Homogeneous Tungsten, Rhenium, and Iridium Catalysts in Alkane Dehydrogenation Driven by Reflux of Substrate or of Cosolvent or by Inert-Gas Flow

Toshiya Aoki[†] and Robert H. Crabtree*

Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06511

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A variety of catalysts have been studied for alkane dehydrogenation activity. The activities have been assayed by using the reflux method of Fujii and Saito, in which the endoergonic alkane dehydrogenation reactions can be driven by continuous removal of H_2 in the reflux process, which displaces the equilibrium of eq 1 toward alkene. **1b** ([$IrH_2(O_2CR)(PCy_3)_2$]; Cy = cyclohexyl, R = C_2F_5) is interesting in that initial deactivation leads to a less active catalyst, but one which is stable to further deactivation. [(triphos)WH_6] (**6**; triphos = $PhP(CH_2CH_2PPh_2)_2$) is also notable in that, for the first time, base-metal homogeneous catalysts are shown to be effective in alkane dehydrogenation. [(triphos)ReH_5] is also active. Using the substrate as reflux fluid limits the temperature at which the reaction can conveniently be run, but if the medium that removes the H_2 is other than the refluxing substrate, this limitation is lifted. We find that refluxing perfluorodecane is effective. Removal of the H_2 can also be effected by bubbling argon.

Alkane dehydrogenation[1] (eq 1) is normally endoergonic and so needs to be driven in some way. A hydrogen acceptor[1-3] (eq 2) or photochemical methods[3] (eq 3) can be used, but in eq 2 only hydrogen transfer, not net dehydrogenation, is achieved, and in eq 3 the efficiency is not high because the photon energy greatly exceeds the reaction endothermicity and the buildup of light-absorbing impurities stops the photoprocess. Typically, only 2-35 catalytic turnovers of product are obtained. All homogeneous catalysts previously described for eqs 1-3 involve precious metals, yet it is difficult to see why the reaction steps invoked should not also be possible with base metals.

$$RCH_2CH_3 \rightarrow RCH{=}CH_2 + H_2 \qquad (1)$$

$$RCH_2CH_3 + t\text{-}BuCH{=}CH_2 \rightarrow RCH{=}CH_2 + t\text{-}BuCH_2CH_3 \qquad (2)$$

$$RCH_2CH_3 \xrightarrow{h\nu} RCH{=}CH_2 + H_2 \qquad (3)$$

Fujii and Saito[4a] made the important observation that refluxing the alkane substrate allows eq 1 proceed spontaneously with Wilkinson's complex as catalyst. They proposed that the hydrogen formed in eq 1 is constantly removed by the reflux process and that this displaces the equilibrium to the right. In later work,[4b] they extended this to heterogeneous catalysts.

We have now used this method to test a variety of catalysts for alkane dehydrogenation activity. We also use reflux of an inert fluorocarbon or an inert-gas flow to drive the dehydrogenation. In addition to the precious-metal homogeneous catalysts, based on Ir, Re, and Ru, for example, we now find that a base-metal polyhydride, WH_6L_3, can be active, providing that L_3 is a chelating triphosphine.

Results and Discussion

Catalyst 1a. We have previously shown that [$IrH_2(O_2CCF_3)(PCy_3)_2$] (**1a**; Cy = cyclohexyl) dehydrogenates cyclooctane via eqs 2 and 3, and we proposed a mechanism.[3] We now find dehydrogenation in the absence of hydrogen acceptor under the reflux conditions of Fujii and Saito (eq 1). We were able to determine both the alkene and the hydrogen evolved by GC methods (see Experimental Section). For example, 1.25 mM **1a** at 151 °C gave an initial dehydrogenation rate of 1.41 turnovers/h. As expected from eq 1, the amounts of cyclooctene (coe) and H_2 formed are the same. After 24 h, 22.4 turnovers (t.o.) both of coe and of H_2 are seen (Table I). The dehydrogenation rate is independent of reflux rate in the range we examined, but we did not study very slow reflux.

