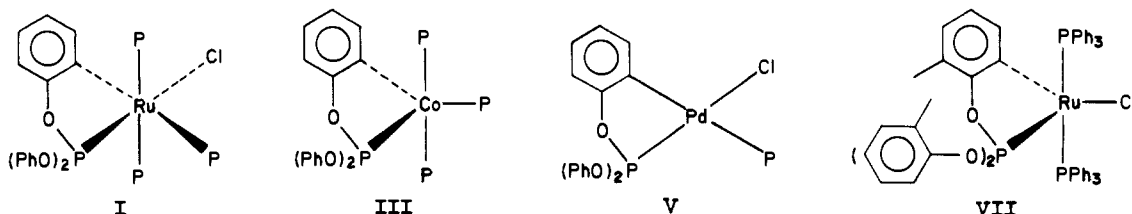


Enhancement of Catalytic Activity through Orthometalation. Synthesis, Structure, and Catalytic Activity of a New Orthometalated Ruthenium Complex

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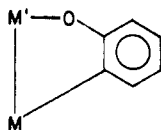
Abstract: Three complexes I, III, and V, $P = P(OPh)_3$, are active catalysts for olefin hydrogenation while the nonorthometalated analogues $HClRu[P(OPh)_3]_4$ (II), $HCo[P(OPh)_3]_4$ (IV), and $Cl_2Pd[P(OPh)_3]_2$ (VI) are not active. Complex VII is synthesized



from $P(o-OC_6H_4)_3$ and $HClRu(PPh_3)_3$ and is a very active catalyst for olefin hydrogenation. The versatility of the catalyst is demonstrated for a number of substrates; its activity is equivalent to $HClRu(PPh_3)_3$ (VIII) and superior to Wilkinson's catalyst, IX. In the absence of air, complex VII remains truly homogeneous, displaying the selectivity expected for a homogeneous catalyst. After air exposure, the catalyst behaves as a heterogeneous (colloidal) catalyst with concomitant increased activity but loss of selectivity. The mechanism of the catalysis is discussed.

Recently the problem of distinguishing between homogeneous and heterogeneous transition-metal catalysts has been addressed.¹⁻³ The selective nature of homogeneous catalysts makes them attractive for the synthesis of a wide variety of molecules. However, catalytic reaction conditions such as the reducing atmosphere encountered in hydrogenation reactions can cause reduction of homogeneous molecular metal species to heterogeneous metallic colloids. The criterion of visual inspection cannot rule out the presence of colloids, which may be as small as 20 Å in diameter.^{2,3} The consequence of forming a colloid under catalytic conditions may be loss of selectivity.⁴

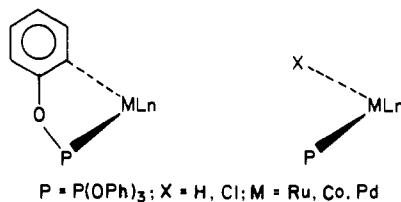
Design of a catalyst that is resistant to irreversible colloid formation while retaining activity is most desirable from a synthetic as well as a mechanistic standpoint. One class of complexes that have received little attention as catalyst precursors are the orthometalated (or cyclometalated) complexes of the type shown, where M is a transition metal and M' is a heteroatom such as P, N, S, etc.⁵⁻⁸



Some stoichiometric insertion reactions are known for these molecules,⁹⁻¹¹ but few attempts have been made to employ these

compounds as catalysts. Complexes containing this moiety offer the potential of being stable to irreversible reduction.

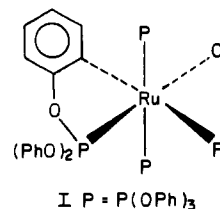
This report discusses the discovery that orthometalation imparts enhanced catalytic activity for olefin hydrogenation. This observation is demonstrated for three pairs of structurally analogous compounds; one of the pair contains an orthometalated group and the other does not.



The first well-characterized five-coordinate ruthenium(II) complex containing an orthometalated group was prepared. The scope of this new highly active olefin hydrogenation catalyst was investigated, and the mechanism of the hydrogenation reactions is discussed.

Results and Discussion

Catalytic Enhancement with Orthometalated Complexes. Recently a study of ruthenium orthometalated complexes in our laboratory^{9,12} showed that these complexes catalyze ortho deuteration and alkylation of phenol. It was found that I was a catalyst for ethylene hydrogenation. Significantly, this hydro-

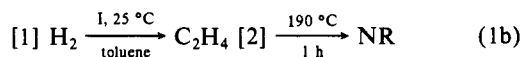
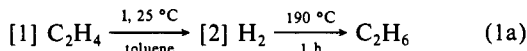


genation reaction was found to be sensitive to the order of addition

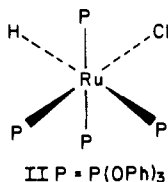
- (1) Hamlin, J. E.; Hirai, K.; Millan, A.; Maitlis, P. M. *J. Mol. Catal.* **1980**, *7*, 543.
- (2) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.
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- (4) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980.
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- (7) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.
- (8) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327.
- (9) Lewis, L. N.; Smith, J. F. *Inorg. Chem.* **1985**, *24*, 4433.
- (10) Pregosin, P. S.; Ruedi, R. *J. Organomet. Chem.* **1984**, *173*, 401.
- (11) Arlen, C.; Pfeffer, M.; Bars, O.; Granjeau, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.

- (12) Lewis, L. N. *J. Am. Chem. Soc.*, in press.

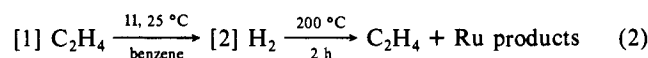
of the gaseous reagents H_2 and C_2H_4 . Thus when ethylene was introduced to a toluene solution containing I followed by pressurization by H_2 , the heated stirred solution gave ethane in >90% conversion. However, if the order of addition of C_2H_4 and H_2 were reversed, no hydrogenation occurred, eq 1.



