle



If the rate-determining step of the catalytic reaction is the reaction of **3a** with molecular hydrogen (eq 15), the rate of formation of cyclohexane is

$$d[\text{cyclohexane}]/dt = d[\text{3b}]/dt = k_{15}[\text{3a}]P(\text{H}_2) \quad (17)$$

Since $[\text{3a}] = K_{13}[\text{3}]P(\text{H}_2)$ by eq 13, then

$$d[\text{cyclohexane}]/dt = k_{15}K_{13}[\text{3}](P(\text{H}_2))^2 \quad (18)$$

It can be seen that eq 18 agrees well with eq 14.

4. Concluding Remarks. These studies have revealed that the binuclear compounds $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-bim})\text{Ir}(\text{COD})]$ and $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TFB})]$ are more active catalysts for the hydrogenation of cyclohexene than the mononuclear parent compounds $[\text{RuH}(\text{Hbim})(\text{CO})(\text{PPh}_3)_2]$, $[\text{Ir}(\text{Hbim})(\text{COD})]$, $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$, and $[\text{Ir}(\text{TFB})(\text{Hpz})_2]\text{BF}_4$. This catalytic synergism is produced by electronic communication between the metal centers through the bridging ligands. *The hydrogenation mainly proceeds via one metal, and the other metal acts as the core of a metal-ligand complex of variable electron density.* On the other hand, the investigation on the kinetics of the hydrogenation of cyclohexene catalyzed by $[\text{Ir}(\mu\text{-pz})(\text{TFB})]_2$ also suggests that the full catalytic cycle involves binuclear species; however, no evidence for the involvement of one or two metal centers during the catalytic cycle has been found for this system.

Experimental Section

General Considerations. All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under nitrogen prior to use. Cyclohexene (Merck) was passed through an alumina column.

Physical Measurements. ^1H and $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded on a Varian XL 200 spectrophotometer. Chemical shifts are expressed in parts per million upfield from $\text{Si}(\text{CH}_3)_4$ (^1H) and 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 240 B microanalyzer.

The catalytic reactions were followed, at constant pressure, by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256). The analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector and a β,β' -oxydipropionitrile on Chromosorb W-HP 80/100-mesh ($4\text{ m} \times 1/8$ in.) column at 70°C for the cyclohexene hydrogenation and with an FFAP on Chromosorb GHP 80/100-mesh ($3.6\text{ m} \times 1/8$ in.) column at 140°C for the TFB hydrogenation.

Materials. TFB²⁶ and the complexes $[\text{Ir}(\text{Hbim})(\text{COD})]^{27}$ $[\text{RuH}(\text{Hbim})(\text{CO})(\text{PPh}_3)_2]$, $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-bim})\text{Ir}(\text{COD})]$ (**1**),¹² $[\text{Ir}(\mu\text{-pz})(\text{COD})]_2$ (**4**),^{13b} $[\text{Ir}(\mu\text{-pz})(\text{TFB})]_2$ (**3**), $[\text{RuHCl}(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$,¹¹ and $[\text{Ir}(\mu\text{-OMe})(\text{TFB})]_2$ ²⁸ were prepared by published methods. The compound $[\text{Ir}(\text{TFB})(\text{Hpz})_2]\text{BF}_4$ was prepared by the procedure described for the analogous complex $[\text{Ir}(\text{TFB})(2\text{-Mepy})_2]\text{BF}_4$.²⁹ The purity of these compounds was checked by elemental analyses and IR and NMR (^1H and ^{31}P) spectra.

The complexes $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$ and $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TFB})]$ were obtained as described below.

