3362 Organometallics 1992, 11, 3362–3369

Hydrogenation of Benzylideneacetone Catalyzed by $OsHCl(CO)(PR_3)_2$ (PR_3 = P-*i*-Pr_3, PMe-*t*-Bu_2): New Roles of Dihydrogen Complexes in Homogeneous Catalytic Hydrogenation

Miguel A. Esteruelas, Luis A. Oro,* and Cristina Valero

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, E-50009 Zaragoza, Spain

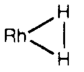
Received February 20, 1992

The five-coordinated hydrido carbonyl complexes $OsHCl(CO)(PR_3)_2$ (PR_3 = P-*i*-Pr_3 (1), PMe-*t*-Bu_2 (12)) catalyze the selective hydrogenation of benzylideneacetone to 4-phenylbutan-2-one. In 2-propanol solutions, selectivities close to 100% are achieved. In the presence of 1, the reaction is first-order with respect to the concentrations of catalyst and substrate and independent of the hydrogen pressure. For the reaction catalyzed by 12, the kinetic experimental data are in accordance with an expression of the form $-d[\text{benzylideneacetone}]/dt = k[12]^2[\text{benzylideneacetone}](P(H_2))$. The mechanisms deduced for these reactions, on the basis of the rate laws and spectroscopic observations, illustrate new roles of the dihydrogen complexes in homogeneous catalytic hydrogenation. 1, initially nonactive, is activated as a result of the formation of *trans(hydride,dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)$(P-*i*-$Pr_3)_2$ (6), which isomerizes to *cis(hydride,dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)$(P-*i*-$Pr_3)_2$ (14) and subsequently dissociates molecular hydrogen. The reaction catalyzed by 12 is proposed to go by the intermediate *trans*-$[OsCl(CO)(PMe\text{-}t\text{-}Bu_2)_2]_2H_4$ (18), which could be formed by reaction of 12 with *cis(hydride,dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (20). According to the theoretical works of Burdett and Pourian, this binuclear intermediate could contain a planar 4-gon of cyclically bound hydrogen atoms.

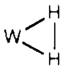
Introduction

The study of the mechanism of homogeneous hydrogenation catalyzed by transition-metal complexes has led to a better understanding of catalytic reactions. The discovery, in the last few years, of the dihydrogen complexes[1] has been an important contribution to the field. These compounds have distinctive properties of great utility in rationalizing some fundamental steps of the catalytic cycles.

Early, Halpern[2] proposed that the activation of hydrogen involved attack of the bonding electrons of the hydrogen molecule on a vacant metal d orbital. Recent theoretic studies[3] on the oxidative addition of molecular hydrogen to $RhCl(PPh_3)_3$ show the existence of a strong three-center interaction between molecular hydrogen and the rhodium atom. The structure of the calculated



fragment is similar to that determined experimentally for the



fragment in the complex $W(CO)_3$(P-*i*-$Pr_3)_2(\eta^2\text{-}H_2)$.[4] In agreement with this, spectroscopic observations indicate that the solutions of some dihydrogen complexes contain a dihydride equilibrium fraction which is formed by oxidative addition of the η^2-H_2 ligand.[5]

The coordinated η^2-H_2 ligand, which might be considered as an isolated intermediate on the way to oxidative addition, is readily deprotonated.[6] The acidic character of this ligand has suggested that the dihydrogen complexes may be important in the heterolytic activation of hydrogen.[7] Recent kinetic studies on the hydrogenation of alkynes to alkenes catalyzed by $[FeH(\eta^2\text{-}H_2)(PP_3)]BPh_4$ ($PP_3 = P(CH_2CH_2PPh_2)_3$) have proved that reduction of the substrates occurs via an intramolecular acid/base reaction involving η^2-H_2 and σ-vinyl ligands mutually cis disposed.[8] In this way the metal gives the same products that would have been obtained through an oxidative-addition/reductive-elimination pathway, but avoiding the oxidative step.

The η^2-H_2 ligand can be easily substituted by several molecules such as N_2, CO, CNR, PR_3, olefins, etc.[9] This

---

[1] (a) Kubas, G. J. *Comments Inorg. Chem.* **1988**, 7, 17. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

[2] Halpern, J. *Adv. Catal.* **1959**, *11*, 301.

[3] Daniel, C.; Koga, N.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773.

[4] Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

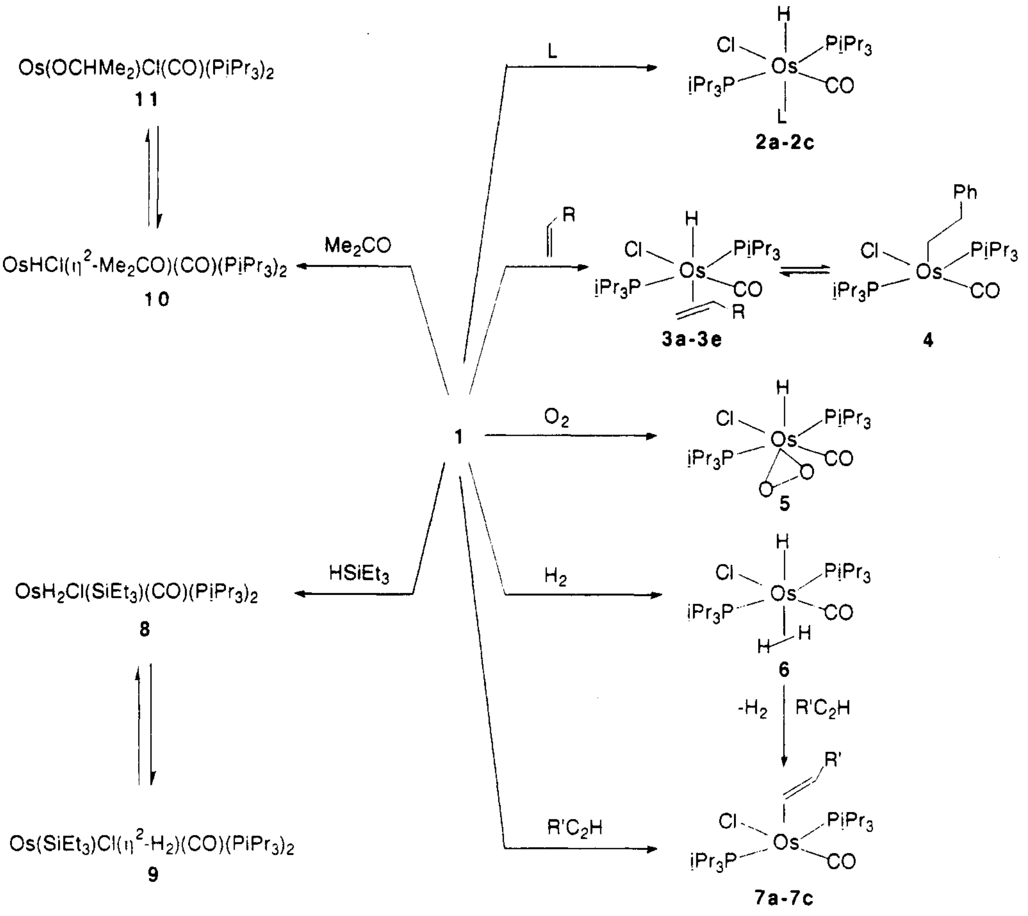
[5] (a) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (b) Clark, H. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 3829. (c) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (d) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (e) Arliguie, T.; Chaudret, B. *J. Chem. Soc., Chem. Commun.* **1989**, 155. (f) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Stepan Van Der Sluys, L.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855. (g) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (h) Haward, M. T.; George, M. W.; Hamley, P.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1101.