The cause of the dependence on order of addition lay in the reactivity between I and H_2 . Parshall and co-workers showed that the product of I and hydrogen was II, a complex lacking an

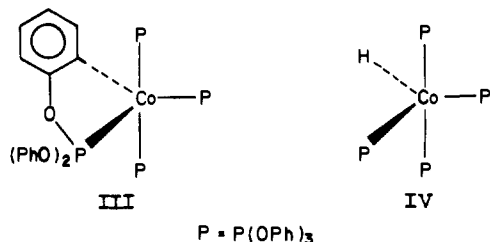


orthometalated bond.¹³ When an authentic sample of II was employed as a potential catalyst for ethylene hydrogenation, no ethylene reduction was noted, eq 2.

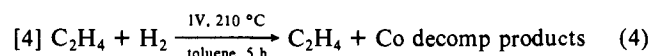
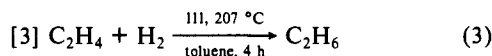


Complex I, while inactive at 25 °C, was quite robust at elevated temperatures. Gas uptake was monitored in the course of ethylene hydrogenation catalyzed by I in eq 1. The hydrogenation reaction commenced above 80 °C as evidenced by the observation that a linear pressure rise with increasing temperature occurred until 80 °C followed by a less gradual increase in pressure with temperature above 80 °C. Hydrogenation of 1-hexene in the presence of I was carried out at 155 °C to give 100% conversion to *n*-hexane, corresponding to 890 catalyst turnovers. Following hexene or ethylene hydrogenation by I, active catalyst solutions were recharged with olefin and H_2 and were shown to retain their activity; hydrogenation recommenced after heating. This recharge procedure could be repeated several times without noticeable loss of activity. The solution was then passed through a 0.5- μ m filter, recharged with ethylene and hydrogen, and reheated; ethane was again produced quantitatively.

The fact that catalyst I was a catalyst for hydrogenation while complex II was not suggested that the orthometalated group imparted enhanced activity for catalysis. Additional examples of this phenomenon were studied. Two cobalt complexes, III¹⁴ and IV,¹⁵ display the same structural relationship of complexes I and II; complex III is the orthometalated analogue of IV.



Complex III was active as a catalyst for ethylene hydrogenation while IV was inactive as a catalyst, eq 3 and 4. Complex III was



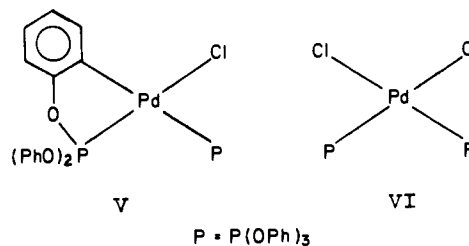
(13) Parshall, G. W.; Knoth, W. H.; Shunn, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990.

(14) Gosser, L. W. *Inorg. Chem.* **1975**, *14*, 1453.

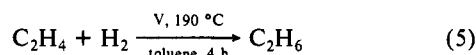
(15) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 96.

also active for the hydrogenation of 1-hexene to *n*-hexane. The solution following 1-hexene hydrogenation catalyzed by III was filtered through a 0.5- μ m filter, recharged with 1-hexene and H_2 , and reheated. *n*-Hexane was again produced with 100% conversion.

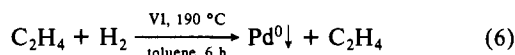
Two palladium complexes, V¹⁶ and VI,¹⁷ were also investigated



for their catalytic activity. Ethylene was hydrogenated to ethane in the presence of V, eq 5, while complex VI was found to be



inactive as a catalyst for this reaction. Decomposition of VI to a Pd mirror occurred in the course of an attempted hydrogenation of ethylene in the presence of VI, eq 6.



In the previous examples with Ru and Co, active catalyst solutions were passed through 0.5- μ m filters, and the filtrates were shown to retain catalytic activity suggesting they were homogeneous. While these solutions appear visually homogeneous, the filtration procedure does not rule out the presence of filterable active colloids. Anton and Crabtree¹⁸ have addressed the problem of distinguishing between homogeneous compounds and colloidal metals. A useful test for the presence of active colloidal metals was described in which nitrobenzene was reduced by H_2 to aniline in the presence of platinum group metal colloids but *not* in the presence of any known homogeneous compound. For instance, Pd/C is active in promoting the hydrogenolysis of nitrobenzene with H_2 at 25 °C. This test was extended to the palladium complex V. Thus, 1-hexene was hydrogenated by H_2 to give *n*-hexane in the presence of V. Following hydrogenation, nitrobenzene was added to the solution. The solution was then pressurized with H_2 and stirred for 24 h at 25 °C; no aniline was produced. However, this solution was still active for hydrogenation of 1-hexene. These results suggest that a homogeneous compound (no colloids) was responsible for the observed catalysis. The nitrobenzene reduction test was not valid for Ru or Co as neither Ru/C nor Co metal were active catalysts for nitrobenzene reduction. Likewise, the active catalyst solutions containing I or III were not active catalysts for conversion of nitrobenzene to aniline.

A summary of the effect of the orthometalated group on catalytic activity is shown in Table I. These data suggest that orthometalation imparts enhanced catalytic activity for olefin hydrogenation. The mechanism of enhancement provided by the orthometalated group is not known. It appears, however, that the orthometalated moiety provides stability against irreversible reduction, cf. reduction of VI to a Pd mirror in eq 6.

