$R = 2.08\%$, $wR = 3.20\%$, and GOF = 2.184. The R value for all 2698 data was 2.59%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$ where w is the weight of a given observation. The p factor,[28] used to reduce the weight of intense reflections, was set to 0.02 in the last cycles of refinement. The analytical forms of the scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[30] Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.48 e/Å^3 and was located near one of the ethyl groups of the dithiocarbamate ligand. The positional and thermal parameters of the non-hydrogen atoms are given in Table V.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. **2**, 76772-61-7; **3**, 97011-30-8; **4**, 97011-31-9; **5**, 97011-32-0; **6**, 97011-33-1; **7**, 97011-34-2; **8**, 97011-35-3; **9**, 96503-79-6; **10**, 97011-36-4; $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, 1291-32-3; $Al(SiMe_3)_3$, 65343-66-0; $(\eta^5\text{-}C_5H_5)_2HfCl_2$, 12116-66-4; $KOSiMe_3$, 10519-96-7; NaS_2CNEt_2, 148-18-5; $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2O$, 12097-04-0.

Supplementary Material Available: Tables of anisotropic thermal parameters for **5**, the values of F_o and F_c, the positions of the hydrogen atoms, and least-squares planes and torsion angles (20 pages). Ordering information is given on any current masthead page.

---

[30] Cromer, D. T., ref 29, Table 2.3.1.

[31] Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Communications

Mechanisms of Reactions of Binuclear Iron Bis(μ-phosphido) Carbonyl Complexes with Protic Acid, Hydride, and Alkyl Halides

Shin-Guang Shyu and Andrew Wojcicki*

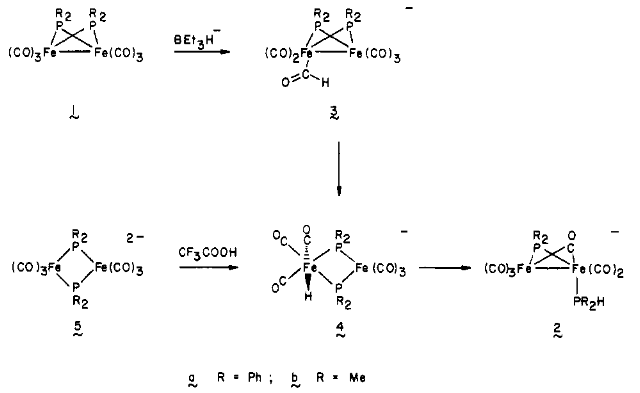
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received May 24, 1985

Summary: The mechanisms of the reactions of $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ (**1a**, R = Ph; **1b**, R = Me) with 1 equiv of BEt_3H^- (and BEt_3D^-) and of $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]^{2-}$ (**5**) with 1 equiv of CF_3COOH, both of which proceed with $\overline{Fe\text{-}(\mu\text{-}PR_2)}$ bond cleavage to yield $[(CO)_3Fe(\mu\text{-}PR_2)(\mu\text{-}CO)Fe(CO)_2(PR_2H)]^-$ (**2**), were investigated by variable-temperature ^{31}P, ^2H, and ^1H NMR in THF solution. Treatment of **1** with BEt_3H^- first affords spectroscopically characterized binuclear iron-formyl anions $[Fe_2(CO)_5(C(O)H)(\mu\text{-}PR_2)_2]^-$ (**3**). These rearrange at −25 to −20 °C to the hydrido complexes $[Fe_2(CO)_6(H)(\mu\text{-}PR_2)_2]^-$ (**4**), which at −5 to 0 °C reductively eliminate H and μ-PR_2 to furnish **2**. Protonation of **5** with CF_3COOH in THF at −25 °C yields the same binuclear iron hydrides **4**, which convert to **2** on warming. Alkylation reactions of **5a** with 1 equiv of R′I (R′ = Me and Et) in THF occur at −70 to 25 °C without an observable (by ^{31}P NMR) intermediate to give the binuclear iron acyls $[Fe_2(CO)_5(C(O)R')(\mu\text{-}PR_2)_2]^-$ (**6a**). In contrast, **5b** and R′I (R′ = Me (and CD_3), Et, and allyl) yield intermediate species **7b** at −75 to −70 °C. From ^{31}P and ^2H NMR, **7b** are assigned binuclear iron-alkyl structures $[Fe_2(CO)_6(R')(\mu\text{-}PR_2)_2]^-$ analogous to those of the iron hydrides **4**. On warming, **7b** convert to the acyl complexes **6b** (rather than reductively eliminate R′ and μ-PR_2) in the order R′ = Et > Me > allyl, consistent with the greater propensity of metal alkyls than of metal hydrides to participate in intramolecular CO insertion.