[6] (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (c) Cappellani, E. P.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Steele, M. R. *Inorg. Chem.* **1989**, *28*, 4437. (d) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (e) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1990**, *390*, C16. (f) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581. (g) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (h) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (i) Cazanoue, M.; He, Z.; Neibecker, D.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1991**, 307. (j) Stepan Van Der Sluys, L.; Miller, M. M.; Kubas, G. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 2513. (k) Jia, G.; Morris, R. H.; Schweitzer, C. T. *Inorg. Chem.* **1991**, *30*, 593.

[7] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988.

[8] Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. *Organometallics* **1992**, *11*, 138.

Scheme I



	a	b	c	d	e
L	CO	PMe$_3$	P(OMe)$_3$		
R	H	CN	CO$_2$Me	COMe	Ph
R'	H	Me	Ph		

weak Lewis base character permits it to stabilize unsaturated species in solution, without bothering the coordination of the substrate to the metallic center. Several catalytic systems based upon this strategy have been reported,[10] and some other catalysts, studied before 1984, could also contain the η^2-H$_2$ ligand. Along these lines, it has recently been described that [IrH$_2$(η^2-H$_2$)(PPh$_2$Me)$_3$]$^+$ catalyzes the hydrogenation of 2-butyne.[11] Thus, it is very likely that intermediates [IrH$_2$(η^2-H$_2$)$_2$(PR$_3$)$_2$]$^+$ formed from [Ir(COD)(PR$_3$)$_2$]$^+$ under hydrogen in noncoordinating solvents catalyze the hydrogenation of olefins via a mechanism broadly similar to that described earlier by Schrock and Osborn, for the same reactions, in the presence of [RhH$_2$(Me$_2$CO)$_2$(PR$_3$)$_2$]$^+$.[12]

Six years ago, the synthesis of OsHCl(CO)(P-*i*-Pr$_3$)$_2$ (1) was reported.[13] At room temperature, it adds Lewis bases that are not bulky (e.g. CO, PMe$_3$, and P(OMe)$_3$) to form octahedral compounds of formula OsHCl(CO)L(P-*i*-Pr$_3$)$_2$ (2a–c) (Scheme I). Oxygen, hydrogen, and olefins such as ethylene, methyl acrylate, acrylonitrile, and methyl vinyl ketone are also coordinated.[13,14] Upon reaction with HSiEt$_3$, the dihydrogen complex 9 is formed.[15] Alkynes, styrene, and acetone undergo insertion into the Os–H bond of 1.[16-18] As the complexes 2–11 can be considered as models for catalytic intermediates, 1 has been used as a

---

(9) (a) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. (b) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (c) Henderson, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1670. (d) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429. (e) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072. (f) Boyd, S. E.; Field, L. D.; Hambley, T. W.; Young, D. J. *Inorg. Chem.* **1990**, *29*, 1496. (g) Amendola, P.; Antoniutti, S.; Albertin, G.; Bordignon, E. *Inorg. Chem.* **1990**, *29*, 318. (h) Jia, G.; Meek, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 757. (i) Bianchini, C.; Pérez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.

(10) (a) Crabtree, R. H. *Inorg. Chim. Acta* **1986**, *125*, L7. (b) Linn, D. E.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969. (c) Hampton, C.; Cullen, W. R.; James, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 6918. (d) Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855.

(11) (a) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165. (b) Marinelli, G.; Rachidi, I. E.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 2346.

(12) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143. (c) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 4450.

(13) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

(14) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563.

(15) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462.

(16) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.

(17) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431.

(18) Esteruelas, M. A.; Valero, C.; Oro, L. A.; Meyer, U.; Werner, H. *Inorg. Chem.* **1991**, *30*, 1159.

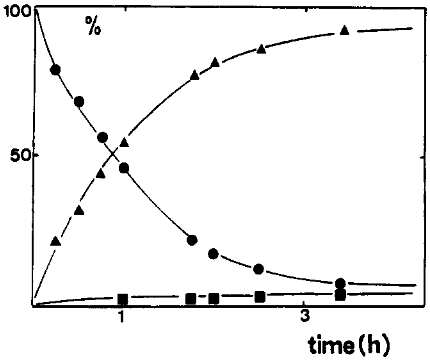


Figure 1. Hydrogenation of benzylideneacetone catalyzed by $OsHCl(CO)(P-i-Pr_3)_2$ in 2-propanol at 60 °C (1 atm of H_2; 2.5×10^{-3} M $OsHCl(CO)(P-i-Pr_3)_2$; 0.25 M $PhHC{=}CHC(O)CH_3$): (●) benzylideneacetone; (▲) 4-phenylbutan-2-one; (■) 4-phenylbutan-2-ol.

