J. Am. Chem. Soc. **1995,** *117,* 3617−3618 3617

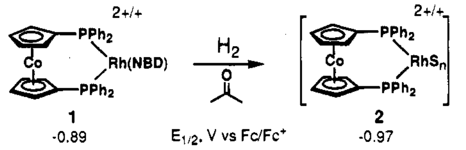
Use of the Redox-Active Ligand 1,1′-Bis(diphenylphosphino)cobaltocene To Reversibly Alter the Rate of the Rhodium(I)-Catalyzed Reduction and Isomerization of Ketones and Alkenes

Ivan M. Lorkovic, Ronald R. Duff, Jr., and
Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received October 17, 1994

Toward our goal of characterizing well-defined catalysts having multiple redox and reactivity states, we report the synthesis and characterization of the reversibly redox-active hydrogenation catalyst precursor $[Rh(dppc)NBD]^{2+/+}$ $(PF_6)_{2/1}$ (NBD, bicyclo[2.2.1]hepta-2,5-diene; dppc, 1,1′-bis(diphenylphosphino)cobaltocene) (**1**). **1** reacts in both states of charge with H_2 in acetone to give $[Rh(dppc)(acetone)_n]^{2+/+}$ (**2**), eq 1.[1]



(1)

There have been many reports of the use of redox-active ligands to perturb the electronic properties[2−6] and stoichiometric reactivity[2c,5b] of the transition metals to which they are bound. It is also well-documented that ligand "donicity" affects the reactivity and selectivity of homogeneous transition metal catalysts.[7] While cationic Rh reduction catalysts containing both achiral[8] and chiral[9] ferrocene-based phosphines are well-studied, there have been no reports which describe the effect of changes in the ligand state of charge on catalytic reactivity. We show here that, between the two states of charge of **2**, $\mathbf{2}_{ox}$ is the faster and more durable hydrosilation catalyst, while $\mathbf{2}_{red}$ is the faster hydrogenation catalyst (Scheme 1). Furthermore, the differences in catalytic reactivity between $\mathbf{2}_{ox}$ and $\mathbf{2}_{red}$ may be observed *in situ* by addition of stoichiometric amounts of simple redox reagents such as cobaltocene ($CoCp_2$) or $[Fe(\eta^5\text{-}C_5Me_5)_2]PF_6$ (Fc^*PF_6) to the solution.

Scheme 1. Catalytic Properties of $\mathbf{2}_{ox}$ Versus $\mathbf{2}_{red}$

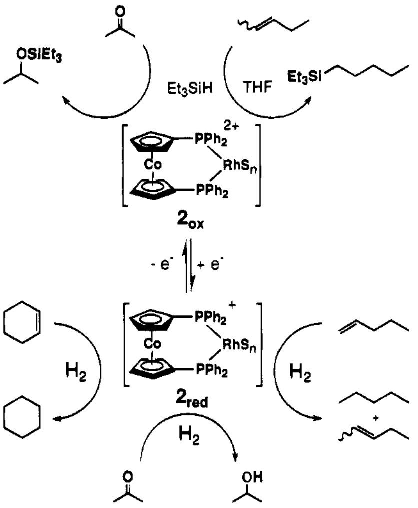


Figure 1 shows results from the hydrogenation of cyclohexene to cyclohexane catalyzed by a 4.0 mM solution of **2** prepared from $\mathbf{1}_{red}$ at 20 °C in acetone.[10] $\mathbf{2}_{red}$ clearly yields a faster rate than $\mathbf{2}_{ox}$. The hydrogenation rate of 0.23 mM/min observed after the chemical oxidation of $\mathbf{2}_{red}$ by Fc^*PF_6 is comparable to the 0.14 mM/min observed using a 4.0 mM solution of $\mathbf{2}_{ox}$ (prepared from $\mathbf{1}_{ox}$). In addition, full recovery of catalytic activity is observed when the solution is chemically re-reduced by the addition of 1 equiv of $CoCp_2$. We see similar results in the hydrogenation/isomerization of 1-pentene to pentane and 2-pentene, Figure 2. In this case, again, the reactivity of $\mathbf{2}_{red}$ formed by chemical reduction of $\mathbf{2}_{ox}$ *in situ* is similar to that of $\mathbf{2}_{red}$ prepared from $\mathbf{1}_{red}$. When the same solution is re-oxidized by addition of Fc^*PF_6, we observe that the rate of hydrogenation to form pentane is slowed, as expected, but that isomerization continues just as rapidly. $\mathbf{2}_{red}$ is much more reactive than $\mathbf{2}_{ox}$

---

* Author to whom correspondence should be addressed.