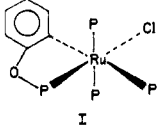
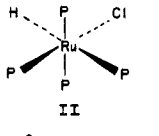
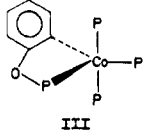
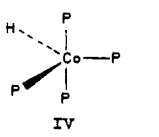
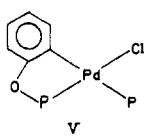
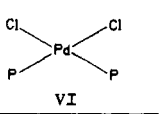
Synthesis of a Five-Coordinate Ru(II) Complex Containing an Orthometalated Group. A New Catalyst. In an attempt to exploit the observation of enhanced activity by orthometalated complexes, a new complex containing an orthometalated group was synthesized and tested for its catalytic activity. Five-coordinate Ru(II) complexes are among the best known homogeneous hydrogenation catalysts.¹⁹ This fact and the present observation that ortho-

(16) Ahmad, N.; Ainscough, E. W.; James, T. A.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1151.

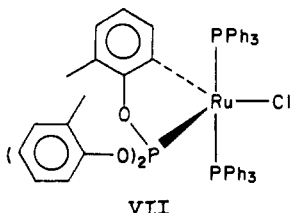
(17) Reference 16, p 1148.

(18) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

Table I. Summary of the Effect of Orthometalation on Catalytic Activity

complex	catalyst for olefin hydrogenation?
	yes
	no
	yes
	no
	yes
	no

metalation gave rise to enhanced catalytic activity was the basis for the design of complex VII. The synthesis of VII is shown



in eq 7. The empirical formula of VII was evident from elemental analysis and the structure was assigned on the basis of $^{31}\text{P}\{\text{H}\}$ NMR. Two resonances were observed at 167.7 (t, $J = 45$ Hz) and 41.8 (d, $J = 45$ Hz). The downfield resonance was assigned as an orthometalated phosphite ligand.²⁰ A single-crystal X-ray diffraction analysis of disordered crystals of VII ($R = 16\%$) confirmed the gross structural features proposed for VII. (See Figures 1 and 2, supplementary material.)

Scope of Catalytic Activity of VII. In order to determine the scope of the catalyst, a variety of substrates were hydrogenated in the presence of VII. Unlike the catalysts I, III, and V, which required high temperatures, complex VII was quite active under mild conditions. In a typical hydrogenation reaction, distilled olefin and complex VII (dissolved in a minimum of benzene or toluene) were combined in a thick-walled glass bottle under N_2 . The bottle was then charged with H_2 to 50–100 psig, and the contents were heated if necessary to initiate reaction. The hydrogenations were run until no further hydrogen uptake was noted. These results

are summarized in Table II. Catalyst VII was synthetically useful as a catalyst for hydrogenation of a variety of olefins that possess a number of functional groups including alkyl, phenyl, ester, siloxane, keto, and cyano. The hydrogenation reactions were run under mild conditions of temperature and pressure.

(19) Bennett, M. A.; Matheson, T. W. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4.

(20) Stewart, R. P.; Isbrandt, L. R.; Benedict, J. J. *Inorg. Chem.* **1976**, *15*, 2013.

Table II. Effect of Functional Groups on Catalyst Activity

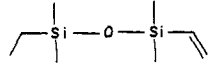
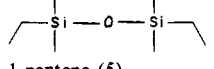
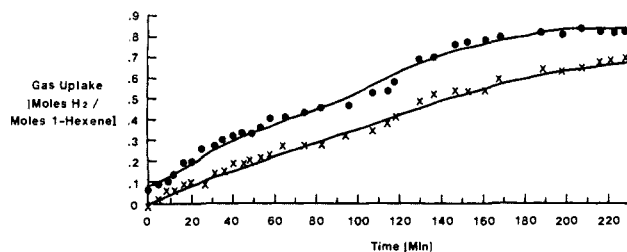
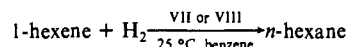
substrate	mol % cat.	time, h	temp, °C	P, psi	products (%)
ethylene	0.8	8	25	60	ethane (100)
1-hexene	0.08	3	25	50	<i>n</i> -hexane (100)
styrene	0.1	3.5	165	80	ethyl benzene (96)
vinyl acetate	0.2	2	170	80	ethyl acetate (20)
cyclohexene	0.4	5	130	50	cyclohexane (100)
1,3-divinyln-tetra- <i>a</i> -methyl-disiloxane	0.7	3	120	45	 (21)
					 (69)
pentyne	0.2	48	25	50	1-pentene (5) 1-pentane (5)
pentyne	0.2	17	110	50	pentenes (50) <i>n</i> -pentane (50)
cyclo-dodecatriene	0.6	2	120	65	cyclododecadiene (75)
carbone	0.5	6	95	54	cyclododecene (25) dihydrocarvone (98)
1,4-dicyano-2-butene	0.5	20	130	70	1,4-dicyanobutane (78)

Table III. Comparison of Catalysts for Olefin Hydrogenation^a

substr	product	% conversion, %		
		cat. VII	cat. VIII	cat. IX
ethylene	ethane	100	50	0
1-hexene	<i>n</i> -hexane	100	100 ^b	6
styrene	ethyl benzene	96		100 ^c
vinyl acetate	ethyl acetate	20		13
cyclohexene	cyclohexane	100		80
carvone	dihydrocarvone	98		75 ^d

^a All run under identical conditions to Table II except where noted. ^b Catalyst decomposed upon air exposure. ^c 100 °C, 2 h. ^d 110 °C, 17 h.

**Figure 3.** Relative rate of gas uptake in absence of air: (●) VIII; (×) VII.

are summarized in Table II. Catalyst VII was synthetically useful as a catalyst for hydrogenation of a variety of olefins that possess a number of functional groups including alkyl, phenyl, ester, siloxane, keto, and cyano. The hydrogenation reactions were run under mild conditions of temperature and pressure.