homogeneous catalyst precursor. Thus, in the presence of KOH or $NaBH_4$, it catalyzes hydrogen-transfer reactions from 2-propanol to cyclohexanone, acetophenone,[19] benzylideneacetone, benzylideneacetophenone,[20] and phenylacetylene.[21] Under a hydrogen atmosphere, 1 is a very active homogeneous hydrogenation catalyst for styrene, cyclohexene, cyclohexadienes, phenylacetylene, and diphenylacetylene,[14] and in the presence of $HSiEt_3$, phenylacetylene is transformed into *trans*- and *cis*-$PhHC{=}CH(SiEt_3)$. This catalytic hydrosilylation proceeds via the silyl–dihydrogen species 9 according to the reactions

$$1 + HSiEt_3 \xrightarrow{\text{slow}} 9 \quad (1)$$

$$9 + PhC_2H \xrightarrow{\text{fast}} 1 + \textit{trans-}\text{ and }\textit{cis-}PhHC{=}CH(SiEt_3) \quad (2)$$

In a continuation of our catalytic studies, we have now found that 1 and its related complex $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (12) also catalyze the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one. Although the range of catalysts available for the hydrogenation of unsaturated ketones is great, and simple enones may be reduced to ketones in the presence of $OsHBr(CO)(PPh_3)_3$,[22] $OsH_2Cl_2(P-i-Pr_3)_2$,[23] $CoH_3(P(O-i-Pr)_3)_3$,[24] $RhCl(PPh_3)_3$,[25] $RhHCl_2(PCy_3)_2$,[26] $[Rh(NBD)(PR_3)_2]^+$,[27] $[Ir(COD)(py)(PCy_3)]^+$,[28] $IrH_3(PR_3)_3$, $IrH_5(PR_3)_2$,[29] Pd(DIAN)(alkene)[30] (DIAN = *N,N'*-diaryldiiminoacenaphthene), or $Pt(C_2H_4)$(chelating diphosphine),[31] mechanistic proposals supported by rate law and spectroscopic studies of the reactions have not been reported. In the present article we describe the results obtained from a kinetic and spectroscopic study on the hydrogenation of benzylideneacetone catalyzed by 1 and 12. We believe that these results are of interest because they permit us to propose new "mechanisms" which illustrate new roles of the dihydrogen complexes in homogeneous catalytic hydrogenation.

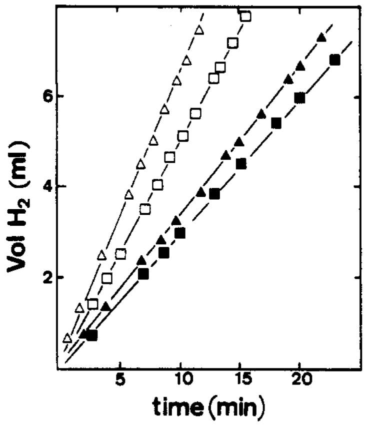


Figure 2. H_2 gas uptake plots for the $OsHCl(CO)(P-i-Pr_3)_2$-catalyzed hydrogenation of benzylideneacetone to 4-phenylbutan-2-one in 2-propanol at 60 °C (1 atm of H_2; 2.5×10^{-3} M $OsHCl(CO)(P-i-Pr_3)_2$). $[PhHC{=}CHC(O)CH_3]$ = 0.25 M (■), 0.34 M (▲), 0.52 M (□), 0.60 M (△).

Results and Discussion

1. Hydrogenation of Benzylideneacetone Catalyzed by 1. The hydrogenation of benzylideneacetone to 4-phenylbutan-2-one in the presence of 1 was performed in a 2-propanol solution. Figure 1 summarizes the course of a typical reaction. The reduction of the C=C bond of the α,β-unsaturated ketone is preferred to that of the C=O bond. Although two reaction paths can be envisaged for the hydrogenation of unsaturated ketones (C=C reduction or C=O reduction), careful GC measurements showed that, in this case, no unsaturated alcohol is formed. After 3 h, at 60 °C and under an atmospheric pressure of hydrogen, conversions close to 90% are achieved. During the same time, under an argon atmosphere, the conversion was no more than 3%, showing that hydrogen transfer from the solvent does not represent an important contribution to the overall reaction.

A simple rate law for a catalytic hydrogenation of benzylideneacetone to 4-phenylbutan-2-one is

$$-d[\text{benzylideneacetone}]/dt = -d[H_2]/dt = k_3[\text{benzylideneacetone}]^m[\text{cat.}]^n[H_2]^q \quad (3)$$

At constant temperature and with a large excess of α,β-unsaturated ketone, this rate law is further simplified to

$$-d[\text{benzylideneacetone}]/dt = -d[H_2]/dt = k_{obs}[\text{cat.}]^n(P(H_2))^q \quad (4)$$

where $P(H_2)$ is the hydrogen pressure.

The reactions were followed by measuring the hydrogen consumption as a function of time. The volume of H_2

---

(19) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *J. Mol. Catal.* **1988**, *45*, 1.

(20) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *J. Mol. Catal.* **1989**, *53*, 43.

(21) Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187.

(22) Sanchez-Delgado, R.; Andriollo, A.; González, E.; Valencia, N.; León, V.; Espidel, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1859.

(23) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

(24) Rakowski, M. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 739.

(25) Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; D. Reidel: Dordrecht, The Netherlands, 1985; Chapter 3, p 48, and references therein.

(26) Grushin, V. V.; Alper, H. *Organometallics* **1991**, *10*, 831.

(27) Fujitsu, H.; Matsumura, E.; Takeshita, K.; Mochida, I. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2650.

(28) Suggs, J. W.; Cox, S. D.; Crabtree, R. H.; Quirk, J. M. *Tetrahedron Lett.* **1981**, *22*, 303.

(29) (a) Farnetti, E.; Pesce, M.; Kaspar, J.; Spogliarich, R.; Graziani, M. *J. Chem. Soc., Chem. Commun.* **1986**, 746. (b) Farnetti, E.; Nardin, G.; Graziani, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1264. (c) Farnetti, E.; Kaspar, J.; Spogliarich, R.; Graziani, M. *J. Chem. Soc., Dalton Trans.* **1988**, 947. (d) Spogliarich, R.; Farnetti, E.; Kaspar, J.; Graziani, M.; Cesarotti, E. *J. Mol. Catal.* **1989**, *50*, 19.

(30) Van Asselt, R.; Elsevier, C. J. *J. Mol. Catal.* **1991**, *65*, L13.

(31) Paganelli, S.; Matteoli, U.; Scrivanti, A.; Botteghi, C. *J. Organomet. Chem.* **1990**, *397*, 375.