Reflux is required for the reaction to proceed. If the temperature is reduced to 140 °C under 1 atm pressure, both the reflux and the dehydrogenation processes stop. If the pressure is then reduced so that the system starts refluxing at 140 °C, the dehydrogenation resumes, but at a slightly slower rate (0.42 t.o./h). These observations are entirely consistent with the proposal that the role of the reflux is to remove the H_2 and displace the equilibrium of eq 1 in favor of alkene.

Differential reflux temperatures and solvation effects associated with mixed solvents prevented us from determining the order in alkane. A time course for the production of coe from cyclooctane (coa) in the range 130-159 °C is shown in Figure 1. A plot (Figure 2) of the log of the initial rates versus temperature in the range 140-160 °C gave an apparent activation energy of 36 kcal/mol.

[†] Permanent address: Mizushima Laboratories, Asahi Chemical Industry Co., Ltd., Kurashiki City, Okayama 711, Japan.

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Table I. Results of Cyclooctane Dehydrogenation with the Iridium Catalysts 1 ($[IrH_2(O_2CR)(PCy_3)_2]$; Cy = Cyclohexyl)

catalyst, R group[a]	conditions[b]	time, h	amt of products, mol/mol of metal: coe	H_2	initial rate, t.o./h	deact half-life, h
1a, CF_3	rflx, 151 °C, 760 mmHg	24	22.4	22.4	1.41	15
		48	28.5	27.1		
	non-rflx, 140 °C, 760 mmHg	27	0.3		<0.03	
	non-rflx, 140 °C, 760 mmHg	53	1.6	1.3	0.06	
	rflx, 140 °C, 600 mmHg	24	8.6	>6.8	0.42	58
	rflx, 130 °C, 400 mmHg	24	3.7	>3.5	0.16	300
1b, C_2F_5	rflx, 151 °C, 760 mmHg	24	20.1	22.7	1.05	34
		48[c]	35.8	29.4	0.69	≫100
1c, $PhCH_2$	rflx, 151 °C, 760 mmHg	23	4.5	2.8	0.22	14

[a] R group in the carboxylate ligand of the Ir complex. [b] Catalyst: 1.25 mM (**1a**), 1.20 mM (**1b**), 1.25 mM (**1c**). [c] **1b** partially deactivates with time to give a stable product of unknown structure; the figures refer to this deactivation product.

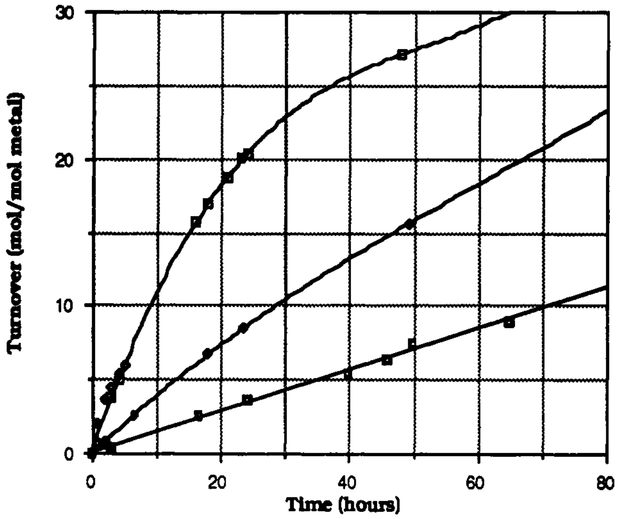

Figure 1. Time course of coe production from coa with **1a** (0.06 mmol in 50 mL of coa) as catalyst at 151 °C (□), 140 °C (◆), and 130 °C (■) under reflux.

