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Selective Catalytic Dehydrogenation of Alkanes to Alkenes

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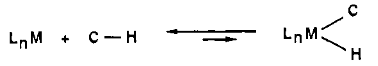
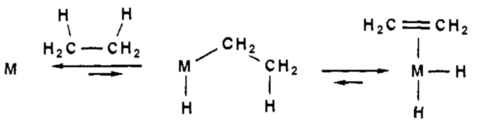
Abstract: Linear and cyclic alkanes can be selectively dehydrogenated to the corresponding alkenes both thermally and photochemically (254 nm) with iridium complexes as catalysts. In the photochemical case, a sacrificial hydrogen acceptor is not required and H_2 is evolved directly. Preferential initial formation of the least stable alkene (e.g., methylenecyclohexane from methylcyclohexane) is explained by attack at unhindered C–H bonds by an oxidative addition to the metal. A subsequent β-elimination gives the alkene. A key feature of the catalyst, $[IrH_2(\eta^2\text{-}O_2CCF_3)(PR_3)_2]$ (**4**), is that the chelating acetate group can open up to allow β-elimination to take place in the alkyl hydride intermediate $[IrH(R)(\eta^2\text{-}O_2CCF_3)(PR_3)_2]$. Prolonged reaction times lead to progressive isomerization of the alkene to give the thermodynamic product (e.g., 1-methylcyclohexene from methylcyclohexane). Up to 32 turnovers of dehydrogenation are seen. Deactivation of the catalyst takes place by P–C hydrogenolysis of the PAr_3 ligand in the thermal case; the rise in the amount of ArH formed parallels the fall-off in activity of the catalyst. P–C cleavage does not take place in the photochemical system (R = cyclohexyl). A reversible cyclometalation of the catalyst **4a** (R = $p\text{-}FC_6H_4$) is observed after removal of the hydride ligands with $t\text{-}BuCH{=}CH_2$. In the presence of C_6H_6, a C–H oxidative addition product, $[IrH(Ph)(\eta^2\text{-}O_2CCF_3)(PR_3)_2]$, is formed instead ($k_H/k_D = 4.5$) and can be isolated from the reaction mixtures; this supports the oxidative addition pathway proposed for the alkanes. Equilibrium constants for the reaction of **4a** with alkenes to give $[IrH_2(\text{alkene})(\eta^1\text{-}O_2CCF_3)(PR_3)_2]$ are reported.

Alkane C–H bond activation by transition-metal complexes is a topic of current interest. Of the many possible approaches,[1] we will consider here only the oxidation addition pathway (eq 1).


(1)

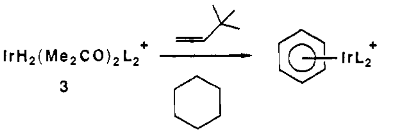

(2)

As indicated in the equation, the reaction seems usually to be thermodynamically unfavorable for the d-block metals, the M–C bond being substantially weaker than the M–H bond.[1,2] This situation contrasts to that for H_2 addition (eq 2), which is thermodynamically favorable, and many cases of H_2 addition to metal complexes are known. We have always been interested in catalytic applications of C–H bond-breaking reactions, and so the instability of the alkyl hydride (**1**) in eq 1 and 3 is *not* a disadvantage. We only need to channel the decomposition in the direction of β-elimination to an alkene dihydride (**2**), rather than reductive elimination to alkane (eq 3).


(3)

As indicated in the equation, when the alkane is dissected to give **1**, the two 1e donor fragments, R and H, together constitute a net 2e donor system, and so a 16e starting metal fragment can in principle give this reaction (eq 1). Several photochemically generated 16e fragments have been observed to give adducts of type **1**.[3] The corresponding net electron count for the C=C and the two H ligands of **2**, in contrast, is 4e, and so a 14e fragment (or its equivalent) would be required to dissect an alkane to give **2**. We do not necessarily imply that any 14e fragment need have an independent existence. We merely require that the catalyst precursor be capable of rearrangement or ligand dissociation to liberate vacant sites at the metal. These sites must be capable of holding the C=C and the two H ligands derived from the alkane and therefore must be capable of accepting 4e.