Comparison to Other Homogeneous Hydrogenation Catalysts. One of the most active homogeneous hydrogenation catalysts is $\text{HClRu}(\text{PPh}_3)_3$ (VIII).²¹ Complex VIII, though a very active catalyst, is extremely air-sensitive and is easily poisoned by impurities. Thus, complex VIII has not found much practical utility in synthesis. The typical catalyst for routine homogeneous olefin hydrogenation is Wilkinson's catalyst, $\text{ClRh}(\text{PPh}_3)_3$ (IX).²² While the rate of olefin hydrogenation catalyzed by IX is 15–20 times slower than that of VIII, complex IX is quite robust,²¹ and no special efforts are necessary to protect the reaction solution from air or moisture.

(21) Hallman, P. S.; McGarvey, B. P.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

(22) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organometallic Chemistry"; University Science Books: Mill Valley, CA, 1980.

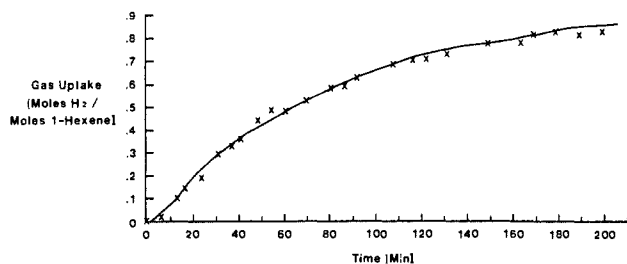
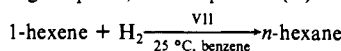


Figure 4. Rate of gas uptake, after exposure: (x) VII.



Complexes VII, VIII, and IX were compared as catalysts for olefin hydrogenation, Table III. Complex VII was more active than IX (Wilkinson's catalyst) for hydrogenation of terminal and internal olefins. This work demonstrated that the new complex, VII, and complex VIII²¹ are active catalysts for hydrogenation of ethylene, while complex IX is not active.

Complexes VII and VIII catalyze the hydrogenation of olefins at a rate of 16 times faster than the rate catalyzed by Wilkinson's complex. The rates of 1-hexene hydrogenation catalyzed by VII and VIII were compared in the absence of air, Figure 3. The rate of 1-hexene hydrogenation catalyzed by VII was about 0.67 times the rate of that catalyzed by VIII. After air exposure, however, the solution containing complex VIII became cloudy and was no longer active for hexene hydrogenation. The rate of hexene hydrogenation catalyzed by complex VII after air exposure was the same as the rate of hexene hydrogenation catalyzed by VIII in the absence of air, Figure 4. In addition, isomers of 1-hexene could be observed after air exposure. These results suggest that the original catalyst had reacted with air to form a more active catalyst.

Similar results were obtained for ethylene. The initial rate of ethylene hydrogenation catalyzed by VIII was greater than that catalyzed by VII. However, complex VIII decomposed during the reaction and hydrogenation stopped. On the other hand, catalyst solutions containing complex VII could be repeatedly recharged with ethylene and hydrogen; hydrogenation of ethylene was observed after each recharge. Analysis of a reaction solution containing catalyst VII by ³¹P NMR and FDMS following ethylene hydrogenation showed the catalyst was unchanged.

Earlier workers had found that alkynes inhibited hydrogenation catalyzed by ruthenium complexes.²¹ Similarly, it was found that 1-pentyne was poorly hydrogenated at 25 °C in the presence of VII (10% conversion, 48 h) in contrast to 1-hexene (100% conversion, 25 °C, 3 h). However, after exposure to air and recharging with hydrogen, complete conversion of pentyne to a mixture of pentenes and pentane occurred. In addition, pentene isomers were noted after air exposure as was the case in hexene hydrogenation. Surprisingly, further conversion of pentenes to pentane required higher temperatures than was needed for 1-hexene hydrogenation. The catalyst was inhibited by the initial exposure to pentyne.

Mechanistic Considerations. Homogeneity and Selectivity. "The major virtue of homogeneous catalysis (compared to heterogeneous) that has led to its widespread adoption by industry is selectivity, the ability to produce pure products in high yield."²⁴ It was of interest to determine if VII was truly a homogeneous catalyst and, more importantly, to determine the extent of the selectivity of catalyst VII.

A number of homogeneous catalysts are unaffected by the presence of Hg, while colloidal-based catalysts are completely deactivated by mercury.¹⁸ Mercury did not inhibit the rate of hydrogenation of hexene in the presence of VII in the absence of air. However, after air exposure, the presence of Hg completely inhibited 1-hexene hydrogenation. These results are consistent with catalyst VII being homogeneous in the absence of air and colloidal after air exposure.

Direct observation of Ru colloid was accomplished by employing laser light scattering. Initial catalyst solutions containing VII and 1-hexene in benzene were free of particles greater than 10 Å (lower

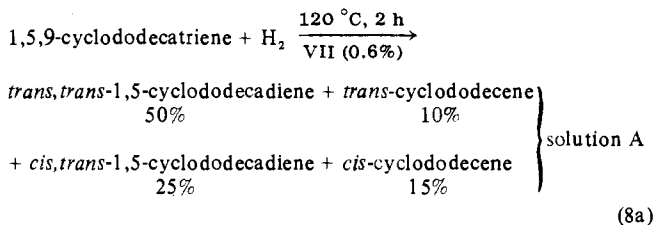
detection limit of instrument). Likewise, after a hydrogenation run in the absence of air, no colloids were detected; however, after air exposure 30-μm Ru colloids were observed by light scattering. These results give direct evidence for catalyst VII changing from homogeneous to heterogeneous after air exposure.

While Ru/C was not an active catalyst for reduction of nitrobenzene (vide supra), Rh/C did promote this reduction. Wilkinson's catalyst was tested for the presence of colloidal rhodium. Following a cyclohexene hydrogenation reaction catalyzed by IX, nitrobenzene was added and then the solution was charged with H₂ and heated to 110 °C for 45 min. Analysis of the solution by GC showed 29% conversion of nitrobenzene to aniline, consistent with the presence of Rh colloids.