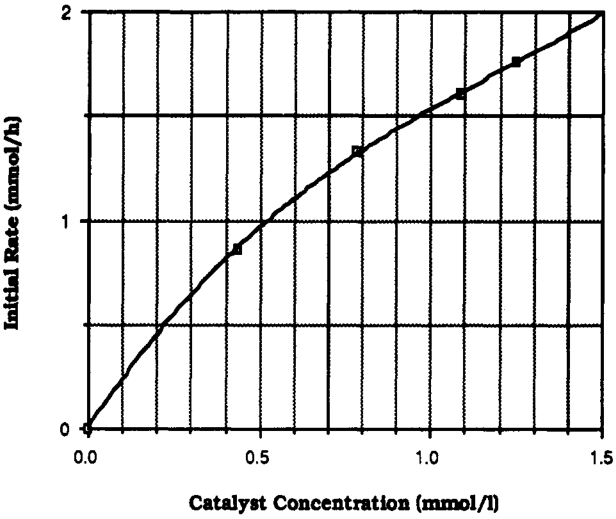

Figure 3. Dependence of the rate of alkane dehydrogenation (151 °C, reflux) on catalyst concentration for **1a** ($[IrH_2(CF_3CO_2)(PCy_3)_2]$).

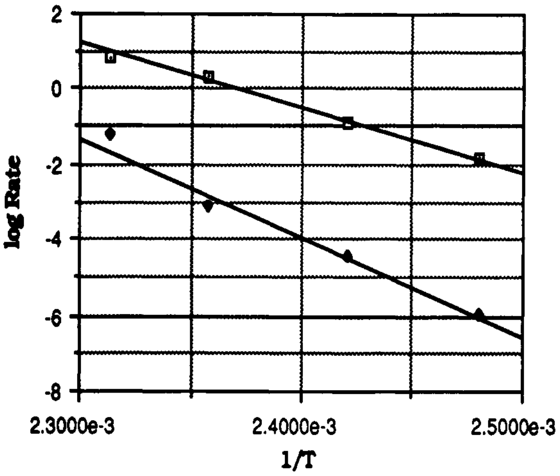

Figure 2. Temperature dependence of the initial dehydrogenation rate (□) and the deactivation rate (◆) of **1a** (0.062 mmol in 50 mL of coa) under reflux.

This is only 12 kcal/mol larger than the endothermicity[5] of eq 1 (23.5 kcal/mol), suggesting that the catalyst is efficient. There was no inhibition by metallic mercury, suggesting a homogeneous origin for the chemistry.[6] The initial rate was not exactly first order in catalyst (Figure 3). We think the departure from linearity is real or it may be the result of mass transport limitations. In our experiment, the H_2 evolved builds up in the ca. 70 mL headspace above the reflux zone and in the gas buret, all originally filled with N_2.

Because of catalyst deactivation, we were not able to follow the reaction for a sufficient time to find out if it stops when the partial pressure of H_2 in the gas buret reaches the equilibrium value, but we did show that dehydrogenation does not occur under an atmosphere of H_2. Indeed, with Pd/C, alkene can be hydrogenated under H_2, even at reflux. This implies that H_2 is dissolving in the condensing alkane to some extent and returning to the liquid phase; thus, reflux-induced dehydrogenation would eventually come to equilibrium even if the catalyst did not deactivate.

Figure 1, the time courses for the production of coe at various temperatures, shows that higher temperature gives higher dehydrogenation activity but also much higher deactivation rates. The catalytic rate for **1a** shows decay with time (Figure 4), which we ascribe to the deactivation process. If we define the deactivation as ($rate_i - rate_t$)/$rate_i$, then we can follow the deactivation with time at different temperatures. It proves to be a first-order process, and at 151 °C, the deactivation half-life is 15 h. The temperature dependence of the deactivation rate over the range 130–160 °C leads to an apparent activation energy of 46 kcal/mol for the deactivation process (Figure 2). The deactivation is accompanied by the appearance of ca. 0.5 mol of cyclohexane and cyclohexene per mole of Ir complex deactivated, which we ascribe to P–C bond

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(5) Stull, D. R.; Westrum, E. F.; Sinke, J. E. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