Table I. Kinetic Data for the Hydrogenation of Benzylideneacetone to 4-Phenylbutan-2-one Catalyzed by $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (1)

T, K	$P(H_2)$, atm	10^3[Os], M	[substrate], M	$10^6(-dV/dt)$,[a] L s^{-1}	10^2k_{obs}, s^{-1}	10^2k_6, M^{-1} s^{-1}
333	1.00	0.73	0.43	3.15	2.0	4.6
	1.00	1.01	0.43	4.00	1.8	4.2
	1.00	1.23	0.43	6.87	2.6	5.9
	1.00	1.70	0.43	5.33	1.4	3.3
	1.00	1.97	0.43	10.25	2.4	5.5
	1.00	2.50	0.43	8.73	1.6	3.7
	1.00	2.50	0.25	5.18	1.0	3.8
	1.00	2.50	0.29	5.33	1.0	3.4
	1.00	2.50	0.34	6.00	1.1	3.2
	1.00	2.50	0.39	8.58	1.6	4.0
	1.00	2.50	0.52	8.83	1.6	3.1
	1.00	2.50	0.60	10.37	1.9	3.2
	0.70	2.50	0.43	10.13	1.9	4.3
	0.84	2.50	0.43	8.33	1.5	3.6
	1.26	2.50	0.43	9.63	1.8	4.1
293	1.00	2.50	0.43	0.33	0.1	0.2
313	1.00	2.50	0.43	1.42	0.3	0.6
323	1.00	2.50	0.43	3.00	0.6	1.3
338	1.00	2.50	0.43	10.17	1.9	4.3
343	1.00	2.50	0.43	15.67	2.9	6.7
348	1.00	2.50	0.43	24.67	4.5	10.0

[a] Corrected to P = 1 atm.

corrected to 1 atm was converted to the pseudo-zero-order rate constant k_{obs} using eq 5, where $-dV/dt$ is the initial rate, R is the molar gas constant, T is the temperature (K), and V_{sol} is the total volume (L) of the reacting solution.

$$-(dV/dt)/RTV_{sol} = k_{obs}[\text{cat.}]^n(P(H_2))^q \quad (5)$$

Initial hydrogenation rates were obtained from gas uptake experiments, as exemplified in Figure 2. In order to determine the rate dependence on the various reaction components, hydrogenation runs were performed at different catalyst (1) and benzylideneacetone concentrations and at different hydrogen pressures (Table I). Plots of log ($-dV/dt$) versus log [1] and log ($-dV/dt$) versus log [benzylideneacetone] yielded straight lines with slopes of 0.96 and 0.85, respectively, suggesting that the reduction of the α,β-unsaturated ketone is first-order in catalyst and substrate concentration. On the other hand, the data collected in Table I indicate that the reaction rate is practically independent of the hydrogen pressure; the catalytic rate law therefore is

$$-d[\text{benzylideneacetone}]/dt = k_6[\mathbf{1}][\text{benzylideneacetone}] \quad (6)$$

and

$$k_{obs} = k_6[\text{benzylideneacetone}] \quad (7)$$

A plot of k_{obs} versus [benzylideneacetone] (Figure 3) yields a value for k_6 at 333 K of (3.19 ± 0.29) × 10^{-2} M^{-1} s^{-1}. From the temperature dependence of k_6 the following parameters are deduced at 333 K: $\Delta H^‡ = 14.8 \pm 0.7$ kcal mol^{-1}, $\Delta S^‡ = -21.1 \pm 1.9$ cal mol^{-1} K^{-1}, and $\Delta G^‡ = 21.9 \pm 1.4$ kcal mol^{-1}.

Hydrogenation Mechanism. According to eq 6, the mechanism of benzylideneacetone hydrogenation catalyzed by 1 can be described in its simpler form by eqs 8 and 9.

$$[Os]\text{-}H + S \xrightarrow{\text{slow}} [Os]\text{-}SH \quad (8)$$

$$[Os]\text{-}SH + H_2 \xrightarrow{\text{fast}} [Os]\text{-}H + SH_2 \quad (9)$$

$[Os] = OsCl(CO)(P\text{-}i\text{-}Pr_3)_2$; S = benzylideneacetone

In order to obtain more information about the intimate details of the slow step of this catalytic reaction (eq 8), a spectroscopic study of the reactivity of 1 toward benzylideneacetone was carried out. Addition of an excess of α,β-unsaturated ketone (ca. 4 equiv) to 1 in benzene-d_6 at room temperature, in an NMR tube under argon, does not produce any changes in the catalyst signals. Although a nondetectable $OsHCl(\eta^2\text{-}PhHC{=}CHC(O)Me)(CO)(P\text{-}i\text{-}Pr_3)_2$ (13) intermediate, similar to 3d, could be formed, the intramolecular insertion of the α,β-unsaturated ketone olefinic bond into the Os–H bond is not favored due to the trans disposition of these ligands. Consistently, phenomena of H–D exchange between Os–D and benzylideneacetone were not observed when the substrate was added to a solution of $OsDCl(CO)(P\text{-}i\text{-}Pr_3)_2$, under the abovementioned experimental conditions. However, under a hydrogen atmosphere, fast formation of 6 and subsequent reduction of benzylideneacetone to 4-phenylbutane-2-one take place. These observations suggest that 6 plays a fundamental role in the rate-determining step of the catalytic reaction.[32] According to this, the ^{31}P NMR spectra of the catalytic solutions show a signal at 36.1 ppm, which is assigned to 6 by comparison of these spectra with a pure sample.

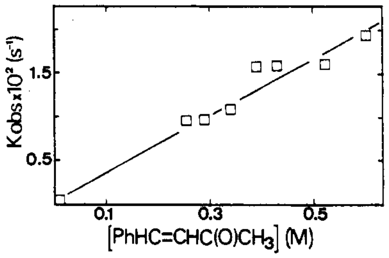


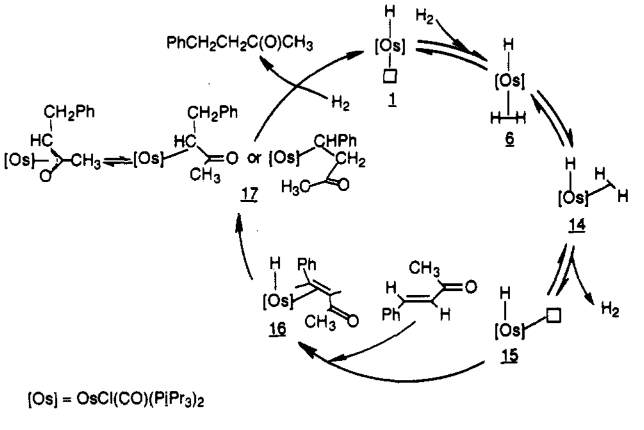
Figure 3. Rate constant plot for the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ in 2-propanol at 60 °C (1 atm of H_2; 2.5 × 10^{-3} M $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$).