We have previously used $[IrH_2(Me_2CO)_2L_2]^+$ (**3**) (L = PPh_3) in this connection and have shown that this species dehydrogenates alkanes beyond the alkene stage to arenes,[4a] cyclopentadienyls,[4b,c] and related species (eq 4 and 5). Since the H_2 and both Me_2CO ligands of **3** are lost in eq 4 and 5, this complex can be considered as equivalent to a 12e reagent. The dehydrogenation products, benzene and cyclopentadienyl, are too tightly bound to be released thermally under mild enough conditions to avoid destruction of the IrL_2^+ fragment, and so these reactions are not catalytic. We wondered whether we could divert the process to give alkenes selectively as products by using a reagent equivalent to a 14e fragment and so stopping the dehydrogenation at the alkene stage. Since alkenes often dissociate from metal complexes relatively easily, we believed that the overall process might then be catalytic. We thought that a neutral catalyst might be useful, because it should be alkane soluble, and so we aimed for a 14e "IrL_2X" system (X = anionic ligand). This paper describes the development of such a catalyst.[5]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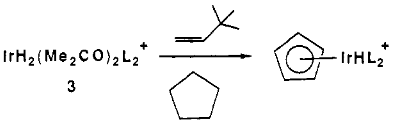
(5)

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Felkin et al.[6] have observed catalytic alkane dehydrogenation with a variety of transition-metal polyhydrides, notably ReH_7L_2 and $IrH_5(P(i\text{-}Pr)_3)_2$, and with $t\text{-}BuCH{=}CH_2$ (tbe), a reagent we originally introduced as a hydrogen acceptor.[4b,c] The presence of tbe is required to make the overall process thermodynamically favorable. Up to 40–70 turnovers of cyclooctene (coe) can be obtained in this way from cyclooctane. In the presence of tbe, $IrH_5(P(i\text{-}Pr)_3)_2$ dehydrogenates pentane to 1-pentene (0.3 turnover), but this is subsequently largely isomerized to 2-pentene. Methylcyclohexane gives up to 3.6 turnovers of alkenes, most of which consists of methylenecyclohexene.[6c] We hoped in our work to make a catalyst that would be generally useful for the dehydrogenation of a variety of alkanes and also to explore ways of avoiding the apparent necessity for having a hydrogen acceptor present. Some of this work has appeared in a preliminary form.[5]

Results and Discussion

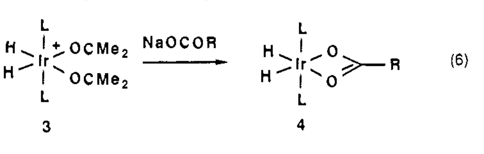
Early Attempts To Obtain "$IrXL_2$" Fragments. Our first step was to try X = H; $IrHL_2$ has now been proposed as the active species in IrH_5L_2 catalysts.[6c] For this we felt we need only deprotonate the $[IrH_2(Me_2CO)_2L_2]^+$ complex. This would have the additional merit of labilizing the acetone groups, because loss of the net cationic charge should make the metal less oxophilic.

Proton Sponge (1,8-bis(dimethylamino)naphthalene) in cyclooctane/tbe proved to be a suitable base. Heating the mixture resulted in the dissolution of **1a** ($[IrH_2(Me_2CO)_2[(p\text{-}FC_6H_4)_3P]_2]SbF_6$), the precipitation of the protonated form of the base, and in the formation of 8 turnovers of cyclooctene/mol of **1a** after 24 h at 140 °C. Full activity required 1 equiv of Proton Sponge, but the presence of excess base partially inhibited the reaction.

We felt we could obtain a more convenient system by starting with a neutral complex. We first considered a formate complex $[IrH_2(\eta^2\text{-}O_2CH)L_2]$ because we thought this might lose CO_2 under the conditions of the reaction.[8] Unfortunately, the formate proved to be very labile, losing CO_2 near room temperature. CO_2 loss is probably reversible, however, because the complex could be isolated by treatment of **3** with NaOCHO under CO_2. Two turnovers of coe were formed with the formate complex as catalyst at 140 °C for 24 h.

In the course of this work, we found that formate ion reacts (25 °C, 1 h) with $[(cod)IrL_2]^+$ to give $[(cod)IrHL_2]$ and CO_2. Evidently formate acts as a selective, mild H^--equivalent reagent in this case. Other similar examples are known.[8]

The best catalyst was found through exploration of other carboxylates. Two synthetic routes proved useful. The first, which was most useful for arylphosphine complexes, involves treatment of **3** with the sodium salt of the carboxylic acid (eq 6) to give **4a** (L = $(p\text{-}FC_6H_4)_3P$, R = CF_3). On the other hand, the alkylphosphine species such as **4b** (L = $P(C_6H_{11})_3$, R = CF_3) were best prepared by eq 7. These species are analogous to the known complex $[IrH_2(\eta^2\text{-}O_2CCH_3)(PPh_3)_2]$,[9] which in our hands is catalytically inactive, however. The red intermediate $[Ir(cod)(\mu\text{-}OCOR)]_2$ shown in eq 7 is known for R = CH_3.[10]