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

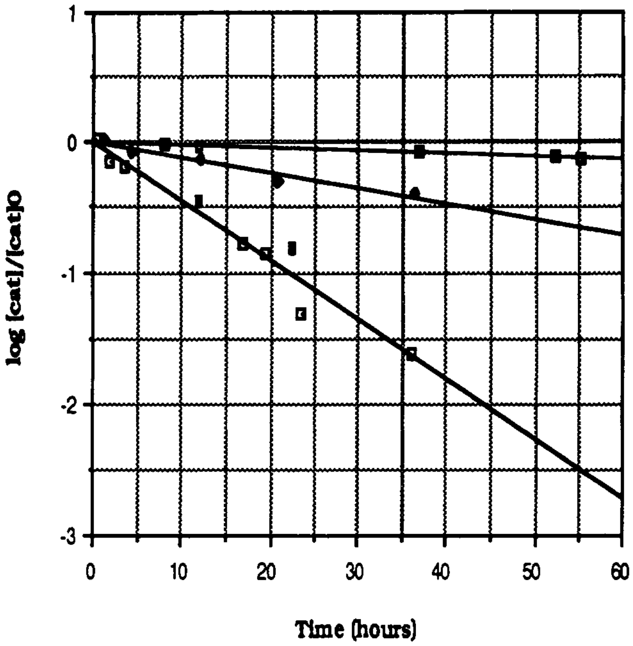

Figure 4. Time dependence of log {(rate$_i$–rate$_t$)/rate$_i$} at various temperatures: 151 °C (■), 140 °C (◆), and 130 °C (□) for coa dehydrogenation with **1a** (0.0624 mmol in 50 mL of coa) under reflux conditions.

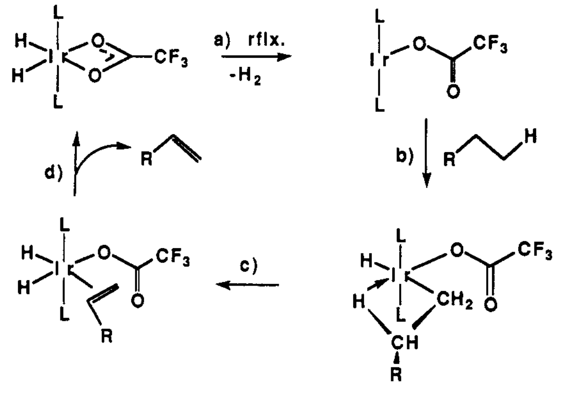

Figure 5. Mechanism previously proposed[3] for alkane dehydrogenation with **1a**, adapted to take account of the reflux conditions used here.

cleavage[7] of the phosphine. P–Ar bond cleavage was previously noted[3] as the deactivation pathway in the related catalysts [$IrH_2(O_2CCF_3)(PAr_3)_2$], where ArH builds up in the reaction mixture as deactivation proceeds. It is presumably P–C bond cleavage that is rate-determining in the deactivation. Deactivation is not simply due to buildup of coe, as we found by deliberately adding coe (10 equiv) to the reaction mixture.

The catalytic cycle previously proposed[3] for **1** (Figure 5) may apply to the reflux system. An important difference is that the present reaction proceeds in the absence of photons, and so the loss of H_2 from the dihydride must be thermal; this (step a of Figure 5) could well be the rate-determining step. We verified that the reaction proceeds in the presence of metallic Hg, suggesting a homogeneous origin for the catalytic activity.[3]

Catalysts 1b,c. The related catalysts **1b,c** ([$IrH_2(O_2CR)(PCy_3)_2$]; Cy = cyclohexyl; R = C_2F_5 (**b**), $PhCH_2$ (**c**)) were studied to see if we could slow deactivation by altering R. They are also active (Table I) and show improved (**1b**) or comparable (**1c**) deactivation half-lives. In particular, **1b** showed an initial deactivation with a half-life of ca. 34 h to give a species which was somewhat less catalytically active but which did not show a significant falloff in activity with time. This shows that phosphine degradation can in principle be prevented by alteration of the non-phosphine ligands and so provides a strategy for further work.