The initial addition of molecular hydrogen to the catalyst is difficult to reconcile with the observed kinetics, unless the hydrogen dependence of this step is compensated by an inverse hydrogen dependence corresponding to the dissociation of the $\eta^2\text{-}H_2$ ligand. In order to understand the role of the $\eta^2\text{-}H_2$ ligand in the catalysis

---

[32] As shown in Scheme I, alkynes and styrene undergo insertion into the Os–H bond of 1, suggesting that 6 does not play, most probably, a fundamental role in the catalytic hydrogenation of these substrates.

Scheme II. Catalytic Cycle for the Hydrogenation of Benzylideneacetone to 4-Phenylbutan-2-one Catalyzed by $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (1)



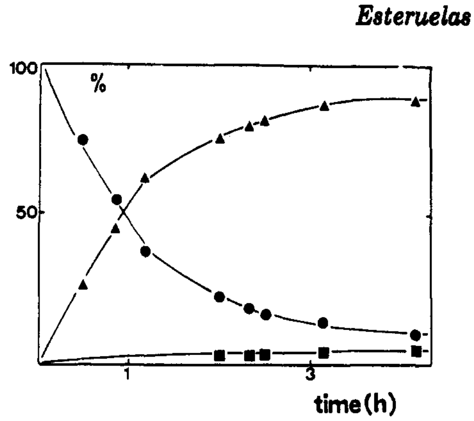


Figure 4. Hydrogenation of benzylideneacetone catalyzed by $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ in 2-propanol at 43 °C (1 atm of H_2; 2.54 × 10^{-3} M $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$; 0.25 M $PhHC{=}CHC(O)CH_3$): (●) benzylideneacetone; (▲) 4-phenylbutan-2-one; (■) 4-phenylbutan-2-ol.

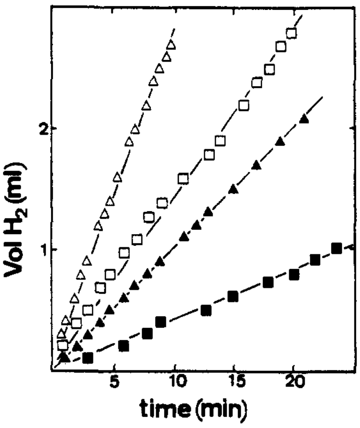


Figure 5. H_2 gas uptake plots for the $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$-catalyzed hydrogenation of benzylideneacetone to 4-phenylbutan-2-one in 2-propanol at 41 °C (1 atm of H_2; 1.27 × 10^{-3} M $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$). $[PhHC{=}CHC(O)CH_3]$ = 0.07 M (■), 0.16 M (▲), 0.26 M (□), 0.43 M (△).

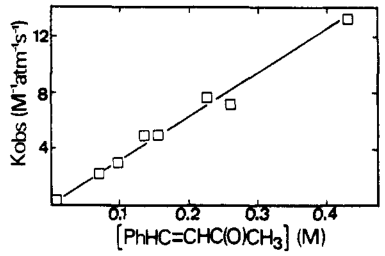


Figure 6. Rate constant plot for the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ in 2-propanol at 41 °C (1 atm of H_2; 1.27 × 10^{-3} M $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$).

rate-determining step, reaction of 1 with D_2 under ambient conditions was studied. As a result of this study, we found that the complex $OsDCl(\eta^2\text{-}D_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ was rapidly formed, indicating that for 6 $Os\text{–}H/Os\text{–}(\eta^2\text{-}H_2)$ and coordinated H_2/free H_2 exchange phenomena take place faster than on the NMR time scale. Three possible mechanisms for the $MH/M(\eta^2\text{-}H_2)$ exchange process have been proposed:[33] (i) homolytic cleavage of the H–H bond of the $\eta^2\text{-}H_2$ ligand to give a fluxional trihydride intermediate, (ii) rapid equilibrium trans ⇌ cis isomerization of the octahedral complex to bring the exchanging groups cis to each other, and (iii) formal deprotonation of the $\eta^2\text{-}H_2$ ligand by the hydride ligand, which can act as a base. In our case, according to eq 6 and the experimental spectroscopic observations mentioned above, (ii) is the only possible mechanism. The trans ⇌ cis isomerization process could occur via a fluxional trihydride intermediate formed by homolytic cleavage of the H–H bond.

Scheme II shows a catalytic cycle for the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by 1, which agrees with all that has previously been described. As the insertion of the substrate into the Os–H bond of 1 is not favored due, most probably, to the trans disposition of the hydride ligand and the coordination vacancy, formation of 6, following isomerization to 14 and subsequent hydrogen dissociation, produces a rearrangement of the ligands of the catalyst to give a new isomer, 15, containing the hydride ligand and the coordination vacancy in a cis disposition. Then, coordination of the substrate and its subsequent insertion into the Os–H bond must lead to an alkyl intermediate, which by reaction with molecular hydrogen gives 4-phenylbutan-2-one and regenerates 1. Scheme II, on the other hand, illustrates a new role of the dihydrogen compounds in catalysis. As a consequence of the isomerization of 6 into 14 and subsequent dissociation of the $\eta^2\text{-}H_2$ ligand, the starting species 1 is activated.

2. Hydrogenation of Benzylideneacetone Catalyzed by 12. Under the above-mentioned experimental conditions, 12 also catalyzes the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one. Figure 4 summarizes the course of a typical reaction. In order to obtain more information about the reaction mechanism, the kinetics of the hydrogenation was studied. Typical gas uptake measurements are shown in Figure 5. Following a kinetics analysis analogous to that described above for 1, from the data collected in Table II we can deduce that the reaction is second-order with respect to catalyst[34] and first-order with respect to hydrogen and benzylideneacetone. Thus, the catalytic rate law can be written as

$$-\mathrm{d}[\text{benzylideneacetone}]/\mathrm{d}t = k_{10}[12]^2[\text{benzylideneacetone}](P(H_2)) \quad (10)$$

and

$$k_{\text{obs}} = k_{10}[\text{benzylideneacetone}] \quad (11)$$

A plot of k_{obs} versus [benzylideneacetone] (Figure 6) yields a value for k_{10} at 314 K of 30 ± 2 $M^{-2}\ atm^{-1}\ s^{-1}$. In

---

[33] Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876.