Phosphido-bridged transition-metal complexes represent an important class of binuclear and polynuclear compounds.[1] The binuclear complexes have received attention in the synthesis of metal clusters and in studies of cooperative reactivity effects. In general, phosphido ligands provide stable bridges between metals which retard fragmentation of the molecular framework.[2] However, ex-

Scheme I



---

[1] Representative recent publications: (a) Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5934. (b) Glaser, R.; Kountz, D. J.; Waid, R. D.; Gallucci, J. C.; Meek, D. W. *Ibid.* **1984**, *106*, 6324. (c) Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 633. (d) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 1020. (e) Casey, C. P.; Bullock, R. M. *Ibid.* **1984**, *3*, 1100. (f) Kyba, E. P.; Mather, J. D.; Hassett, K. L.; McKennis, J. S.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 5371. (g) Bender, R.; Braunstein, P.; Metz, B.; Lemoine, P. *Organometallics* **1984**, *3*, 381. (h) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stuart, A. L.; Wright, T. C.; Whittlesey, B. R. *Ibid.* **1984**, *3*, 114. (i) Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazany, A. M. *Ibid.* **1984**, *3*, 1121. (j) Finke, R. G.; Gaughan, G; Pierpont, C.; Noordik, J. H. *Ibid.* **1983**, *2*, 1481. (k) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabreze, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763. (l) Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47. (m) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D., *Chem. Ber.* **1983**, *116*, 1219. (n) Schneider, J.; Huttner, G. *Ibid.* **1983**, *116*, 917. (o) Ritchey, J. M.; Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501.

[2] (a) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846. (b) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069. (c) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726. (d) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113. (e) Finke, R. G.; Gaughan, P.; Pierpont, C.; Cass; M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394.

0276-7333/85/2304-1457$01.50/0 © 1985 American Chemical Society

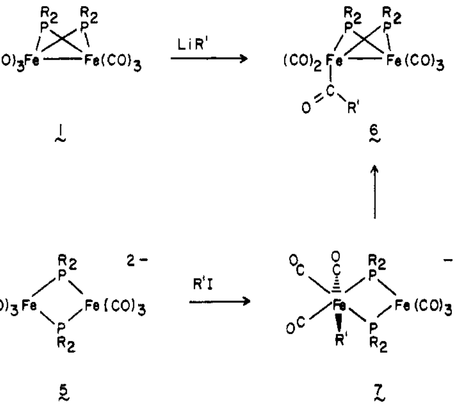
amples have recently become available of reactions that lead to cleavage of M–(μ-PR_2) bonds sometimes with degradation to lower nuclearity complexes.[3] Mechanisms of such reactions are largely unexplored. Herein we report on the mechanism of cleavage of the Fe–(μ-PR_2) bonds in $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]^n$ (n = 0 and 2–) by protonation and treatment with hydride and on the mechanism of related alkylation reactions.