Table II. Cyclooctane Dehydrogenation with Various Catalysts

catalyst[a]	time, h	amt of products, mol/mol of metal		initial rate, t.o./h	deact half-life, h
		coe	H_2		
2, $IrH_2(CF_3CO_2)(PPh_3)_2$	46	1.2	2.9	0.20	5
3, $IrCl(PPh_3)_3$	70	1.6	0.8	0.09	12
4a, Pd/C	28	14.6	16.9	4.48	2
5a, Rh/C	18	5.6	(2.6)	1.82	1.5
4b, Pd/C recycle of **4a**[b]	24	13.2			
5b, Rh/C recycle of **5a**[b]	24	5.1			
6, [$(triphos)WH_6$]	3	4.5	4.5	1.5	5
7, [$(triphos)ReH_5$]	18	4.6	5	1.25	<5

[a] triphos = $PhP(CH_2CH_2PPh_2)_2$. Conditions: reflux, 151 °C; catalyst 0.030 mmol, coa 25 mL (**2a**, **3**, **4b**, **5b**, **6**, and **7**); catalyst 0.0625 mmol, coa 50 mL (**4a** and **5a**). [b] **4b** and **5b** refer to **4a** and **5a** recovered from the reaction mixture and washed with pure hexanes before reexposure to pure cyclooctane under the reaction conditions.

The identity of the deactivation product from **1b** is of great interest, but no progress was made in isolating and characterizing it. No P–C bond-cleavage products were detected, and so the deactivation of **1b** probably does not occur in the same way as for **1a**. The deactivation product does not crystallize, nor does it show any hydride resonances, but it does show the ususal resonances for the carboxylate and phosphine ligands. Further work is in progress.

Other Precious-Metal Homogeneous and Heterogeneous Catalysts. Other, less successful PPh_3-based catalysts were also studied (Table II). [$IrH_2(O_2CCF_3)(PPh_3)_2$] (**2**) showed rapid deactivation, as did [$IrCl(PPh_3)_3$] (**3**). Surprisingly, heterogeneous catalysts such as Pd/C (**4a**) and Rh/C (**5a**) show even faster deactivation under these conditions. The reason may be a poisoning of the surface by some of the dehydrogenation products, because simple washing of the recovered catalyst with pure hexanes and reexposure to pure cyclooctane under the reaction conditions leads to essentially complete recovery of activity. Saito et al.[4b] have also studied heterogeneous catalysts in reflux-induced dehydrogenation.

Tungsten Catalyst. Only precious-metal homogeneous catalysts have previously been active for alkane dehydrogenation: all our prior efforts with base-metal catalysts have failed. Early work[8] on [$W(PMe_2Ph)_3H_6$] was unsuccessful because alkanes were not dehydrogenated. The metal complex did react, however, and the very stable [$W(PMe_2Ph)_4H_4$] was observed as the major identifiable product from thermolysis of the hexahydride in alkanes at 150 °C. This complex is catalytically inactive.

By preventing the disproportionation of WH_6L_3, we should be able to prevent catalyst deactivation to give WH_4L_4. We therefore tried to prepare a tungsten tetrahydride using the meridional $PhP(CH_2CH_2PPh_2)_2$ (triphos). We find that treatment of the known[9] complex [$WCl_4(PPh_3)_2$]·CH_2Cl_2 with triphos gives [$(triphos)WCl_4$].

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(7) Ortiz, J. V.; Havels, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.

(8) Crabtree, R. H.; Hlatky, G. G. Unpublished work, 1981.

(9) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1990**, *28*, 33.

Reduction of this species with $LiAlH_4$ leads to the formation of the desired hexahydride, [(triphos)WH_6] (**6**), in good yield.[10] The complex can be identified from its characteristic ^1H NMR resonance at −3.85 ppm ($J_{H,P}$ = 23 Hz, $J_{H,W}$ = 29 Hz), which shows coupling both to phosphorus and to tungsten. In the IR spectrum, M–H stretching bands appear at 1866, 1824, and 1770 cm^{-1}. The spectral data for **2** seem entirely consistent with a classical complex, and a tricapped-trigonal-prismatic structure is probably adopted.