[34] The same dependence on catalyst was observed when 1,2-dichloromethane was used as solvent.

Table II. Kinetic Data for the Hydrogenation of Benzylideneacetone to 4-Phenylbutan-2-one Catalyzed by $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (12)

T, K	$P(H_2)$, atm	10^3[Os], M	[substrate], M	$10^6(-dV/dt)$,[a] L s^{-1}	k_{obs}, M^{-1} atm^{-1} s^{-1}	k_{10}, M^{-2} atm^{-1} s^{-1}
314	1.00	1.90	0.10	2.32	3.1	31
	1.00	3.15	0.10	5.37	2.6	26
	1.00	3.83	0.10	6.98	2.3	23
	1.00	0.76	0.43	1.75	14.7	34
	1.00	1.28	0.43	4.53	13.4	31
	1.00	1.91	0.43	7.08	9.4	22
	1.00	2.20	0.43	13.50	13.5	31
	1.00	2.56	0.43	24.90	18.4	43
	1.00	1.27	0.07	0.72	2.2	31
	1.00	1.27	0.10	0.97	2.9	29
	1.00	1.27	0.14	1.65	5.0	37
	1.00	1.27	0.16	1.66	5.0	31
	1.00	1.27	0.22	2.55	7.7	34
	1.00	1.27	0.26	2.30	7.0	27
	0.81	1.27	0.14	1.33	4.9	35
	1.17	1.27	0.14	2.16	5.5	39
	1.51	1.27	0.14	2.83	5.5	39
309	1.00	1.29	0.43	2.93	8.6	20
320	1.00	1.27	0.43	5.28	15.5	36
326	1.00	1.28	0.43	5.98	16.8	39
331	1.00	1.27	0.43	9.33	26.7	62

[a] Corrected to P = 1 atm.

light of eq 10, the following set of reactions could be consistent with the catalytic cycle:[35]

$$\underset{12}{2[Os]} + H_2 \underset{}{\overset{K_{12}}{\rightleftharpoons}} \underset{18}{[Os]_2H_2} \qquad (12)$$

$$\underset{18}{[Os]_2H_2} + S \xrightarrow[\text{slow}]{k_{13}} \underset{12}{2[Os]} + SH_2 \qquad (13)$$

$[Os] = OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$,
S = benzylideneacetone

The formation rate of 4-phenylbutan-2-one (SH_2) follows the kinetic law

$$d[SH_2]/dt = -d[S]/dt = k_{13}[18][S] \qquad (14)$$

Since $[18] = K_{12}[12]^2(P(H_2))$, then

$$d[SH_2]/dt = -d[S]/dt = k_{13}K_{12}[12]^2[S](P(H_2)) \qquad (15)$$

As can be seen in eq 15, the rate of the catalytic reaction is directly proportional to [benzylideneacetone] and $P(H_2)$ and second-order with respect to [12], which agrees well with the experimental data (see eq 10).

Hydrogenation Mechanism. In order to determine the nature of 18, we have carried out the spectroscopic investigation of the reaction of 12 with molecular hydrogen. Figure 7 shows the spectra of 12 in the hydride region with toluene-d_8 as solvent under a hydrogen atmosphere, at temperatures ranging from −79 to +52 °C.

The ^1H NMR spectrum of 12, in the hydride region, in toluene-d_8 under an argon atmosphere and at room temperature shows a triplet at δ −34.20 with a P–H coupling of 14 Hz.[36] Under a hydrogen atmosphere, this triplet disappears and a broad signal at about −28 ppm (A) is observed. When the temperature is lowered to 0 °C, A disappears and the spectrum contains a new broad signal at about −2 ppm (B), which shows T_1 = 3.4 ms. From −36 to −58 °C, the spectra show three signals: B, C + D, and A. At −79 °C, C + D resolves into a broad signal and a triplet with a P–H coupling of about 18 Hz. The dynamic behavior of C + D is typical for cis(hydride,dihydrogen) complexes where the classical and the nonclassical ligands are exchanging at the metal. However, the dynamic behavior observed for A can be rationalized in terms of a

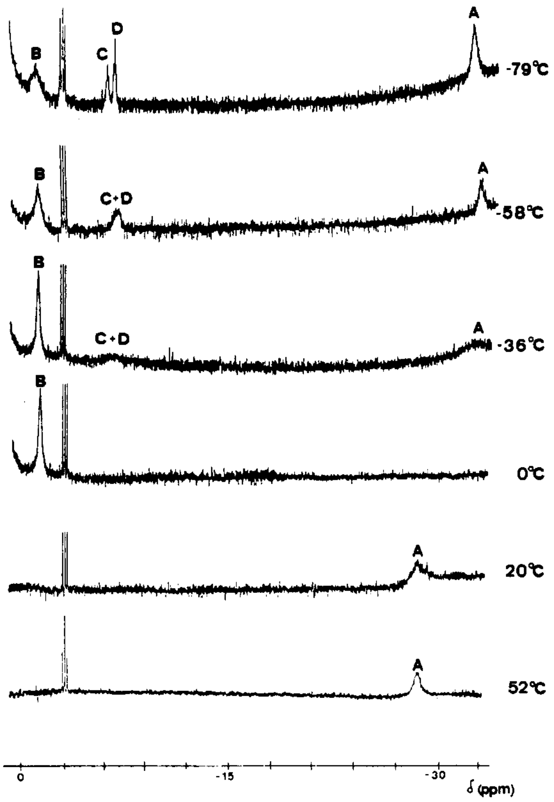


Figure 7. ^1H NMR spectra (toluene-d_8) of the hydride region from +52 to −79 °C for $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ under an H_2 atmosphere. The triplet at δ −2.40 ppm (J_{P-H} = 30 Hz, 1 H, Os*H*) is assigned to $OsHCl(\eta^2\text{-}O_2)(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (5).[17]

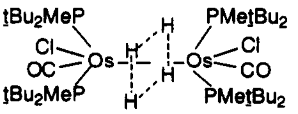


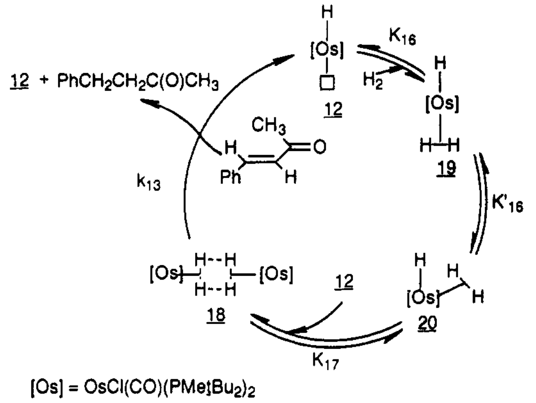
Figure 8. Structure proposed for 18 on the basis of the theoretical studies of Burdett and Pourian.