(6)

Table I. Thermal Alkane Dehydrogenation with **4a**[a]

alkane	time, days	products (turnovers)	total turnovers
cyclopentane	2	cyclopentene (1.4)	1.4^b
cyclohexane	2	cyclohexene (3)	3
	14	cyclohexene (8)	8
methyl-cyclohexane	14	methylenecyclohexane (0.46)	
		1-methylcyclohexene (2.6)	
		3-methylcyclohexene (0.6)	
		4-methylcyclohexene (0.8)	4.46
cyclooctane	2	cyclooctene (9)	9
	5	cyclooctene (20)	20^c
	14	cyclooctene (34)	34
cyclooctane/cyclohexane	14	cyclooctene (17)	17
		cyclohexene (3)	3
n-hexane	14	1-hexene (0.2)	
		trans-2-hexene (2.83)	
		cis-2-hexene (0.92)	
		trans-3-hexene (0.7)	
		cis-3-hexene (0.4)	5.05^d

[a] Conditions: **4a** (7.1 mM), tbe (50 mol equiv) in the neat alkane at 150 °,c; see also the Experimental Section. [b] $ReH_7(P(p\text{-}FC_6H_4)_3)_2$ gives 1.1 turnovers after 30 min at 80 °C.[6a] [c] $IrH_5(P(p\text{-}FC_6H_4)_3)_2$ gives 30–35 turnovers after 5 days at 150 °C.[6b] [d] $IrH_5(P(i\text{-}Pr)_3)_2$ gives 9 turnovers after 30 min at 80 °C.[6d]

$$[Ir(cod)Cl]_2 \xrightarrow{AgOCOR} [Ir(cod)(\mu\text{-}OCOR)]_2 \xrightarrow[\text{ii) } H_2]{\text{i) } 4L} \underset{\mathbf{4}}{[IrH_2(OCOR)L_2]} \qquad (7)$$

Molecular weight determinations, together with IR and NMR spectral studies, confirmed that **4** has the structure shown in eq 6. In particular, the Ir–H protons appear as a triplet ($J_{PH} \sim 16$ Hz) at −28.5 to −33.5 ppm, appropriate[11a] for an Ir(III)–H trans to an O-donor ligand, and the IR shows bands at ca. 1450 and 1625 cm^{-1} as expected for this structure.[11b] While the carboxylates are chelating in **4**, it was anticipated that these ligands could open to the η^1 form, during the catalytic cycle. Evidence for this view is presented in a later section.

Catalytic Studies with 4. **4a** proved to be an effective catalyst for thermal alkane dehydrogenation. Thirty-four turnovers of coe were obtained from coa and tbe after 14 days of reaction in a glass vessel sealed with a Teflon stopcock (7.1 mM catalyst, 355 mM tbe, 150 °C).

Table I shows that alkanes other than coa can also be dehydrogenated. **2a** is therefore a generally applicable catalyst.

The identification and determination of the mixture of product alkenes in the presence of a large excess of the corresponding alkanes is a challenging problem for which we were able to develop a general solution. As described in detail elsewhere,[12] we brominated the alkenes with $[C_6H_5NH][Br_3]$ and then determined the resulting alkene dibromides by capillary GC.

All the possible linear hexenes were formed from *n*-hexane under these conditions. These alkenes could have been formed either by direct methods or by isomerization of an initial kinetic product mixture. Only in the first case would the product distribution give information about the site of attack. Subjecting 1-hexene in cyclohexane to the reaction conditions for 2 days gave a very similar product mixture to that shown in Table I (hexenes from *n*-hexane shown first, hexenes from 1-hexene in parentheses):

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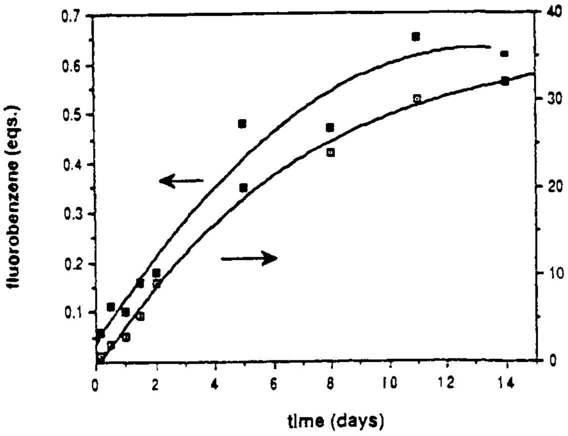


Figure 1. Time course study of the rate of production of fluorobenzene (solid points, left scale) in the deactivation of catalyst **4a** compared with the activity of the catalyst as measured by cyclooctene (coe) production from cyclooctane (squares dotted, right scale).