Preparation of $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$. A solution of $[\text{RuHCl}(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$ (303.2 mg, 0.4 mmol) in dichloromethane (20 mL) was treated with stoichiometric amounts of KOH in methanol (0.4 mmol) and pyrazole (27.2 mg, 0.4 mmol). The reaction mixture was stirred for 4 h at room temperature and filtered through kieselguhr. The filtrate was concentrated until the precipitation of a white solid, and then methanol was added to complete the precipitation; yield 281 mg (89%). ^1H NMR (CDCl_3 , 20°C): δ -11.65 (t, $J_{\text{P-H}} = 20.2$ Hz, 1 H, RuH); 5.53 (t, 1 H) and 5.96 (t, 1 H) (H4 and H4', pz₂); 6.61 (d, 1 H), 7.05 (d, 1 H), 7.09 (d, 1 H), and 7.11 (d, 1 H) (H3, H3', H5, and H5', pz₂). ^{31}P NMR (CDCl_3 , 20°C): δ 45.64 (s). IR: $\nu_{\text{CO}}(\text{Cl}_2\text{CH}_2)$ 1925 cm^{-1} ; $\nu_{\text{Ru-H}}$ (Nujol) 1980 cm^{-1} . Anal. Calcd for $\text{C}_{43}\text{H}_{38}\text{N}_4\text{OP}_2\text{Ru}$: C, 65.39; H, 4.85; N, 7.09. Found: C, 65.33; H, 5.06; N, 7.10.

Preparation of $[\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ru}(\mu\text{-pz})_2\text{Ir}(\text{TFB})]$ (2**).** A stoichiometric amount of $[\text{Ir}(\mu\text{-OMe})(\text{TFB})]_2$ (89.3 mg, 0.1 mmol) was added to a suspension of $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$ (158 mg, 0.2 mmol) in acetone (25 mL), and the mixture was stirred for 24 h at reflux temperature. The resulting suspension was cooled to room temperature, the solvent was partially evaporated, and the yellow solid formed was filtered off, washed with acetone and hexane, and vacuum dried; yield 166 mg (69%). ^1H NMR (CDCl_3 , 20°C): δ -11.77 (t, $J_{\text{P-H}} = 20.1$ Hz, 1 H, RuH); 2.3 (m, 4 H, =CH, TFB); 5.1 (m, 2 H, CH, TFB); 5.23 (t, 1 H) and 5.76 (t, 1 H) (H4 and H4', (pz)₂); 6.25 (d, 1 H), 6.54 (d, 1 H), 6.65 (d, 1 H), and 6.84 (d, 1 H) (H3, H3', H5, and H5', pz₂). ^{31}P NMR (CDCl_3 , 20°C): δ 45.86 (s). IR: $\nu_{\text{CO}}(\text{Cl}_2\text{CH}_2)$ 1912 cm^{-1} ; $\nu_{\text{Ru-H}}$ (Nujol) 1970 cm^{-1} . Anal. Calcd for $\text{C}_{53}\text{H}_{43}\text{N}_4\text{F}_4\text{IrOP}_2\text{Ru}$: C, 54.72; H, 3.59; N, 4.64. Found: C, 54.76; H, 3.93; N, 4.62.

Catalytic Reactions. A degassed solution of the catalyst in toluene (4 mL) was syringed through a silicone septum into a 25-mL flask attached to a gas buret, which was in turn connected to a Schlenck manifold. The system was evacuated and refilled with hydrogen three times, and the flask was then immersed in a 60°C bath. The substrate, dissolved in deaerated 2-propanol (4 mL), was subsequently introduced through the septum, and the mixture was vigorously shaken during the run. For the experiments with complexes **3** and **4** involving pretreatment, the catalyst solution (2 mL of toluene + 4 mL of 2-propanol) was shaken under hydrogen for 1 h at 60°C prior to introduction of the substrate dissolved in deaerated 2-isopropanol (2 mL).

Acknowledgment. We acknowledge useful discussions with Prof. J. A. Osborn, and we thank DGICYT (Proyect PB 88-0386, Programa de Promoción General del Conocimiento) for financial support.

Registry No. **1**, 121616-19-1; **2**, 130095-99-7; **3**, 129450-88-0; TFB, 5162-34-5; $[\text{RuH}(\text{pz})(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$, 130063-77-3; $[\text{RuHCl}(\text{CO})(\text{Hpz})(\text{PPh}_3)_2]$, 129434-13-5; $[\text{Ir}(\mu\text{-OMe})(\text{TFB})]_2$, 94401-81-7; cyclohexene, 110-83-8; cyclohexane, 110-82-7.

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