[1] $\mathbf{1}_{ox}$ and $\mathbf{1}_{red}$ were prepared using a procedure analogous to that of Schrock and Osborn [Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397] for the synthesis of $[(NBD)Rh(PMe_2Ph)_2]^+ClO_4$, but using $NaPF_6$ in place of $NaClO_4$ and $(dppc)PF_6$ [Rudie, A. W.; Lichtenberg, D. W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* **1978**, *17*, 2859] ($\mathbf{1}_{ox}$) or dppc [Dubois, D. L.; Eigenbrot, C. W., Jr.; Miedaner, A.; Smart, J. C. *Organometallics* **1986**, *5*, 1405] ($\mathbf{1}_{red}$) in place of $2PMe_2Ph$. $\mathbf{1}_{red}$ was recrystallized from CH_2Cl_2/MeOH. Analytical data: both $\mathbf{1}_{ox}$ and $\mathbf{1}_{red}$ gave satisfactory elemental analyses. Electrochemistry was performed in a 0.1 M $[n\text{-}Bu_4N]PF_6$ acetone solution with glassy carbon working, Pt counter, and Ag wire quasireference electrodes. Spectroscopic data: $\mathbf{1}_{ox}$, ^1H NMR (acetone-d_6) δ 7.95 (m, 8H), 7.75 (m, 12H), 6.10 (b, 4H), 6.08 (b, 4H), 4.80 (m, 4H), 4.14 (m, 2H), 1.58 (m, 2H); ^{31}P NMR δ (relative to H_3PO_4 ext. ref.) 28.0 (d, $J_{Rh-P} = 159$ Hz); UV/vis λ_{max} in acetone, nm (ϵ, M^{-1} cm^{-1}) 460 (2400); $\mathbf{1}_{red}$, ^1H NMR (acetone-d_6) δ 8.30 (b, 8H), 7.56 (t, $J = 7.3$ Hz, 4H), 7.00 (b, 8H), 4.06 (b, 2H), 3.15 (b, 2H), 2.92 (b, 4H), −12.2 (b, 4H), −52.0 (b, 4H); UV/vis 470 (2800), 544 (1300); $\mathbf{2}_{ox}$, ^1H NMR (acetone-d_6) δ 8.00 (q, $J = 6$ Hz, 8H), 7.67 (t, $J = 7$ Hz, 4H), 7.58 (t, $J = 7$ Hz, 8H), 6.09 (b, 4H), 6.06 (b, 4H); ^{31}P NMR δ 51.3 (d, $J_{Rh-P} = 209$ Hz); $\mathbf{2}_{red}$, ^1H NMR (acetone-d_6) δ 8.00 (b, 8H), 7.37 (t, $J = 7.3$ Hz, 4H), 6.82 (b, 8H), −9.5 (b, 4H), −50 (b, 4H). Chemically oxidizing (reducing) a solution of $\mathbf{2}_{red}$ ($\mathbf{2}_{ox}$) in acetone-d_6 prepared from $\mathbf{1}_{red}$ ($\mathbf{1}_{ox}$) with Fc^*PF_6 ($CoCp_2$) yielded a solution having a NMR spectrum identical to that of $\mathbf{2}_{ox}$ ($\mathbf{2}_{red}$) prepared from $\mathbf{1}_{ox}$ ($\mathbf{1}_{red}$).

[2] (a) Elschenbroich, C.; Stohler, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 174. (b) Miller, T. M.; Ahmed, K. J.; Wrighton, M. S. *Inorg. Chem.* **1989**, *28*, 2347. (c) Lorkovic, I. M.; Wrighton, M. S.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6220. (d) Wolf, M. O.; Wrighton, M. S. *Chem. Mater.* **1994**, *6*, 1526.

[3] (a) Colbran, S. B.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1361. (b) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 943. (c) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1983**, *2*, 952. (d) Colbran, S. B.; Robinson, B. H.; Simpson, J. *Organometallics* **1984**, *3*, 1344.

[4] (a) Hartl, F.; Vlcek, A., Jr.; deLearie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 1073. (b) Hartl, F.; Vlcek, A., Jr. *Inorg. Chem.* **1991**, *30*, 3048. (c) Hartl, F.; Vlcek, A., Jr. *Inorg. Chem.* **1992**, *31*, 2869. (d) Hartl, F.; Vlcek, A., Jr. *Inorg. Chim. Acta* **1992**, *192*, 25.