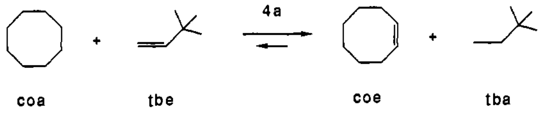
1, 4% (3%); trans-2, 56% (53.5%); cis-2, 18 (17.5%); trans-3, 14% (18.5%); cis-3, 8% (7.5%). In addition, the isomerization system also gave some cyclohexene (ca. 2 turnovers) from the dehydrogenation of the solvent cyclohexane. The results suggest that the product ratio observed in the thermal alkane dehydrogenation results from isomerization of an initial kinetic product. Similarly, 1-methylcyclohexene, the thermodynamically most stable alkene, is formed from the dehydrogenation of methylcyclohexane with our catalyst (Table I), probably also as a result of isomerization. ReH_7L_2[6a] gives mostly 2- and -methylcyclohexene, indicating preferential attack at the least hindered ring methylene groups. $IrH_5(P(i\text{-}Pr)_3)_2$[6c] also dehydrogenates methylcyclohexane, but at 150 °C after 65 h, isomerization is essentially complete and the thermodynamic ratio of alkenes has been attained. In contrast, the trifluoroacetate catalyst is a poor isomerization catalyst, and the product mixture is still far from the equilibrium ratio of alkenes even after 14 days at 150 °C. This suggests that the active species derived from the two catalysts are different.

The more efficient dehydrogenation of cyclooctane compared to the other substrates is probably a result of the transannular steric repulsions in coa, which are less severe in coe; the heat of hydrogenation of coe is therefore unusually low (ca. 23 kcal/mol). Cyclodecane is a good substrate for the same reason. Interestingly, cyclooctane is one of the poorest substrates for reaction with Cp*IrL.[3a] This is not unreasonable. We are not so much concerned with the initial rate of C–H oxidative addition as with the rate at which the intermediate alkyl hydride decomposes to alkene dihydride, which may well be the turnover limiting step of the catalytic system.

Any catalyst active enough to break alkane C–H bonds is usually sufficiently reactive to attack its own ligands and so lead to catalyst deactivation. This is a major problem for homogeneous catalytic alkane conversion in general and has led us to explore the possibility of avoiding the use of ligands altogether, as discussed below. Catalyst deactivation was evident from the formation of fluorobenzene in the hydrogenolysis of the P–C bonds of the $(p\text{-}FC_6H_4)_3P$ ligands, as detected in the alkene dehydrogenation products. The corresponding $(p\text{-}CH_3C_6H_4)_3P$ catalyst gave toluene under the same conditions. Figure 1 shows that the growth of the C_6H_5F over 14 days correlates with the fall-off in the rate of coe formation. This reaction is probably an important pathway for catalyst deactivation in general, and yet it may often be missed because the small amount of arene formed can easily escape detection in the product mixture. Garrou[13] has reviewed the area in detail. Direct oxidative addition of the P–C bond to the metal followed by reductive elimination of the resulting aryliridium species with a hydride is the likely mechanism.[14] Figure 1 suggests that 1 P–C cleavage per metal is sufficient to deactivate the system, so an "$L_2Ir_2(\mu\text{-}PR_2)$" species may be the metal-containing deactivation product. Fluorobenzene formation is much more rapid at higher catalyst concentration (0.9 equiv is formed after 2 days at a 71 mM catalyst concentration), so the reaction may be bimolecular. Felkin et al.[6] also found that yields of alkene were reduced upon raising the catalyst concentration and observed the formation of ArH from $ReH_7(PAr_3)_2$[6a] and of propane from $IrH_5(P(i\text{-}Pr)_3)_2$.[6e] The rate of both fluorobenzene and cyclooctene formation was essentially independent of the concentration in the range 0.35–2.1 M. Tbe therefore does not compete effectively with the neat alkane for binding to the metal and is probably not involved in the turnover limiting step. No alkane dehydrogenation takes place in the absence of tbe however. The observed product mixture is far from the thermodynamic equilibrium for eq 8, and so conversion is limited by catalyst deactivation.