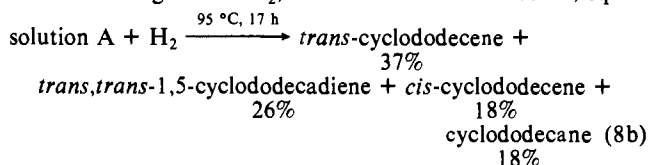
It was interesting that IX tested positive for rhodium colloids under the above hydrogenation conditions. Wilkinson's catalyst is accepted as a true homogeneous catalyst.^{4,22} However, it is typically employed at 25 °C, 1 atm pressure. Under forcing conditions, it is not surprising that it is reduced to a Rh colloid. This rhodium colloid clearly retained catalytic activity, but as a heterogeneous catalyst it may not have retained the selectivity of VII.

Selectivity of VII. Three examples from the literature were applied as tests for the selectivity of complex VII as a hydrogenation catalyst. In 1972, Parshall²³ described the use of tetraalkylammonium trichlorotin salt media containing homogeneous platinum complexes as selective hydrogenation catalysts for conversion of 1,5,9-cyclododecatriene to cyclododecene. In the present work, it was found that a true heterogeneous catalyst (1% Ru/C) catalyzes the hydrogenation of 1,5,9-cyclododecatriene to cyclododecene.

The hydrogenation of 1,5,9-cyclododecatriene is catalyzed by complex VII in the absence of air to give a mixture of cyclododecadienes and cyclododecenes, eq 8a (Table II). Note that

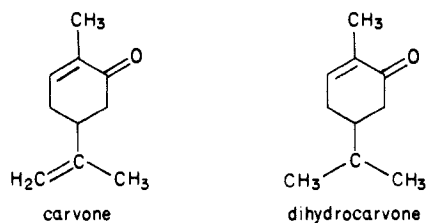


the conditions in the molten salt platinum medium required 160 °C and 100 atm for 8 h.²³ No further hydrogenation of the reaction solution occurred upon additional heating under H₂ at 160 °C for 8 h. When the reaction solution was exposed to air and then charged with H₂, further conversion occurred, eq 8b.



(See Figure 5, supplementary data, for ¹³C NMR spectra from eq 8a and 8b.) These results further support the contention that upon air exposure, the nature of the catalyst based on VII changed in activity and selectivity and that a colloidal catalyst was produced.

Most standard heterogeneous catalysts such as Pd/C and Raney Ni are not selective for carvone hydrogenation. Carvone is hydrogenated to a mixture of dihydrocarvones or completely hy-



grated intensity of CH₃ signals 1:2; ³¹P{¹H} NMR (in CDCl₃) δ 167.71 (t, *J* = 45 Hz), 41.80 (d, *J* = 45 Hz).

Structural Analysis. A crystal suitable for X-ray structural analysis was obtained by slow diffusion of hexane into a toluene solution of VII. The structure was solved by Mary Garbaskas of the GE R&D Center. The best *R* factor was about 16%. Table IV, supplementary material, summarizes the crystallographic data.

Hydrogenation of Ethylene by I, eq 1. Complex I (0.144 g, 0.10 mmol) was dissolved in 10 mL of toluene in a 250-mL thick-walled glass bottle. The bottle was degassed with N₂ and then charged with ethylene (50 psi, 33 mmol) and then hydrogen (50 psi, 33 mmol). The contents were stirred overnight at room temperature. There was no change in pressure after this time. The contents were then heated with stirring to 186 °C for 7 h. In the course of heating, the pressure rose linearly with temperature until 80 °C. At that point, the pressure decreased somewhat and rose only slowly, reaching a final pressure of 90 psi (at 186 °C). The bottle was cooled to room temperature (*P* = 50 psi). The bottle was vented by passing the gas above the solution and through a cold trap at -78 °C, and then the noncondensed gas was collected in a gas IR cell. The IR showed that the gases contained >90% ethane. (See Figures 6 and 7, supplementary material, for IR spectra of ethane and ethylene.³⁰)

The hydrogenation reaction was repeated with added triphenyl phosphite. The pressure at the end of the reaction after cooling to room temperature was 100 psi. Analysis of the gases by IR showed only ethylene to be present. Thus, the hydrogenation was inhibited by added triphenyl phosphite.

Control. Toluene, 5 mL, was placed in a 90-mL F/P bottle. The bottle was degassed with N₂ and then charged first with ethylene (50 psi, 0.012 mol) and then H₂ (50 psi, 0.012 mol). The bottle was heated with stirring to 190 °C for 4½ h. The bottle was cooled to room temperature (*P* = 80 psi). The gases were analyzed by IR and found to contain ethylene.

Ordering Effect of H₂ and Ethylene, eq 1b. I (0.0187 g, 0.0136 mmol) was added to 5 mL of toluene in a 90-mL F/P bottle. The bottle was degassed with N₂ and then charged first with H₂ (50 psi, 0.0118 mol) and then ethylene (50 psi, 0.0118 mol). The bottle was heated with stirring to 186 °C for 2 h. The reaction was cooled and the gases were analyzed by IR and found to contain only ethylene.

Hexene Hydrogenation by I. I (0.051 g, 0.037 mmol) and 1-hexene (4 mL, 32.9 mmol) were combined in a 250-mL F/P bottle. The bottle was degassed with N₂ and charged with H₂ (100 psi, 69.5 mmol). The bottle was heated with stirring to 156 °C for 15 h. The bottle was cooled to room temperature (*P* = 55 psi) and vented, and the contents were analyzed by GC and GCMS, which showed that *n*-hexane was produced in 100% yield.

Attempted Hydrogenation with II, eq 2. Complex II (0.068 g, 0.049 mmol) was combined with 10 mL of benzene and placed in a 90-mL F/P bottle. The bottle was degassed with N₂ and then charged first with ethylene (50 psi, 0.011 mol) and then H₂ (50 psi, 0.011 mol). The bottle was heated with stirring to 200 °C for 2 h. The gases were analyzed by IR and shown to contain 100% ethylene.