Complexes $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ (**1a**, R = Ph; **1b**, R = Me) react with $LiBEt_3H$ to afford $[(CO)_3Fe(\mu\text{-}PR_2)(\mu\text{-}CO)Fe(CO)_2(PR_2H)]^-$ (**2**) in solution.[4] Monitoring mixtures of equimolar **1** and $LiBEt_3H$ in THF by ^{31}P NMR with increasing temperature revealed that the formation of **2** commences at –5 to 0 °C and, under these conditions, furnishes no observable intermediates. However, if a mixture of **1a** and 1 equiv of $LiBEt_3H$ (or $LiBEt_3D$) at low temperature is rapidly warmed to ca. 0 °C and then immediately cooled back to ca. –50 °C, intermediate species can be observed and their chemistry (Scheme I) followed by ^{31}P, ^2H, and/or ^1H NMR. Thus, the $^{31}P\{^1H\}$ NMR spectrum at –50 to –45 °C shows two new complexes formulated as **3a** and **4a**. The former is assigned a binuclear anionic metal–formyl structure on the basis of a remarkable similarity of its $^{31}P\{^1H\}$ NMR spectrum[5] to that of the analogous iron–acyl complexes[6] (**6a**) and from a low-field ^2H NMR signal at δ 13.7, which is in the normal range for metal–formyl complexes.[7] The latter (**4a**) is formulated as a binuclear metal–hydrido complex without an Fe–Fe bond from its high-field ^{31}P and ^2H (and ^1H) NMR signals.[8] Raising the temperature to between –25 and –20 °C leads to the disappearance of the ^{31}P NMR signals of **3a** and an increase in the intensity of the signal of **4a**. At –5 to 0 °C, the resonances of **2a** grow in and that of **4a** is barely discernible and disappears on further warming. A similar behavior was noted for the reacting **1b** and $NaBEt_3H$, with **3b**[9] rearranging to **4b**[10] at –25 to –20 °C. Further warming results in a complete conversion of **4b** to **2b** at ca. 0 °C.

Anions **2** are also accessible by protonation of $Na_2[Fe_2(CO)_6(\mu\text{-}PR_2)_2]$ ($(Na^+)_2$**5a**, R = Ph; $(Na^+)_2$**5b**, R = Me) with 1 equiv of CF_3COOH at room temperature. When these reactions are carried out at –25 °C, the iron hydrides **4** are observed and convert to **2** on warming (Scheme I).

The foregoing studies demonstrate that the reduction of **1** with BEt_3H^- and the protonation of **5** with CF_3COOH proceed via a common binuclear iron–hydrido intermediate, **4**. This intermediate then converts to the anion **2**.

Scheme II



a R = Ph ; b R=Me

Interestingly, the related, linked bis(μ-phosphido) complex $(CO)_3Fe(\mu,\mu'\text{-}(1\text{-}PPh\text{-}2\text{-}PPhC_6H_4))Fe(CO)_3$ reacts with $LiBEt_3H$ to yield a product analogous to **2** by attack of H^- at phosphorus.[11] A mechanism parallel to that reported here is precluded by the inability of the linked bis(μ-phosphido) system to assume a structure with a planar P_2Fe_2 core, which would be expected for an intermediate corresponding to **4**.

Alkylation reactions of **5** with 1 equiv of alkyl iodides (R′I) proceed to the binuclear metal–acyl anions **6**, which are also obtained by treatment of **1** with LiR′[12] (Scheme II). When **5a** was employed, no intermediates were detected by ^{31}P NMR spectroscopy at temperatures –70 °C and above for MeI and EtI. With the former, **6a**-*Me*[12] appears[6] even at ca. –70 °C. As expected, EtI reacts with **5a** more slowly than MeI, and **6a**-*Et*[12] is observed[6] at room temperature. In contrast to **5a**, **5b**[13] undergoes reactions with R′I via an observable (by ^{31}P and ^2H NMR) intermediate. The iodides MeI (or CD_3I), EtI, and C_3H_5I (C_3H_5 = allyl) each alkylate **5b** at –75 to –70 °C to afford what we formulate from spectroscopic data as binuclear iron–alkyl anions **7b**[14] structurally analogous[15] to the hydride **4b**. On warming, **7b** convert to the iron–acyl complexes **6b**[16] in the order Et (at ca. –60 °C) > Me (at ca. –35 °C) > C_3H_5 (at –20 to –10 °C). This order parallels the usual relative rates of migratory CO insertion in mononuclear complexes.[17]

It is significant that the structurally related intermediates **4** and **7** rearrange via different pathways. The former undergoes reductive elimination of H and Fe(μ-PR_2) as Fe(PR_2H), whereas the latter undergoes migratory

---

(3) (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (b) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 814. (c) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Ibid.* **1983**, *2*, 53. (d) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L. *Inorg. Chem.* **1984**, *23*, 1779. (e) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519. (f) Yu, Y.-F.; Chau, C.-N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *Ibid.* **1984**, *106*, 3704. (g) Shyu, S.-G.; Wojcicki, A. *Organometallics* **1984**, *3*, 809.