Table II. Photochemical Alkane Dehydrogenation

alkene	co-reactant	time, days	products (turnovers)	total
cyclooctane	tbe	7	cyclooctene (12)	12
cyclooctane	tbe	14	cyclooctene (23)	23
cyclooctane	none	7	cyclooctene (8)	8
methylcyclohexane	tbe	7	methylenecyclohexane (2.77) 1-methylcyclohexene (2.19) 3-methylcyclohexene (0.85) 4-methylcyclohexene (1.26)	7.07
	none	7	methylenecyclohexane (1.6) 1-methylcyclohexene (3.84) 3-methylcyclohexene (0.32) 4-methylcyclohexene (0.82)	6.58
cyclohexane	tbe	7	cyclohexene (3.2)	3.2
cyclohexane	none	7	cyclohexene (3.9)	3.9
n-hexane	tbe	7	1-hexene (1.18) *trans*-2-hexene (2.48) *cis*-2-hexene (0.47) *trans*-3-hexene (0.52) *cis*-3-hexene (0.2)	4.85



(8)

We applied the usual Hg test[15] to check for homogeneity. The rate of reaction was unaffected, and this supports our view that the reaction is authentically homogeneous.

Changing the carboxylate ligand to acetate gave a catalytically inactive complex: neither alkene nor fluorobenzene was observed. Similar activity differences were observed in RCHO hydrogenation with $[RuX(O_2CR)(CO)(PPh_3)_2]$,[16] and the likely origin for the difference is the much higher tendency for CF_3CO_2 to open to the η^1 form, experimental evidence for which is presented below.

Changing the phosphine to $(p\text{-}CH_3C_6H_4)_3P$ led to an increased rate of P–C cleavage and decreased catalyst lifetime. $P(C_6H_{11})_3$ and $P(i\text{-}Pr)_3$ gave poor catalysts: only small yields of alkenes were observed.

Photochemical Alkane Dehydrogenation. We considered whether we could also dehydrogenate alkanes under photochemical conditions. If the role of the tbe in the thermal catalyst system is to remove the H_2 from the catalyst precursor and so prepare it for alkane oxidative addition, then irradiation might serve the same purpose. Stoichiometric photochemical alkane C–H activation is well-known,[3] and Shilov[17a] has observed stoichiometric formation of alkene complexes on irradiation of $PtCl_6^{2-}$ in the presence of alkane.

While the thermal catalyst **4a** proved inactive, **4b** did dehydrogenate alkanes catalytically under photochemical conditions. **3a** (7.7 mM) and tbe (385 mM) in cyclooctane gave 12 turnovers

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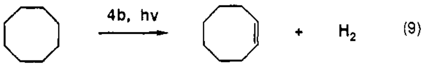
of coe after 7 days at 25 °C (8-W low-pressure Hg lamp, quartz vessel). The 254-nm line appears to be responsible for the photochemistry, because a Pyrex filter stopped the reaction. Table II summarizes the results. This was the first example of the transition-metal-mediated photochemical functionalization of an alkane (eq 9).[5] Hill[17b] has recently reported a photochemical polyoxometalate system that gives amides, ketones, and alkanes.



(9)

coa coe

The products from methylcyclohexane are decidely different from the thermodynamic mixture of alkenes obtained in the thermal system. To test the isomerization activity of the photochemical system, methylenecyclohexane (12 mol equiv) was subjected to the reaction conditions and gave only 25% conversion to 1-methylcyclohexene, suggesting that only about half of the 1-methylcyclohexene shown in Table II may have come from isomerization. Methylenecyclohexane is therefore the preferred kinetic product in this system, as is seen for $IrH_5(P(i\text{-}Pr)_3)_2$.[6c] The preferential attack at the 1° C–H bonds seen in these systems argues in favor of an oxidative addition pathway and compares with the similar results of Bergman,[3a] Graham,[3b] Jones,[3c] and their collaborators for stoichiometric oxidative addition of alkane C–H bonds to Ir, Rh, and Re species. A radical or carbonium ion mechanism would have shown a preference for 3° C–H activation. In contrast, the transition state for oxidative addition is very sensitive to steric effects.[3,6,18] This, together with the isolation of an oxidative addition product from benzene, discussed below, makes it difficult to avoid the conclusion that alkane C–H oxidative addition is involved in these systems. By extrapolation, the same mechanism is likely both in our original work[4b,c] and in the Felkin[6] systems.