In cyclooctane dehydrogenation, 1.2 mM **6** gave an initial rate of 1.5 t.o./h under reflux conditions. This appears to be the first case in which a base metal has given an active catalyst for alkane dehydrogenation. Unfortunately, the deactivation appears to be quite rapid.

Rhenium Catalyst. [ReH_5(triphos)][10] (**7**) was also assayed for alkane dehydrogenation activity. The initial rate was comparable to that found for **6**, but deactivation was more rapid. The related complex [ReH_5(P{OCH_2}$_3$CMe)$_3$][10] was almost inactive (initial rate 0.03 t.o./h), and [ReH_3(CO)(PMe_2Ph)$_3$] was entirely inactive.

Utility of Reflux Method for Assaying Catalyst Activity. This reflux method provides a very convenient method of testing a variety of catalysts for alkane dehydrogenation activity. Previous assays[1-3] involved photochemistry or the presence of a hydrogen acceptor. Photochemical reactivity may not be relevant to the thermal processes and may also require a judicious choice of wavelength for the irradiation. The hydrogen acceptor may bind strongly and so block sites at the metal or may otherwise react with the catalyst to give a catalytically inactive species. In contrast, the reflux assay tests the ability of the complex to dehydrogenate alkanes thermally without other factors complicating the interpretation of the results.

Driving the Reaction by Reflux of Cosolvent and Bubbling Inert Gas. Reflux of substrate limits the temperature range over which the reaction can be carried out, and a different approach is needed to extend the method to high-boiling substrates. Two different possibilities were considered: (1) using an inert volatile cosolvent to act as the refluxing medium and (2) bubbling an inert gas through the solution. If reflux serves only to displace the equilibrium of eq 1, it should not matter whether the refluxing liquid is the substrate itself or an inert solvent or an inert gas. Perfluorodcalin (PFD) is more volatile than coa and is chemically inert; therefore, we tried it as a cosolvent. With 0.77 mM **1** in 50:50 (v/v) PFD/coa at 127 °C, the reflux temperature, 5.8 t.o. of coe were formed after 24 h. The PFD reaction is efficient and has almost double the turnovers compared to reflux of neat coa under reduced pressure at essentially the same temperature (3.0 t.o. at 130 °C under 400 mmHg for 22 h). This may be a solvent effect, or PFD may be more efficient at entraining H_2 in the system.

Bubbling an inert gas was also effective, but for coa as substrate, this caused excessive loss of coa by evaporation; we therefore moved to the relatively involatile cyclodecane as substrate. In neat alkane as solvent, 2.9 t.o. of dehydrogenation were observed at 145 °C after 6 h with 1.25 mM **1** as catalyst. The PFD and bubbling Ar reactions are significant in that alkanes with boiling points unsuitable for the usual reflux process can now be studied.

Conclusion

We have used the technique of Fujii and Saito to test a number of catalysts under conditions which avoid both photochemical conditions and the presence of a hydrogen acceptor. We find that a number of Ir catalysts are active but they deactivate with time. In one case (**1a**), the deactivation process was shown to involve P–C cleavage in the phosphine. In another case (**1b**), deactivation occurred by a different route to give a species which was less active but did not show a falloff in activity with time. Finally, a base metal polyhydride, [(triphos)WH_6] (**6**), was shown to be active, providing a triphosphine was used to prevent formation of catalytically inactive WH_4L_4 species, as happens with the monophosphine analogues of **6**. Reflux of an inert fluorocarbon cosolvent or bubbling an inert gas is also effective in driving reaction 1. This allows the method to be used with a larger variety of alkanes than before.