[5] (a) Fenske, D. *Chem. Ber.* **1979**, *112*, 363. (b) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, *111*, 130. (c) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (d) Mao, F.; Tyler, D. R.; Bruce, M. R. M.; Bruce, A.; Rieger, A. L.; Rieger, P. L. *J. Am. Chem. Soc.* **1992**, *114*, 6418.

[6] (a) Atkinson, F. L.; Christofides, A.; Connelly, N. G.; Lawson, H. J.; Lowyns, A. C.; Orpen, A. G.; Rosair, G. M.; Worth, G. H. *J. Chem. Soc., Dalton Trans.* **1993**, 1441. (b) Carriedo, G. A.; Connelly, N. G.; Perez-Carreno, E.; Orpen, A. G.; Rieger, A. L.; Rieger, P. H.; Riera, V.; Rosair, G. M. *J. Chem. Soc., Dalton Trans.* **1993**, 3103. (c) Bardaji, M.; Brown, N. C.; Connelly, N. G.; Davies, R.; Orpen, A. G.; Rosair, G. M.; Seear, N. R. *J. Organomet. Chem.* **1994**, *474*, C21.

[7] For example: (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Jacobsen, E. N.; Zhang, W.; Güler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703. (c) Nishiyama, H.; Yanaguchi, S.; Kondo, M.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 4306. (d) Rajanbabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6265. (e) Rajanbabu, T. V.; Ayers, T. A.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 4101.

[8] (a) Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1983**, *2*, 714. (b) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Jones, T.; Einstein, F. W. B. *J. Chem. Soc., Chem. Commun.* **1984**, 719. (c) Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1985**, *4*, 346. (d) Allgeier, A. M.; Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Organometallics* **1994**, *13*, 2928.

[9] (a) Hayashi, T.; Mise, T.; Mitachi, S.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1976**, 1133. (b) Hayashi, T.; Mise, M.; Kumada, M. *Tetrahedron Lett.* **1976**, 4351. (c) Cullen, W. R.; Yeh, E.-S. *J. Organomet. Chem.* **1977**, *139*, C13. (d) Cullen, W. R.; Einstein, F. W. B.; Huang, C.-H.; Willis, A. C.; Yeh, E.-S. *J. Am. Chem. Soc.* **1980**, *102*, 988. (e) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138. (f) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395. (g) Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7. (h) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

0002-7863/95/1517-3617$09.00/0

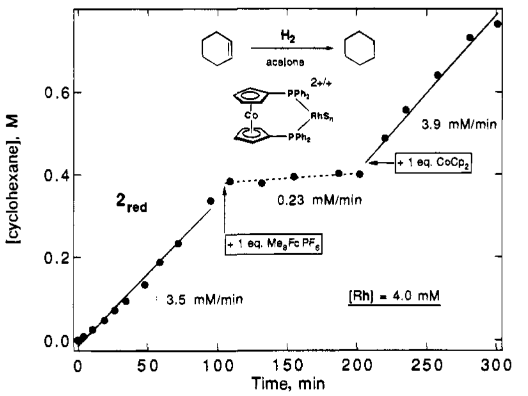


Figure 1. Progress of the hydrogenation of cyclohexene in acetone at 20.0 °C catalyzed by a solution of **2** prepared from 0.044 mmol of $\mathbf{1}_{\mathrm{red}}$. At 65 and 125 min, 0.044 mmol of Fc*PF$_6$ and CoCp$_2$ were added, respectively.