Such a photochemical system does not necessarily require a hydrogen acceptor because the 254-nm quantum carries 112 kcal/einstein, enough to easily overcome the heat of hydrogenation of any alkane. We were pleased to find experimentally that the rate and extent of alkane dehydrogenation were essentially unchanged in the presence or absence of tbe. As can be seen from the table, isomerization of the product alkene is more extensive in the absence of tbe. 1-Methylcyclohexene is now the major product from methylcyclohexane, for example.

Even in the presence of tbe, the tbe does not act as hydrogen acceptor for all the H_2 removed from the alkane. For example, **4b** and tbe (4 mol equiv) in C_6D_{12} gave 3 turnovers of C_6D_{10} after 7 days but only 1.2 turnovers of tbe were formed. We conclude that some free H_2 is formed even in the presence of tbe. No reaction took place between **4b** and tbe in the absence of 254-nm light.

The H_2 formed in these photochemical systems were detected by passing the gases evolved into a solution of $[Ir(cod)L_2]SbF_6$ in acetone-d_6 at 0 °C; $[IrH_2(Me_2CO\text{-}d_6)_2L_2]SbF_6$ was produced quantitatively and detected by ^1H NMR.

The photochemical system degrades very slowly with time. The rate of alkene production is essentially linear (e.g., 12 turnovers of coe are formed from coa after 7 days, 23 turnovers after 14 days), and 70% of the catalyst can be recovered after 7 days. The system is therefore much more resistant to P–C cleavage than was the thermal one, although it is not yet clear whether this is because it is photochemical or because $P(C_6H_{11})_3$ may be inherently more P–C cleavage resistant than PAr_3; the latter is expected to be the case from Hoffmann's arguments.[14]

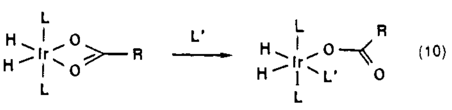
With C_6D_{12} as substrate, the ^2H NMR of the recovered catalyst **4b** showed deuteriation of the Ir–H groups as well as of the cyclohexyl rings, indicating reversible cyclometalation of this ligand. The degree of deuterium incorporation was greater in the absence of tbe, consistent with the stabilizing coordinatively unsaturated intermediates.

Once again, the system is homogeneous by the Hg test. During these experiments, mercury-photosensitized alkane coupling also occurred.[19] In following up this result, some interesting new mercury-sensitized alkane functionalization reactions were discovered.[20] These are of practical interest, because multigram quantities of alcohols, ethers, aldehydes, and silanes are obtained in this way from any of a wide variety of alkanes.

The electronic absorbtion spectrum of **4b** shows three bands, one at 344 nm (ϵ = 650 L/cm·mol), one at 264 nm (ϵ = 5740), and the third at 225 nm (ϵ = 12 040), of which the 264-nm band is probably responsible for the photochemistry. A Pyrex filter was sufficient to prevent alkene formation, so the 344-nm band is inactive. The photochemically inactive complex **4a** has two UV–visible absorbtion bands, one at 332 nm (ϵ = 610) and the other at 249 nm (ϵ = 23 100). The latter may be a ligand transition (cf. $P(p\text{-}C_6H_4F)_3P$: 252 nm (ϵ = 23 000)), and this may account for the lack of photochemical activity: the energy is dissipated in the ligands when the phosphine is aromatic.

Some Chemistry of 4 Related to the Mechanism of Alkane Dehydrogenation. A plausible first step in the thermal alkane reactions is binding of tbe to **4a** followed by transfer of the hydride ligands to the olefin to give tba and a reactive metal fragment. We find that reaction of complexes of type **4** in an NMR tube with a variety of ligands shows the greater tendency of the trifluoroacetate group to adopt an η^1 form. While CO opens the chelate ring in both acetate and trifluoroacetate complexes, the weaker ligand MeCN gives an adduct only with the trifluoroacetate **4a**. In the case of **4b** the product seems instead to be $[IrH_2(MeCN)_2[P(C_6H_{11})_3]_2]O_2CCF_3$. Only the trifluoroacetates were found to be active in alkane dehydrogenation, and we imagine that this is due to their greater tendency to open the η^1 form. Table III lists the NMR and IR data for these adducts.

Adding olefins, including tbe, to **4a** allowed the proposed equilibrium (eq 10) to be observed directly at low temperature. Table IV lists the ^1H NMR data for these species as well as the values of K_{eq} for eq 10. Of particular interest is the observation that tbe is one of the poorest ligands studied.