Experimental Section

Materials were obtained from Aldrich, PCR, Pfaltz and Bauer, and Strem Chemical Co. Alkanes were purified as previously described;[3] solvents and reagents were purified by standard techniques. Spectra were obtained on a Bruker WM250 instrument (NMR) and a Nicolet 5-SX FT-IR spectrometer. The synthesis of the tungsten compound is described in another paper.[10]

Dihydrido(η^2-pentafluoropropionato)bis(tricyclohexylphosphine)iridium(III) (1b). A mixture of [Ir(coe)Cl]$_2$ (0.30 g, 0.45 mmol; coe = cyclooctene) and $AgO_2CC_2F_5$ (0.24 g, 0.90 mmol) in CH_2Cl_2 (20 mL) was stirred in the dark for 30 min. The resulting red solution was filtered through Celite, and PCy_3 (0.50 g, 1.8 mmol) added. The resulting orange solution was stirred for 5 min; H_2 (1 atm., 50 mL/min) was then bubbled for 20 min, during which time the solution turned colorless, and it was concentrated to ca. 5 mL. The addition of methanol (10 mL) precipitated **1b** as a white solid, which was filtered, washed with methanol (2 × 3 mL), and dried in vacuo; yield 0.66 g (80%). The compound can be recrystallized from CH_2Cl_2/methanol or benzene/methanol. Anal. Calcd for $C_{39}H_{68}F_5O_2P_2Ir{\cdot}CH_2Cl_2$: C, 47.89; H, 7.03. Found: C, 47.69; H, 6.83. ^1H NMR: δ −34.0 (t, 15.1 Hz, Ir–H), 1.2–2.1 (c, Cy).

Dihydrido(η^2-phenylacetato)bis(tricyclohexylphosphine)iridium(III) (1c). A mixture of [Ir(coe)Cl]$_2$ (0.30 g, 0.45 mmol) and AgO_2CCH_2Ph (0.21 g, 0.90 mmol) in CH_2Cl_2 (20 mL) was stirred in the dark for 40 min. The resulting red solution was filtered through Celite, and PCy_3 (0.50 g, 1.8 mmol) was then added. The resulting orange solution was stirred for 4 min. H_2 was bubbled for 20 min, during which time the solution turned colorless; it was concentrated to ca. 5 mL. The addition of heptane (15 mL) precipitated **1c** as a white solid, which was filtered, washed with heptane (2 × 3 mL), and dried in vacuo; yield 0.66 g (82%). The compound can be recrystallized from CH_2Cl_2/heptane or benzene/heptane. Anal. Calcd for $C_{39}H_{68}F_5O_2P_2Ir{\cdot}2CH_2Cl_2$: C, 52.12; H, 7.51. Found: C, 51.99; H, 7.85. ^1H NMR: δ −31.0 (t, 15.1 Hz, Ir–H), 1.0–1.9 (c, Cy and CH_2), 7.2–7.9 (c, Ph).

Other Catalysts. The iridium complexes [IrH_2(O_2CCF_3)(PCy_3)$_2$] (**1a**)[3] and $IrCl(PPh_3)_3$ (**3**)[11] were prepared by the published methods. The heterogeneous catalysts 5% Pd/C and 5% Rh/C were from Aldrich Chemical Co. and were used without reduction or other pretreatment. The syntheses of the W and Re triphos complexes will be described in a future paper.[10]

Thermal Cyclooctane Dehydrogenations. All manipulations were carried out under argon. Thermal cyclooctane dehydrogenations were performed with three different reaction systems. Type I: a Schlenk tube (100 mL) was equipped with

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[10] Michos, D.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.*, in press.

[11] Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.

a thermocouple and a reflux condenser. The condenser was connected to a 50-mL gas buret (containing Nujol as working fluid and with a leveling bulb to maintain 1 atm total pressure) to measure the evolved gas, and the stopcock exits were sealed with rubber septa. Type II: as for type I, except that instead of gas burets the reflux condensers were attached to a pressure gauge and micro-metering values (orifice size 0.51 mm). These values allowed the pressure to be controlled to a tolerance of ca. 5 mmHg by either using the vacuum pumps or attaching a high-pressure Ar tank. Type III systems were composed of resealable glass vessels (capacity 10–15 mL) equipped with Kontes or Ace glass Teflon stopcocks and made of triple-thickness Pyrex glass. All reaction mixtures were stirred with small Teflon-coated stirbars. All reaction temperatures were maintained to within ±0.2 °C with a fully equilibrated Blue M (MW-115A-2) oil bath. The temperature was monitored with an external thermocouple probe. Type IV: a Schlenk tube (100 mL) was equipped with a gas inlet tube which allowed introduction of the gas through a frit. The system was also equipped with a thermocouple and a reflux condenser. The condenser was connected to a gas bubbler to prevent air leaks; the inner gas and stopcock exits were sealed with rubber septa. The gas inlet tube was connected to an argon gas tank through a pressure-controlling valve.