(4) **2a**: Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1983**, *105*, 4826. Li^+**2b**: $^{31}P\{^1H\}$ NMR (THF, 25 °C) δ 94.3 (d, J_{PP} = 22.0 Hz), 2.5 (s br); ^{31}P NMR δ 94.3 (br), 2.5 (d, J_{PH} = 314.9 Hz; IR (THF, 25 °C) $\nu_{C=O}$ 1620 (m) cm^{-1}.

(5) $^{31}P\{^1H\}$ NMR (THF, –47 °C) δ 157.0 (d, J_{PP} = 94 Hz), 127.9 (d, J_{PP} = 94 Hz).

(6) **6a**-*Me* (THF, –53 °C): δ 151.8 (d, J_{PP} = 94.5 Hz), 118.7 (d, J_{PP} = 94.5 Hz). **6a**-*Et* (THF, –50 °C): δ 150.4 (d, J_{PP} = 92.8 Hz), 118.4 (d, J_{PP} = 92.8 Hz).

(7) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

(8) ^{31}P NMR (THF, –46 °C) δ –59.7 (d, J_{PH} = 32.7 Hz); ^2H NMR (THF, –33 °C) δ –3.2 (s br, Fe*D*Fe); ^1H NMR (THF, –73 °C) δ –3.35 (t, J_{PH} = 35.1 Hz, Fe*H*Fe). ^{31}P NMR signals in the range δ 50 to –300 for μ-PR_2 almost always indicate that no metal–metal bond is present; see: (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Reference 3a.

(9) $^{31}P\{^1H\}$ NMR (THF, –33 °C) δ 120.2 (d, J_{PP} = 98.5 Hz), 91.1 (d, J_{PP} = 98.5 Hz).

(10) ^{31}P NMR (THF, –70 °C) δ –111.9 (d, J_{PH} = 35.3 Hz); ^1H NMR (THF, –73 °C) δ –5.23 (t, J_{PH} = 36.6 Hz, Fe*H*Fe).

(11) Kyba, E. P.; Clubb, C. N.; Liu, S.-T.; McKennis, J. S., private communication.

(12) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146. The intermediacy of **7a** in the reaction of **5a** with R′X was proposed but not demonstrated.

(13) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 746.

(14) **7b**-*Me*: $^{31}P\{^1H\}$ NMR (THF, –68 °C) δ –112.2 (s); ^2H NMR (THF, –78 °C) δ 0.8 (s, $FeCD_3$). **7b**-*Et*: $^{31}P\{^1H\}$ NMR (THF, –66 °C) δ –116.1 (s). **7b**-C_3H_5: $^{31}P\{^1H\}$ NMR (THF, –73 °C) δ –113.2 (s).

(15) From ^{31}P and ^1H NMR data, these anions are assigned structures with facial geometry of the six-coordinate Fe. However, meridional isomers of **7** apparently form during low-temperature reaction of **5a** and **5b** with $PhCH_2I$; this aspect of the alkylation reaction is under investigation.

(16) **6b**-*Me*: $^{31}P\{^1H\}$ NMR (THF, –23 °C) δ 120.7 (d, J_{PP} = 96.3 Hz), 92.7 (d, J_{PP} = 96.3 Hz); ^2H NMR (THF, 25 °C) δ 2.0 (s, $C(O)CD_3$); IR (THF, 25 °C) $\nu_{C=O}$ 1550 (w) cm^{-1}. **6b**-*Et*: $^{31}P\{^1H\}$ NMR (THF, –62 °C) δ 124.6 (d, J_{PP} = 96.3 Hz), 95.2 (d, J_{PP} = 96.3 Hz); ^1H NMR (acetone-d_6, 25 °C) δ 0.70 (t, J_{HH} = 7 Hz, $C(O)CH_2CH_3$), 2.65 (q, J_{HH} = 7 Hz, $C(O)CH_2$); IR (THF, 25 °C) $\nu_{C=O}$ 1550 (vw) cm^{-1}. **6b**-C_3H_5: $^{31}P\{^1H\}$ NMR (THF, –18 °C) δ 121.9 (d, J_{PP} = 96.3 Hz), 93.6 (d, J_{PP} = 96.3 Hz); IR (THF, 25 °C) $\nu_{C=O}$ 1550 (vw) cm^{-1}.