(10)

(L' = alkenes, CO, MeCN)

This is no doubt a reflection of the steric bulk of the *t*-Bu group. A low K_{eq} is a valuable property for a hydrogen acceptor because we do not want the alkene to exclude the alkane from the metal by strong binding. Cyclooctene is a very effective ligand, but it is not hydrogenated by the system. Cyclopentene and cyclodecene are very poor ligands, possibly because of steric congestion in the complexes. $Me_3SiCH{=}CH_2$ is much less hindered and so is expected to bind better than the carbon analogue. Steric effects alone do not explain why this ligand is so much better than 1-hexene, so it may be that the electrophilic metal prefers a more strongly electron releasing alkene. Others have reported K_{eq} values for the reaction of alkenes with various metal complexes, but tbe and $Me_3SiCH{=}CH_2$ were not studied.[21]

Free and bound tbe gave distinct resonances at −80 °C but coalescence took place at ca. −20 °C. By 25 °C, hydrogenation took place slowly, and the hydride peaks of **4a** disappeared over 15 h (1 equiv of tbe) or 1 h (10 equiv of tbe). The acetate, in contrast, did not react with tbe over 5 days, which is probably the reason that this complex is not catalytically active for alkane dehydrogenation.

In the presence of 10 equiv of tbe, an apparent intermediate in the dehydrogenation of **4a** was detected by ^1H NMR. This intermediate grows until it constitutes ca. 95% of the reaction

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Table III. IR and NMR Data for the Adducts of **4** with Various Ligands, L

compound[a]	L	IR[b]	^{1}H NMR	^{31}P NMR[d]
$IrH_2(O_2CCF_3)(PAr_3)_2$ (**4a**)	CO	2099[e] 2008[e] 1680[f]	−21.6, dt (4.4,[h] 14.6[j]), IrH −7.32, dt (4.4,[h] 18.2[j]), IrH 7.15, 7.52, c, Ar	+9.25
$IrH_2(O_2CCF_3)(PCy_3)_2$ (**4b**)	CO	2090[e] 1978[e] 1683[f] 1444[g]	−24.4, dt (5.5,[h] 13.2[j]), IrH −7.93, dt (5.5,[h] 18.2[j]), IrH 1.6–1.9, c, Cy	+28.1
$IrH_2(O_2CCH_3)(PAr_3)_2$	CO	2093[e] 1996[e] 1603[f] 1444[g]	−20.6, dt (5.5,[h] 15.2[j]), IrH −7.93, dt (5.5,[h] 18.8[j]), IrH 1.28, s, OAc 7.15, 7.52, c, Ar	+9.6
$IrH_2(O_2CCH_3)(PCy_3)_2$	CO	2076[e] 1970[e] 1602[f] 1369[g]	−23.4, dt (5.5,[h] 14[j]), IrH −7.93, dt (5.5[h], 18.2[j]), IrH 1.3–1.9, c, OAc & Cy	+25.5
$IrH_2(O_2CCF_3)(PAr_3)_2$ (**4a**)	MeCN	2184[k] 1682[f]	−25.7, dt (6.9,[h] 16.6[j]), IrH −20.1, dt (6.9,[h] 17.1[j]), IrH 1.64, s, MeCN 7.1, 7.6, c, Ar	+17.2

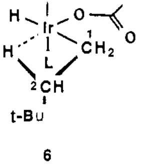
[a] Ar = *p*-FC_6H_5, Cy = cyclohexyl. [b] In CD_2Cl_2. [c] In CD_2Cl_2, reported as position (δ), multiplicity (coupling constant, hertz), assignment. [d] In CD_2Cl_2, relative to external 85% H_3PO_4. [e] ν(Ir–H) or ν(CO). [f] ν(CO) symmetric. [g] ν(CO) asymmetric. [h] $^{2}J_{HH'}$. [j] $^{2}J_{PH}$ cis. [k] ν(C–N).