Reactions under Different Conditions. (i) Reflux (151 °C) at 760 mmHg. In a typical experiment, a type I reactor was charged with $[IrH_2(CF_3CO_2)(PCy_3)_2]$ (1; 54.2 mg, 0.0624 mmol) and degassed cyclooctane (50 mL). After the solution was heated to the reflux temperature (151 °C) with the oil bath (180 °C), the amount of the evolved gas was measured using the gas buret (50 mL). The components both in the gas and in the solution phases were sampled successively through the stopcock with microsyringes and quantified on a Varian Model 3700 GC (methyl-silicone or Carbowax capillary columns) or a Varian Model 920 GC (5-Å molecular sieve column).

(ii) Reflux at 140 °C and 760 mmHg. In a typical experiment, the type I reactor was charged with $[IrH_2(CF_3CO_2)(PCy_3)_2]$ (1; 27.1 mg, 0.0312 mmol) and degassed cyclooctane (25 mL). After the solution was heated to 140 °C with the oil bath (140 °C), the amount of the evolved gas was measured with the gas buret. The components in both the gas and solution were analyzed as above. Although the reaction temperature was below the boiling point (151 °C), a very slow refluxing took place because of the temperature difference between the solution and the reflux condenser.

(iii) Strict Nonreflux Conditions (140 °C) and 760 mmHg. To prevent any reflux at 140 °C, a type III reactor was employed and sunk as deep as possible in the hot oil to avoid temperature variations between different parts of the reactor. In a typical experiment, the reactor was charged with $[IrH_2(CF_3CO_2)(PCy_3)_2]$ (1; 2.7 mg, 0.0031 mmol) and degassed cyclooctane (2.5 mL). The reactor was heated to 140 °C for 27 h, and the products were analyzed as above.

(iv) Reflux (140 °C) and 600 mmHg. In reduced-pressure runs at 140 °C, a type II reactor was employed. In a typical experiment, the reactor was charged with $[IrH_2(CF_3CO_2)(PCy_3)_2]$ (1; 27.1 mg, 0.0312 mmol) and degassed cyclooctane (25 mL). The solution was heated to 140 °C with the oil bath (140 °C); the reactor pressure was reduced to 600 mmHg and controlled with the needle valve. The components both in the gas and in the catalyst solution were sampled and analyzed as above.

(v) Reflux at Various Temperatures and Pressures. The procedure used was identical with that described in (iv), except that the reaction temperatures were changed from 130 °C (400 mmHg) to 159 °C (1000 mmHg).

(vi) Reactions with Heterogeneous Catalysts. The procedure used was identical with that described in (i) except that the catalyst was changed to 5% Pd/C (0.133 g, 0.0625 mmol of Pd) in coa (50 mL) or 5% Rh/C (0.129 g, 0.0625 mmol of Rh) in coa (50 mL). The deactivated catalysts were recycled by filtering, washing several times with *n*-hexanes, and drying with N_2 for 1 h.

(vii) Reactions in the Presence of Mercury. The procedure used was identical with that described in (i) except that 1 drop of Hg (≈2 g) was added to the reaction mixture prior to degassing and heating.

(viii) Hydrogen Pressure in the Gas Phase. The refluxing condensable gas was collected with a gas syringe having a long needle and stopcock. The stopcock was closed after sampling to prevent any undesired contamination. The volumes of hydrogen, argon, and solvents present were measured by GC. The sum of all these volumes at the reflux temperature was always the same within experimental error as the volumes collected at this temperature.

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