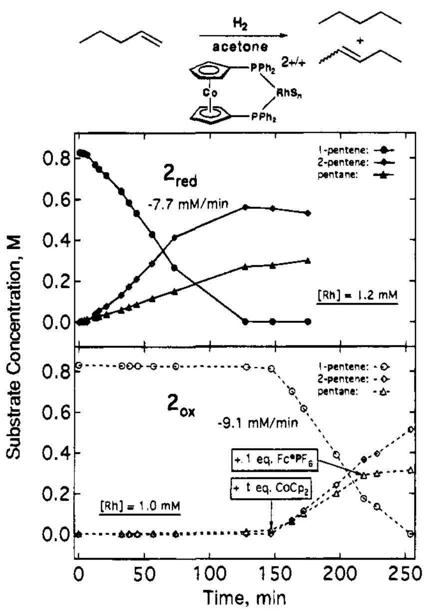


Figure 2. Progress of the hydrogenation/isomerization of 1-pentene to pentane and *cis*- and *trans*-2-pentene in acetone at 20.0 °C catalyzed by solutions of $\mathbf{2}_{\mathrm{red}}$ prepared from 0.013 mmol of $\mathbf{1}_{\mathrm{red}}$ (top) and $\mathbf{2}_{\mathrm{ox}}$ prepared from 0.0095 mmol of $\mathbf{1}_{\mathrm{ox}}$ (bottom). After 146 and 201 min, 0.013 mmol of CoCp$_2$ and Fc*PF$_6$, respectively, were added to the solution containing initially $\mathbf{2}_{\mathrm{ox}}$.

in the hydrogenation of acetone to 2-propanol. Again, at 20 °C in acetone, 0.52, 1.1, and 4.4 mM solutions of $\mathbf{2}_{\mathrm{red}}$ in acetone show the initial rate of 2-propanol formation to be 0.04, 0.06, and 0.11 mM/min, respectively, while a 1.7 mM solution of $\mathbf{2}_{\mathrm{ox}}$ forms 2-propanol at 0.003 mM/min.

In contrast to the results of hydrogenation experiments, $\mathbf{2}_{\mathrm{ox}}$ is faster than $\mathbf{2}_{\mathrm{red}}$ in the hydrosilation of acetone. At 20 °C in acetone containing 0.57 M triethylsilane, a 3.4 mM solution of $\mathbf{2}_{\mathrm{ox}}$ (prepared from $\mathbf{1}_{\mathrm{ox}}$) and a 5.0 mM solution of $\mathbf{2}_{\mathrm{red}}$ (prepared from $\mathbf{1}_{\mathrm{red}}$) catalyze the formation of isopropoxytriethylsilane at an initial rate of 2.0 and 0.45 mM/min, respectively. After chemical reduction of $\mathbf{2}_{\mathrm{ox}}$ *in situ* with CoCp$_2$, the isopropoxytriethylsilane formation rate drops to 0.13 mM/min. As was observed in the hydrogenation/isomerization of 1-pentene, the catalytic properties of $\mathbf{2}_{\mathrm{ox}}$ are not completely recovered when $\mathbf{2}_{\mathrm{red}}$ is re-oxidized *in situ*, increasing to only 0.9 mM/min, indicating that $\mathbf{2}_{\mathrm{red}}$ undergoes some decomposition in this medium. The catalytic isomerization/hydrosilation of 2-pentene to 1-pentyltriethylsilane at 20 °C in THF was also studied. Solutions of $\mathbf{2}_{\mathrm{ox}}$ and $\mathbf{2}_{\mathrm{red}}$ (both 0.9 mM) catalyze the formation of 1-pentyltriethylsilane at initial rates of 1.1 and 0.4 mM/min, respectively. At 20 °C, acetone solutions of $\mathbf{2}_{\mathrm{ox}}$ are air stable, while the air-sensitive $\mathbf{2}_{\mathrm{red}}$ slowly decomposes in acetone under Ar ($t_{1/2}$ = 3 h), with a color change from dark green to brown, to give a complex mixture of diamagnetic species.

The fact that $\mathbf{2}_{\mathrm{red}}$ is a better hydrogenation catalyst than $\mathbf{2}_{\mathrm{ox}}$ is consistent with previous results showing that $[\mathrm{RhL_2S_2}]^+$ hydrogenation catalysts are more active when more basic phosphines are employed,[8a,c,11] possibly because the oxidative addition of hydrogen is promoted by a more electron-rich Rh center. We have shown that reduction of dppc$^+$ or dppf$^+$ in Re(I) carbonyl complexes causes the CO stretch absorbances in their infrared spectra to shift 15 cm^{-1} to lower frequency, which indicates that the difference in phosphine basicity between dppc and dppc$^+$ is roughly equivalent to that between diphos and 1,2-bis(dicyclohexylphosphino)ethane.[2b,c] We have not found a trend in the literature correlating reactivity with changing basicity for hydrosilation of olefins or ketones, but our results indicate different consequences from state of charge changes for hydrogenation compared to hydrosilation upon making the Rh more electron rich.