(17) Wojcicki, A. *Adv. Organomet. Chem.* **1972**, *11*, 88.

CO insertion. This dual behavior is in line with the much greater propensity of M–R′ than of M–H to participate in intramolecular CO insertion.[7] It is of further interest that the related binuclear iron nitrosyl anion $[Fe_2(NO)_4(\mu\text{-}PPh_2)_2]^{2-}$[3f] undergoes alkylation (with R′I) at metal with subsequent reductive elimination of $Fe(PPh_2R')$ rather than migratory insertion involving NO.[18] Details of this latter study will be reported separately.

Acknowledgment. We thank NSF Grant CHE-7911882 for support of this study.

---

[18] Chau, C.-N.; Wojcicki, A., to be submitted for publication.

(Cyclopentadienone)ruthenium Carbonyl Complexes—A New Class of Homogeneous Hydrogenation Catalysts

Y. Blum, D. Czarkie, Y. Rahamim, and Y. Shvo*

Department of Chemistry, Tel-Aviv University
69978 Tel-Aviv, Israel

Received January 25, 1985

Summary: $[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2$ and $[(\eta^4\text{-}Ph_2Me_2C_4CO)(CO)_2Ru]_2$ represent a new class of efficient precatalysts for homogeneous hydrogenation of alkenes, alkynes, ketones, aldehydes, and anthracene under moderate conditions. Mechanistic aspects have been investigated, and a basic catalytic cycle is proposed.

Many transition-metal complexes function as catalysts in homogeneous hydrogenation reactions.[1] Newly discovered systems may be of interest if they are either exceptionally reactive and inexpensive or if they represent a new class of catalysts carrying interesting mechanistic principles.

Herein we report on a new class of ruthenium homogeneous hydrogenation precatalysts examplified by bis[(η^4-tetraphenylcyclopentadienone)dicarbonylruthenium] (1) and bis[(η^4-2,5-dimethyl-3,4-diphenylcyclopentadienone)dicarbonylruthenium] (2). To the best of

$$\underset{\textbf{1}}{[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2}$$

$$\underset{\textbf{2}}{[(\eta^4\text{-}Ph_2Me_2C_4CO)(CO)_2Ru]_2}$$

our knowledge, complexes carrying cyclopentadienone (CPD) ligands were not previously recognized as hydrogenation catalysts. The resistance of the CPD ligand to hydrogenation is surprising. Complex 1 was recently reported by us to catalyze an interesting *dehydrogenation* reaction (eq 1).[2] It is a robust, air-stable complex readily prepared in good yield according to eq 2. An X-ray study[3]

$$2RCH_2OH \xrightarrow{1} RCO_2CH_2R + 2H_2\uparrow \qquad (1)$$

$$Ru_3(CO)_{12} + Ph_4C_4CO \rightarrow \underset{\textbf{3}}{(\eta^4\text{-}Ph_4C_4CO)(CO)_3Ru} \xrightarrow{\Delta} 1 + CO \qquad (2)$$

of the previously reported[4] 3 establishes its structural identity. The dimer 1 has, most probably, the structure[5] $\overline{Ru(CO)_2Ph_4C_4CO{\rightarrow}Ru(CO)_2Ph_4C_4CO}$, similar to that which was proposed for the Fe analogue.[6] The similarly prepared 2 exhibits an IR spectrum [(CCl_4) 2032, 2000, 1977, and 1530 cm^{-1}], which resembles that of 1,[5] and a NMR spectrum [($CDCl_3$) δ 2.06 (s, 6 H), 7.25–7.27 (m, 10 H)] as well as satisfactory elemental analysis.