Catalyst Lifetime. Complex I (0.116 g, 0.084 mmol) was dissolved in 15 mL of toluene and placed in a 250-mL thick-walled glass bottle. The bottle was degassed and then charged first with ethylene (50 psi, 0.033 mol) and then H₂ (50 psi, 0.033 mol). The bottle was heated with stirring to 188 °C for 4 h. The bottle was cooled to room temperature (*P* = 50 psi). Analysis of the gases by IR showed >90% ethane to be present. This solution was then recharged with ethylene (50 psi, 0.033 mol) and H₂ (60 psi, 0.039 mol). The bottle was reheated with stirring to 205 °C for 5 h. The bottle was cooled to room temperature (*P* = 60 psi). Analysis of the gases by IR showed >90% ethane to be present. The solution from this reaction was taken into the glovebox and filtered through a 0.5-μm filter. The solution was golden yellow and homogeneous following filtration. The filtrate was then placed in a 90-mL thick-walled glass bottle and charged with ethylene (50 psi, 0.010 mol) and H₂ (50 psi, 0.010 mol). The bottle was heated with stirring to 170 °C for 6 h. The gases were analyzed by IR and shown to contain >90% ethane.

Hydrogenation by III, eq 3: [(PhO)₃P]₃(C₆H₅O)₂POC₆H₄Co. Complex III (0.087 g, 0.067 mmol) was added to 10 mL of toluene and placed in a 90-mL thick-walled glass bottle. The bottle was degassed with N₂ and then charged with ethylene (50 psi, 0.011 mol) and H₂ (50 psi, 0.011 mol). The bottle was heated with stirring to 207 °C for 4 h. Analysis of the gases by IR showed >90% ethane to be present.

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The hydrogenation of hexene was carried out as follows. Complex III (0.116 g, 0.089 mol) was combined with 1-hexene (1 mL, 7.9 mmol) and 10 mL of benzene in the glovebox and placed in a 90-mL thick-walled glass bottle. The bottle was charged with H₂ (80 psi, 18 mmol) and then heated with stirring to 185 °C for 3 h. The bottle was cooled to room temperature and vented and then the solution was analyzed by GC which showed only *n*-hexane (no hexene) to be present. The solution was then brought into the glovebox and 1-hexene (1 mL, 7.9 mmol) was again added. The solution was filtered through a 0.5-μm filter and then placed back in the 90-mL bottle. The bottle was recharged with H₂ (80 psi, 18 mmol) and then heated with stirring to 199 °C for 4½ h. The solution was analyzed by GC and shown to contain *n*-hexane (no hexene). To this solution was added nitrobenzene (1 mL, 9.7 mmol). The bottle was charged with H₂ (80 psi, 18 mmol) and stirred for 7 h at room temperature. The solution was analyzed by GC and found to contain nitrobenzene (no aniline was observed).

Control. Nitrobenzene (1 mL, 9.7 mmol) was combined with 10 mL of toluene and Co metal powder (0.0051 g, 0.086 mmol) and placed in a 90-mL F/P bottle. The bottle was charged with H₂ (120 psi, 27 mmol) and stirred at room temperature for 6 h. Analysis of the solution by GC showed only nitrobenzene (no aniline) was present.

Attempted Hydrogenation by IV, eq 4: HCo[P(OPH)₃]₄. Complex IV (0.098 g, 0.075 mmol) was added to 15 mL of toluene and placed in a 90-mL thick-walled glass bottle. The bottle was degassed with N₂ and then charged with ethylene (50 psi, 0.010 mol) and H₂ (50 psi, 0.010 mol). The bottle was heated with stirring to 210 °C for 5 h. The solution was colorless with a dark precipitate at this point. The gases were analyzed by IR and found to contain only ethylene.

Hydrogenation by V, eq 5: [(PhO)₃P]₃(C₆H₅O)₂POC₆H₄PdCl. Complex V (0.069 g, 0.091 mmol) was added to 10 mL of toluene in the glovebox and placed in a 90-mL thick-walled glass bottle. The bottle was charged with ethylene (50 psi, 0.011 mol) and H₂ (50 psi, 0.011 mol) and then heated with stirring to 192 °C for 4 h. After the reaction, there was a dark precipitate present. The gases were analyzed by IR and shown to contain >90% ethane. The solution was taken into the glovebox and filtered through a 0.5-μm filter. The filtrate was then placed in a 90-mL thick-walled glass bottle to which 1-hexene (ca. 0.9 mL, 7 mmol) was added. The bottle was charged with H₂ (100 psi, 24 mmol) and heated with stirring to 180 °C for 8 h. This solution was analyzed by GC and shown to contain *n*-hexane (no hexene). Nitrobenzene (1 mL, 9.7 mmol) was added to the above solution. The bottle was charged with H₂ (60 psi, 0.013 mol) and stirred at room temperature for 24 h. Analysis of the solution by GC showed only nitrobenzene was present (no aniline).

Control. Nitrobenzene (1 mL, 9.7 mmol) was combined with 10 mL of toluene and 5% Pd/C (0.044 g, 0.021 mmol Pd) and placed in a 90-mL F/P bottle. The bottle was charged with H₂ (120 psi, 27 mmol) and stirred at room temperature for 6 h. Analysis of the solution by GC showed mostly (>80%) aniline was present with some unreacted nitrobenzene.

Attempted Hydrogenation by VI, eq 6: PdCl₂[P(OPH)₃]₂. Complex VI (0.066 g, 0.083 mmol) was added to 10 mL of toluene and placed in a 90-mL thick-walled glass bottle. The bottle was degassed with N₂ and then charged with ethylene (50 psi, 0.011 mol) and H₂ (50 psi, 0.011 mol). The bottle was heated with stirring to 192 °C for 6 h. A Pd mirror formed in the bottle. Analysis of the gases by IR showed that only ethylene was present.