Confinement of analogues of **1** and **2** to electrode surfaces should be useful in better understanding the consequences of changes in the state of charge of the pendant redox group, since site isolation may preclude catalyst oligomerization,[12,13] which, our preliminary results indicate, is occurring in solution. These experiments and further kinetic studies on $\mathbf{2}_{\mathrm{ox}}$ and $\mathbf{2}_{\mathrm{red}}$ are in progress.[14]

Acknowledgment. We thank the National Science Foundation, the Advanced Research Projects Agency and the Tokyo Electric Power Co. for partial support of this research. I.M.L. thanks the National Science Foundation for a Predoctoral Fellowship. I.M.L. is grateful to Dr. Eric W. Wollman for several stimulating discussions.

JA943380V

---

(10) A typical experiment was performed as follows: under Ar, yellow/burgundy solutions of $\mathbf{1}_{\mathrm{ox/red}}$ (0.2−5 mM) in acetone were prepared in Schlenk flasks with stir bars. The flasks were sealed with wired-down rubber septa, evacuated, and purged twice with H$_2$ ($P_{\mathrm{total}} = 870 \pm 20$ Torr), forming paler yellow/pine green solutions of $\mathbf{2}_{\mathrm{ox/red}}$. For olefin hydrogenations, after the solutions were left to stir under H$_2$ for at least 15 min while immersed in a 20.0 ± 0.5 °C bath, deoxygenated cyclohexene or 1-pentene (to make a 0.8−1 M solution) was added via syringe. Aliquots (50−200 μL) were removed via cannula and quenched with CH$_3$CN (ca. 4 mL). The resulting solutions were then analyzed by GC/MS. The only products detected by GC/MS or ^{1}H NMR for cyclohexene and 1-pentene hydrogenations were cyclohexane and pentane and 2-pentenes, respectively. To change the state of charge of the catalyst in solution, an appropriate amount of a concentrated deoxygenated solution of either CoCp$_2$ or Fc*PF$_6$ in acetone, or CH$_2$Cl$_2$ for reactions run in THF, was added to the stirred solution via syringe. Since the redox potential of **2** is at least 300 mV more positive (negative) than that of CoCp$_2$ (Fc*), the extent to which **2** was chemically reduced (oxidized) is determined by the error (±5%) in the quantity of reducing (oxidizing) agent transferred. For the hydrogenation of acetone, solutions of **1** were prepared with methylcyclohexane (ca. 15 mM) as internal standard. For hydrosilation reactions, the solutions of $\mathbf{1}_{\mathrm{ox/red}}$ were prepared with decane (ca. 0.12 M) internal standard. After formation of $\mathbf{2}_{\mathrm{ox/red}}$ with H$_2$, the solutions were evacuated and purged twice with Ar before addition of Et$_3$SiH (to make a 0.57 M solution) or Et$_3$SiH/2-pentene (1:1, to make a 0.4 M solution). For acetone hydrosilation, besides the expected product isopropoxytriethylsilane, hexaethyldisiloxane and a trace of triethylsilanol were also observed as products, in increasing amounts in acetone with higher [H$_2$O].

(11) (a) Schrock, R. R.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1970**, 567. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134. (c) Vastag, S.; Heil, B.; Marko, L. *J. Mol. Catal.* **1979**, *5*, 189. (d) Tani, K.; Suwa, K.; Tanigawa, E.; Yoshida, T.; Okano, T.; Otsuka, S. *Chem. Lett.* **1982**, 261. (e) Tani, K.; Suwa, K.; Yamagata, T.; Otsuka, Sei. *Chem. Lett.* **1982**, 265. (f) Tani, K.; Suwa, K.; Tanigawa, E.; Otsuka, Sei. *ACS Symp. Ser.* **1982**, *185*, 283. (g) Toros, S.; Kollar, L.; Heil, B.; Marko, J. *J. Organomet. Chem.* **1983**, *253*, 375.

(12) (a) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878. (b) Werner, H.; Wolf, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 296. (c) Meier, E. B.; Burch, R. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2661. (d) Fryzuk, M. D. *Can. J. Chem.* **1983**, *61*, 1347. (e) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *J. Chem. Soc., Chem. Commun.* **1984**, 719.

(13) (a) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055. (b) Halpern, J.; Chan, A. S. C.; Riley, D. P.; Pluth, J. J. *Adv. Chem. Ser.* **1979**, *173*, 16. (c) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936. (d) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 946. (e) Singewald, E. T.; Mirkin, C. A.; Levy, A. D. *Angew. Chem., Int. Ed. Engl.*, in press.

(14) Duff, R. R., Jr.; Wrighton, M. S. Manuscript in preparation.