---

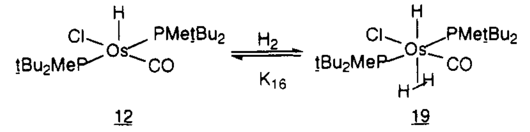
(35) Reaction of 12 with benzylideneacetone was not observed.

(36) (a) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11. (b) Meyer, U. Dissertation, University of Würzburg, 1988.

Scheme III. Catalytic Cycle for the Hydrogenation of Benzylideneacetone to 4-Phenylbutan-2-one Catalyzed by $OsHCl(CO)(PMe$-*t*-$Bu_2)_2$ (12)

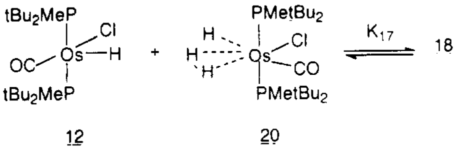


dynamic equilibrium between 12 and $OsHCl(\eta^2\text{-}H_2)(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (19) (eq 16).



(16)

Equation 10 suggests that two molecules of 12 react with one molecule of hydrogen to give the binuclear intermediate 18. Previous theoretical studies[37] have predicted that there is a class of complexes with *n* vertices with good HOMO–LUMO gaps of the type *trans*-$(ML_x)_2H_{n-2}$ for deltahedra with $n = 5$–7, which have a total of 34 valence electrons and a planar $(n - 2)$-gon of cyclically bound hydrogen atoms. If we give *n* the value of 6, in our system, it is possible to find the binuclear compound *trans*-$[OsCl(CO)(PMe\text{-}t\text{-}Bu_2)_2]_2H_4$ (Figure 8), which complies with the above-mentioned prerequisites and explains the kinetic observations. The structure shown in Figure 8 is related geometrically to a set of analogous complexes with four bridging hydrides, several examples of which have been characterized by neutron diffraction: for instance, $[ReH_2(PEt_2Ph)_2]_2H_4$. Interestingly, the hydride ligands of this rhenium compound appear as a broad signal at 0 °C.[38] The spectra shown in Figure 7 at −36, −58, and −79 °C illustrate the equilibrium between the species corresponding to the signal B, C + D, and A, at these temperatures. This equilibrium can be rationalized by assigning 18 to the signal B (eq 17).



(17)

Scheme III shows a catalytic cycle for the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by 12 that is consistent with eq 10. Furthermore, this cycle contains, in equilibrium, the species detected in the spectra of Figure 7. Under catalytic conditions, the dynamic equilibrium shown in eq 16 is dominant, suggesting that K_{16} is greater than K'_{16} and K_{17}. However, at 0 °C K_{17} is greater than K_{16} and K'_{16}, and consequently, B is the only intermediate spectroscopically detected. The interaction of 18 with the substrate to give the saturated ketone and to regenerate the catalyst is the last step of the catalytic cycle. The intimate details of this process are unknown to us.

On the other hand, it is interesting to mention that the mechanism of this hydrogenation catalyzed by the complex containing P-*i*-Pr_3 as phosphorus-donor ligand involves mononuclear species during the full catalytic cycle (Scheme II), while the hydrogenation carried out in the presence of 12 takes place through the binuclear intermediate 18 (eqs 12 and 13). This significant difference can be rationalized in terms of the different stabilities of the trans(hydride,dihydrogen) species 6 and 19. While the complex containing P-*i*-Pr_3 is the main intermediate under a hydrogen atmosphere from −60 to +60 °C, the species containing PMe-*t*-Bu_2, at room temperature, is in a dynamic equilibrium with the monohydride (eq 16). Thus, under catalytic conditions the presence of 12 in significant concentrations is essential for the formation of 18 (eq 17). Furthermore, it is important to note that two isoelectronic and isostructural complexes with phosphines of similar basicities and steric requirements catalyze the same reaction via a completely different mechanism, illustrating different roles of the dihydrogen complexes in catalytic hydrogenation reactions.

3. Concluding Remarks. The studies reported in this paper have revealed that the five-coordinated hydrido carbonyl complexes $OsHCl(CO)(PR_3)_2$ (PR_3 = P-*i*-Pr_3 (1), PMe-*t*-Bu_2 (12)) catalyze the selective hydrogenation of benzylideneacetone to 4-phenylbutan-2-one.

The mechanisms deduced for these reactions, on the basis of kinetic results and spectroscopic observations, illustrate new roles of the dihydrogen complexes in catalysis.

(i) 1, initially nonactive, is activated as a result of the formation of *trans(hydride,dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (6), which isomerizes to *cis(hydride,dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (14) and subsequently dissociates the η^2-H_2 ligand.

(ii) Under catalytic conditions, 12 is in a dynamic equilibrium with *trans(hydride,dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (19), which also isomerizes to *cis(hydride,dihydrogen)*-$OsHCl(\eta^2\text{-}H_2)(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (20). The subsequent reaction of 20 with 12 leads to a binuclear intermediate, which by reaction with benzylideneacetone gives the saturated ketone and regenerates the catalyst. Previous theoretical works suggest that this binuclear intermediate could be *trans*-$[OsCl(CO)(PMe\text{-}t\text{-}Bu_2)_2]_2H_4$, containing a planar 4-gon of cyclically bound hydrogen atoms.

Finally, it is important to note that two isoelectronic and isostructural complexes with phosphines of similar basicities and steric requirements catalyze the same reaction via completely different mechanisms. In light of these results, it is clear that it is only possible to propose a sensible catalytic cycle on the basis of kinetic and spectroscopic studies of the reactions. In general, the catalytic mechanisms involve multistep reactions, where the intermediates are connected by equilibriums that are highly dependent on the electronic properties and steric requirements of the catalyst ligands, as well as on the characteristics of the substrate. Thus, small modifications of these factors can totally change the direction of the equilibriums and, therefore, the contribution of a particular species to the overall catalytic process. Scheme IV summarizes Schemes II and III and illustrates this phenomenon for the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by the complexes 1 and 12.