Ethylene Hydrogenation by VII. Complex VII (0.088 g, 0.087 mmol) was added to 10 mL of toluene and placed in a 90-mL thick-walled glass bottle. The bottle was degassed with N₂ and then charged with ethylene (50 psi, 0.011 mol) and H₂ (50 psi, 0.011 mol). The bottle was stirred at room temperature for 22 h, *P* = 45 psi; at 8 h, *P* = 60 psi. Analysis of the gases by IR showed >90% ethane. Analysis of this solution by ³¹P{¹H} NMR showed triphenyl phosphine oxide and tricresyl phosphate to be present as well as unreacted VII. No other peaks were observed. No hydride resonance was observed by ¹H NMR. Analysis by FDMS showed peaks at *m/e* 1015 (M⁺).

Hydrogenation of Hexene by VII. Complex VII (0.013 g, 0.013 mmol) and 1-hexene (1.5 mL, 12.3 mmol) were combined with 5 mL of C₆D₆ in a 90-mL bottle. The bottle was charged with H₂ (50 psi, 11.8 mmol) and then stirred at 25 °C during which time the pressure was monitored. At 117 min, 20 psi of H₂ (4.7 mmol) was consumed. The bottle was repressurized with H₂ to a total pressure of 51 psi (5.0 mmol added), and stirring was continued for 119 min (total H₂ consumed 44 psi, 10.3 mmol). The bottle was opened to air and then analyzed by ¹H NMR which showed >90% conversion to *n*-hexane. The color of the solution changed from orange to red at this point.

Hexene Recharge. 1-Hexene (1.5 mL, 12.3 mmol) was added to the above solution and the bottle was recharged with H₂ (58 psi, 13.2 mmol) and stirred at 25 °C for 3.5 h. The pressure was monitored during this

time; at 3.5 h, $P = 22$ psi (36 psi of H_2 consumed, 8.2 mmol). 1H NMR analysis at this point showed 83% conversion of 1-hexene to a mixture of *cis*- and *trans*-hexenes and *n*-hexane (hexene:hexane ratio ca. 1:1). Additional 1-hexene (1 mL, 8.2 mmol) was added to the solution, and the bottle was recharged with H_2 (60 psi, 13.5 mmol) and then stirred at 25 °C for 3 h. Analysis by 1H NMR showed >95% conversion of the hexenes to *n*-hexane (>90% of all internal olefin consumed). GCMS analysis showed that there was a trace of 1-hexene and three isomers of hexene (*cis/trans*-2-, 3-hexenes). The major species was *n*-hexane.

Test for Homogeneity. Nitrobenzene (1 mL) was added to the active catalyst solution above, and the same bottle was then charged with H_2 (65 psi, 13.5 mmol) at 25 °C for 17 h. Analysis by GC showed unreacted nitrobenzene (no aniline was observed).

Control with Ru/C. Nitrobenzene (1 mL, 9.8 mmol), Ru/C (1% Ru, 900–1000 m^2/g ; 0.15 g, 0.015 mmol Ru), and benzene (5 mL) were combined in a 90-mL bottle. The bottle was charged with H_2 (60 psi, 14 mmol) and heated to 90 °C for 3 h with stirring. GC analysis showed only unreacted nitrobenzene was present (no aniline was observed).

Hg Inhibition. By use of the same stoichiometry of reagents as for hexene hydrogenation, 1 mL of Hg was stirred with complex VII and 1-hexene under N_2 in benzene for 7 h at 25 °C. The reactor was charged with H_2 and the contents stirred at 25 °C. The rate of production of *n*-hexane was the same as in that not containing mercury. This solution (containing Hg and *n*-hexane) was opened to air; 1-hexene (1 mL) was added and the mixture was recharged with H_2 and stirred at 25 °C. No further conversion of hexene to hexane occurred after air exposure.

Laser Light Scattering. Solutions containing VII and 1-hexene in C_6H_6 as described above were passed through a 0.5- μm filter under N_2 and analyzed for the presence of colloids and shown not to contain particles >10 Å. A solution from a 1-hexene hydrogenation run carried out in the absence of air was similarly analyzed; no particles were observed. Following hydrogenation of 1-hexene in the presence of VII and after air exposure, the solution was filtered through a 0.5- μm filter and shown to contain 30- μm particles. A control sample containing an aqueous platinum colloid³¹ (mean diameter by TEM 15 Å) was shown by this technique to contain 14-Å particles, while an aqueous gold colloid³² (mean diameter by TEM 200 Å) was shown by this technique to contain 220-Å particles.

Hexene Hydrogenation with VIII. Complex VIII (0.014 g, 0.015 mmol) was combined with 1-hexene (1.5 mL, 12.3 mmol) in 5 mL of C_6H_6 in a 90-mL bottle. The bottle was charged with H_2 (50 psi, 11.8 mmol) and then stirred at 25 °C during which time the pressure was monitored. At 117 min, 28 psi of H_2 (66 mmol) had been consumed. The bottle was repressurized with H_2 to a total pressure of 48 psi (6.0 mmol of H_2 added) and then stirring was continued for another 119 min; final $P = 35$ psi (total H_2 consumed, 58 psi, 10 mmol). The tube was then opened to air and the contents analyzed by GC and 1H NMR, which showed >90% *n*-hexane was produced. 1-Hexene (1.5 mL, 12.3 mmol) was added to the above solution and then the bottle was recharged with H_2 (61 psi, 14 mmol) and stirred at 25 °C for 3 h. Gas uptake was not noted and analysis of the solution by 1H NMR showed that no further hydrogenation had occurred.