Table I.[a] **Hydrogenation Data for** $[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2$

compd (mmol)	cat. (mmol)	solv (mL)	time, min	% convn[b] (cycles)[c]
1-octene (17.2)	0.01	bulk	10	100 (1720)
2-pentene (46.5)[d]	0.025	bulk	15	100 (1860)
cyclohexene (49.4)	0.025	bulk	15	100 (1976)
cyclohexene (49.4)[e]	0.025	bulk	60	100 (1976)
1-methylcyclohexene (16.9)	0.01	bulk	20	100 (1690)
styrene (52.4)	0.019	bulk	720	67 (2760)
trans-stilbene (10)	0.05	toluene (5)	180	93 (186)
1-hexyne (10)	0.05	toluene (10)	35	100 (200)
4-octyne (10)	0.05	toluene (10)	35	100 (200)
diphenylacetylene (10)	0.05	toluene (10)	135	100 (326)[f]
anthracene (10)	0.05	toluene (10)	135	100[g] (520)
diethyl ketone (95)	0.047	bulk	45	97 (1940)
cyclohexanone (100)[e]	0.05	bulk	300	98 (1960)
diisopropyl ketone (50)	0.025	bulk	180	88 (1760)
dibenzyl ketone (25)	0.025	toluene (5)	180	100 (1000)
acetophenone (50)	0.025	bulk	255	94 (1880)
benzophenone (10)	0.05	toluene (10)	20	49 (96)
benzaldehyde (10)	0.05	toluene (10)	10	81 (162)[h]
pentanal (10)[e]	0.05	toluene (10)	60	100 (200)[i]

[a] Conditions: glass-lined autoclave; 500-psi initial H_2 pressure; temperature 145 ± 1 °C unless otherwise specified. [b] Determined by GC using authentic samples for product identification. [c] Moles of products/moles of catalyst. [d] Cis–trans mixture. [e] Temperature 100 ± 1 °C. [f] The product contained *trans*-stilbene (37%) and 1,2-diphenylethane (63%). [g] A mixture of tetrahydro- and octahydroanthracenes (MS). [h] The products are benzyl alcohol (95%) and benzyl benzoate (5%). [i] The products are 1-pentanol (40%) and *n*-pentyl *n*-pentanoate (60%).

Both 1 and 2 catalyze hydrogenation of various unsaturated substrates (Table I). The following conclusions can be drawn: (a) Complex 1 is a broad spectrum hydrogenation precatalyst for alkenes, alkynes, ketones, aldehydes, and also anthracene. (b) Generally the rates are very good, exceeding, in several cases, 100 cycles/min under moderate reaction conditions, with conversions of 90–100%. (c) Hydrogenation can be carried out in the bulk or in solvent (toluene). (d) Lowering of the temperature diminishes the rate of the reaction. (e) Alkylacetylenes are hydrogenated to the corresponding alkanes. No attempts have yet been made to selectively hydrogenate one bond. (f) Phenyl olefins react slower than alkyl olefins. (g) No hydrogenolysis was encountered. (h) Esters are byproducts in the hydrogenation of aldehydes. Thus, an irreversible bimolecular dehydrogenation (eq 1) of the primary alcohol to ester[7] or alternatively a slow Tish-

---

[1] Collman, J. P. *Acc. Chem. Res.* **1968,** *1,* 136. Maitlis, P. M. *Ibid.* **1978,** *11,* 301. Muetterties, E. L.; Bleeke, J. R. *Ibid.* **1979,** *12,* 324. Crabtree, R. *Ibid.* **1979,** *12,* 331. James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973.

[2] Blum, Y.; Shvo, Y. *J. Organomet. Chem.* **1985,** *282,* C7.

[3] Blum, Y.; Shvo, Y.; Chodosh, D. F. *Inorg. Chim. Acta* **1985,** *97,* L25.

[4] Bruce, M. I.; Knight, J. R. *J. Organomet. Chem.* **1968,** *12,* 411.

[5] Blum, Y.; Shvo, Y. *Isr. J. Chem.* **1984,** *24,* 144.

[6] Weiss, E.; Merenyi, R.; Hübel, W. *Chem. Ber.* **1962,** *95,* 1170.

0276-7333/85/2304-1459$01.50/0 © 1985 American Chemical Society