Experimental Section

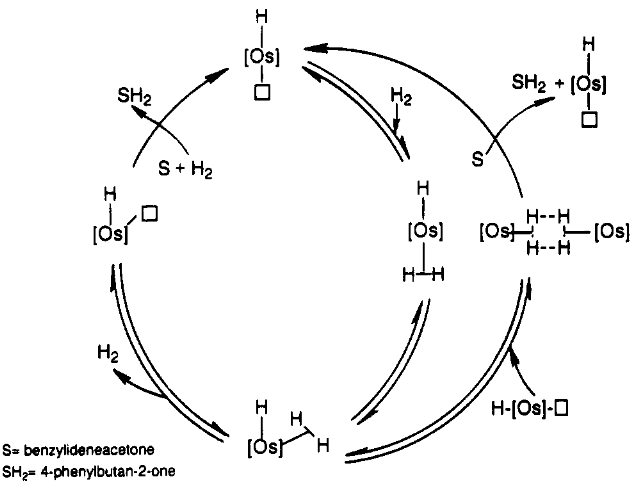
General Considerations. All manipulations were conducted

---

(37) Burdett, J. K.; Pourian, M. R. *Organometallics* **1987**, *6*, 1684.

(38) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

Scheme IV



S= benzylideneacetone
SH$_2$= 4-phenylbutan-2-one

with rigorous exclusion of air. Solvents were dried by known procedures and distilled under argon prior to use. Benzylideneacetone (Merck, 98%) was used without further purification. The complexes $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (1),[13] $OsDCl(CO)(P\text{-}i\text{-}Pr_3)_2$,[17] and $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (12)[36] were prepared by following published methods.

Physical Measurements. NMR spectra were recorded on a Varian 200 XL instrument. Chemical shifts are expressed in parts per million upfield from $Si(CH_3)_4$ (^1H) and 85% H_3PO_4 (^{31}P). The T_1 experiment was performed at 0 °C on a 200-MHz Varian XL spectrometer with a standard 180°–τ–90° pulse sequence. Samples for the $^{31}P\{^1H\}$ NMR spectra were prepared in 5-mm-diameter tubes. These samples were then introduced into 1-cm-diameter tubes containing $CDCl_3$.

The catalytic reactions were followed 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, connected to a Perkin-Elmer M-2 calculation integrator, using an FFAP on Chromosorb GHP 80/100 mesh (3.6 × $^1/_8$ in.) column at 200 °C. The reaction products were identified by comparison of their retention times with those observed for pure samples.

Reaction of 1 with Benzylideneacetone. Benzylideneacetone (20.4 mg, 0.14 mmol) was added to an NMR tube containing a red solution of 1 (20 mg, 0.035 mmol) in 0.6 mL of benzene-d_6 under argon. No color change was observed. According to the NMR spectra, the solution is a mixture of 1 and benzylideneacetone in the ratio 1:4.

Upon removal of the argon atmosphere with hydrogen the color of the solution changed to yellow. The ^{31}P NMR spectra showed a signal at δ 36.5 ppm, which was assigned to 6 by comparison with a pure sample. The solution mixture was passed through a column chromatograph (Al_2O_3; hexane), and benzylideneacetone and 4-phenylbutan-2-one were isolated and characterized by GC.

Reaction of $OsDCl(CO)(P\text{-}i\text{-}Pr_3)_2$ with Benzylideneacetone. This reaction is analogous to that described above, but with $OsDCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (20 mg, 0.035 mmol) as the starting material. According to the NMR spectra, the solution is a mixture of $OsDCl(CO)(P\text{-}i\text{-}Pr_3)_2$ and benzylideneacetone in the ratio 1:4.

Reaction of 1 with D_2: Preparation of $OsDCl(\eta^2\text{-}D_2)(CO)(P\text{-}i\text{-}Pr_3)_2$. In an NMR tube and at room temperature 20 mg (0.035 mmol) of 1 was dissolved in 0.6 mL of benzene-d_6, and D_2 was bubbled through for 1 min, during which time the solution changed from red to colorless. ^1H NMR (benzene-d_6, 20 °C): δ 1.27 (dvt, N = 13.6 Hz, $J_{H\text{-}H}$ = 7.6 Hz, 36 H, $PCHCH_3$), 2.55 (m, 6 H, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C): δ 36.1 (s). In order to confirm the presence of deuterium on the hydridic site, phenylacetylene (40 μL, 0.35 mmol) was added to the reaction mixture, leading immediately to $Os(HC{=}CDPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (see Scheme I). ^1H NMR (benzene-d_6, 20 °C): δ 1.27 (dvt, N = 14.0 Hz, $J_{H\text{-}H}$ = 7.6 Hz, 36 H, $PCHCH_3$), 2.87 (m, 6 H, $PCHCH_3$), 7.12 (m, 5 H, $CH^{\alpha}{=}CDPh$), 8.7 (br, 1 H, $CH^{\alpha}{=}CDPh$). $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C): δ 23.28 (s).

Reaction of $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (12) with H_2. In an NMR tube and at room temperature 20 mg (0.035 mmol) of 12 was dissolved in 1 mL of toluene-d_8, and H_2 was bubbled through for 5 min, during which time the color of the solution did not change. When the temperature was lowered to −79 °C, the solution turned colorless. The reaction was studied by ^1H NMR spectroscopy from −79 to +52 °C (Figure 7).

Catalytic Reactions. A degassed solution of the catalyst in 2-propanol (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 Schlenk manifold. The system was evacuated and refilled with hydrogen three times, and the flask was then immersed in a constant-temperature 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. Plots of kinetic data were fitted by use of conventional linear regression programs.

Acknowledgment. We thank the DGICYT (Project PB 89-0055; Programa de Promoción General del Conocimiento) for their financial support.

Registry No. 1, 102513-18-8; 1-d_1, 143063-96-1; 6-d_3, 143063-97-2; 7c-d_1, 143063-98-3; 12, 104911-48-0; benzylideneacetone, 122-57-6; phenylacetylene, 536-74-3.

OM920088S