Pentyne Hydrogenation by VII. Complex VII (0.010 g, 0.0099 mmol) and 1-pentyne (0.5 mL, 5.1 mmol) were combined in 5 mL of toluene in a 90-mL bottle. The solution changed color from orange to brown upon addition of 1-pentyne to the toluene solution of VII. The bottle was charged with H_2 (50 psi, 11.7 mmol) and then stirred at 25 °C for 48 h. Analysis of the solution at this point by GC and GCMS showed 10% conversion to products (1:1 mixture of *n*-pentane and 1-pentene). This solution was then repressurized with H_2 (50 psi) and heated to 110 °C with stirring for 17 h. Analysis of this solution by GC and GCMS showed complete conversion of 1-pentyne to products: 1:1 mixture of *n*-pentane and pentenes (1-pentene:2-pentene = 2:1, *cis* and *trans* indistinguishable by this technique without authentic samples). The solution was then recharged with H_2 (50 psi) and then heated to 155 °C with stirring for 4 h. Analysis of this solution by GC and GCMS showed that most of the 1-pentene was converted to *n*-pentane; *cis*- and *trans*-2-

pentene remained unreacted. The ratio pentane:1-pentene:*cis*-2-pentene:*trans*-2-pentene was 1.4:1.4:1.0:1.0.

Cyclohexene Hydrogenation by IX, Wilkinson's Catalyst. Complex IX (0.033 g, 0.036 mmol) was combined with cyclohexene (1 mL, 9.9 mmol) in 5 mL of toluene in a 90-mL bottle. The bottle was charged with H_2 (50 psi, 11.7 mmol) and heated to 130 °C with stirring for 5 h. GC analysis showed 80% conversion to cyclohexane. Nitrobenzene (1 mL) was added to the above solution, then pressurized with H_2 (50 psi), and then heated to 110 °C with stirring for 45 min. Analysis by GC showed 29% conversion of the nitrobenzene to aniline.

Hydrogenation of Cyclododecatriene by VII, eq 8a. Complex VII (0.034 g, 0.033 mmol), *trans,trans,cis*-1,5,9-cyclododecatriene (1 mL, 5.5 mmol), and benzene (5 mL) were combined in a 90-mL bottle in the glovebox. The bottle was charged with H_2 (65 psi, 15.4 mmol) and then heated to 120 °C for 2 h with stirring. At this point, 23 psi of H_2 (5.2 mmol) had been consumed. Raising the temperature to 160 °C for an additional 8 h resulted in only an additional 2 psi of H_2 being consumed (solution A). 1H NMR analysis showed ca. 80% conversion to cyclododecadienes: δ 5.18, 4.92 (alkene), 1.90 (allyl), 1.29 (alkyl). Relative intensity of alkene/allyl/alkyl found 1:1.9:2.5; relative intensity for pure cyclododecene, 1:2:8; relative intensity for cyclododecadiene (calcd), 1:2:2. ^{13}C NMR (in $CDCl_3$) (O) *trans*-cyclododecene, (Δ) *cis*-dodecene, (+) 1,5-*trans,trans*-cyclododecadiene, (~) 1,5-*cis,trans*-cyclododecadiene. Alkene δ 132.46 (~), 132.00 (+, ~), 131.51 (+, O), 130.56 (~), 130.49 (Δ), 128.95 (?), 128.28 (~); allyl δ 32.30 (+), 32.26 (O), 30.32 (~), 30.08 (~), 28.46 (~), 28.42 (~), 27.05 (Δ); alkyl δ 26.69 (+), 26.51 (+), 26.34 (O), 25.76 (~), 25.71 (O), 25.66 (~), 25.05 (O), 24.77 (O), 24.58 (Δ), 24.06 (Δ), 24.01 (~), 23.93 (Δ), 23.81 (~), 23.29 (?), 22.23 (Δ). Assignments were made on the basis of comparison to authentic samples of 1,5,9-*trans,trans,cis*-cyclododecatriene, *trans*-cyclododecene, *cis*-cyclododecene, and cyclododecane. GC and GCMS analysis confirmed ca. 80% conversion to cyclododecadienes.

Equation 8b. Reaction solution A was exposed to air (which caused a color change from orange to brown) and recharged with H_2 (70 psi, 16.5 mmol) and then heated to 95 °C for 17 h with stirring. Analysis of this solution by 1H NMR showed δ 5.22, 4.96 (alkene), 1.96 (allyl), 1.32 (alkyl); relative ratio 1:2.3:4.9. Cf. 1H NMR *trans*-cyclododecene δ 5.26, 1.98, 1.44; relative ratio 1.0:7.0:7.71. ^{13}C NMR analysis as well as GC and GCMS analyses showed cyclododecane as a new product (see below and Figure 5, supplementary material).

Cyclododecatriene (1 mL, 5.5 mmol), Ru/C (1%, 0.34 g, 0.034 mmol), and benzene (4 mL) were combined in a 90-mL bottle. The bottle was charged with H_2 (76 psi, 18 mmol) and heated to 98 °C for 14 h with stirring. 1H NMR analysis (δ 1.33) showed complete conversion to cyclododecane had occurred. ^{13}C NMR δ 23.85. The product was isolated as a white crystalline solid (100% yield). mp 56 °C (sharp), lit 59–61 °C (P + B catalog).

Stoichiometric Hydrogenation of Phenylacetylene by VII, eq 14. Complex VII (0.052 g, 0.051 mmol) and $PhC\equiv CH$ (7 μL , 0.064 mmol) were combined in 0.5 mL of $CDCl_3$. No change was observed in the 1H NMR spectrum of VII and $PhC\equiv CH$ at this point. H_2 was bubbled through the solution for 1 min (no visible changes occurred). 1H NMR showed complete conversion to styrene (no ethyl benzene was observed) and that the resonances for VII were present. No new peaks were observed.

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Supplementary Material Available: Figures 1 and 2 and Table IV, crystallographic data for VII, Figure 5, ^{13}C NMR spectra from hydrogenation of cyclododecatriene by VII, and Figures 6 and 7, gas IR data for ethylene hydrogenation (10 pages). Ordering information is given on any current masthead page.