Table IV. ^{1}H NMR and Equilibrium Data for Alkene Complexes of **4a**

		^{1}H NMR[b]	
alkene	K_{eq}[a]	Ir–H	coordinated vinyl
PhCMe=CH_2	~0	no complex observed	
t-BuCH=CH_2	0.58	−27.74, br t (16) −10.8, br t (20.6)	3.16, t, (12) 3.47, d (8.5) 4.66, dd (8.5, 12)
cyclopentene	1.9	−28.75, dt (6, 13.7) −11.1, dt (6, 19.8)	4.2, br
cyclodecene	2.3	−27.25, br −12.95 br t (23)	4.2, br
EtOCH=CH_2	6.3	−24.3, br t (13) −10.8, br t (16)	2.33, 2.98, 3.56, br
n-BuCH=CH_2	17	−27.75, dt (6, 16) −10.7, dt (6, 19)	3.1, br d (8) 3.4, br d (13) 4.3, br dd (8, 13)
PhCH=CH_2	32	−27.3, br −9.94, dt (6, 19)	3.6, 3.7, br 4.65 br t (11)
Me_3SiCH=CH_2	1250	−28.2, br t (13) −11.1, dt (6, 19.8)	[−0.59, s, $SiMe_3$] 3.17, 3.5, 3.56, br
cyclooctene	5500	−27.85, dt (6, 17.5) −10.9, dt (6, 19)	3.45, br
CH_2=CH_2	large	−26.45, dt (6, 16) −8.4, dt (6, 17)	3.15, br
norbornene	large	−27.5 dt (7.5, 16) −9.6, dt (7.5, 17.5)	3.55, br

[a] In CD_2Cl_2 at −80 °C (L mol^{-1}). [b] Reported as in Table III.

products after 1 h and it shows a hydride resonance at −28.7 ppm (J_{PH} = 16 Hz) and a new *t*-Bu group at 0.52 ppm. It also shows a doublet at +18 ppm in the selective ^{1}H-decoupled ^{31}P NMR, which is consistent with it being a monohydride. The ^{13}C NMR shows new resonances coupled to phosphorus at +95.4 ppm (J_{PC} = 8.2 Hz) for C(1) and +139.0 ppm ($J_{PC} \approx$ 1 Hz) for C(2). These rather "vinylic" positions suggest that the intermediate is probably an agostic[22] alkyl hydride, e.g., **6**, broadly related to the known species **7**.[18] Analogous intermediates are not observed in the case



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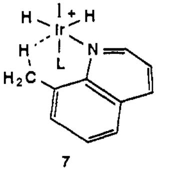

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of any of the other alkenes, but Halpern[23a] has seen a distantly related Rh complex. After several hours, **6** decomposes to give free tba and two new species **8** and **9** are formed. The ^{31}P NMR of **8** shows mutually coupled resonances at +17.1 and −44.3 ppm. The latter is appropriate for a cyclometalated ring, and the large $J_{PP'}$ of 368 Hz is appropriate for a trans arrangement of phosphines. ^{1}H NMR shows a doublet of doublets at −27.6 ppm, and irradiation of either the +17.1 or the −44.3 ppm lines in the ^{31}P spectrum led to collapse of the Ir–*H* peak to a simple doublet, confirming the orthometalated structure for **8**. **9** was characterized as the Ph–H oxidative addition product with the solvent C_6D_6 because it was obtained in a pure form after recrystallization. This supports our view that the first step in the reaction of an alkane with the catalyst is oxidative addition. Up to now, no C–H oxidative addition product has been observed in an alkane conversion catalyst, although Baker and Field[23b] have observed the photochemical decomposition of a pentane-derived complex, $(dmpe)_2Fe$(1-pentyl)H, to give 1-pentene stoichiometrically.

We were able to determine k_H/k_D for the (thermal) oxidation addition of benzene by monitoring the reaction between **4a** and benzene by ^{31}P NMR. The resulting value of 4.5 (±0.1) is normal and higher than the values of 1.4 obtained by Feher and Jones[3c] for the oxidative addition of Ph–H to Cp*Rh(PMe_3) and of 1.38 obtained by Bergman et al.[3a] for cyclohexane and Cp*Ir(PMe_3). Our intermediate is probably much less reactive than Cp*IrL.

The final picture that emerges from this study is shown in Figure 2. Tbe reacts with **4a** to give first **5** and then **6**. Reductive elimination from **6** takes place presumably to give the very reactive $IrL_2(\eta^1\text{-}OCOCF_3)$. This is capable of oxidatively adding C–H bonds as shown by its subsequent conversion to **8** and then (in the presence of C_6H_6) **9**. Of course, in the presence of alkane, the products would be **8** and the corresponding "alkyl hydride" **10**, which can follow the sequence shown in Figure 2 to generate alkene from the alkane. Analogy with **6** suggests that the alkyl hydride **10** may in fact be agostic, and this would increase its thermodynamic stability with respect to the free alkane and so perhaps lower the transition-state energy both for the formation reaction and for its β-elimination to give alkene. A key feature of the system, which allows catalysis to proceed, is the facile opening of the trifluoroacetate chelate ring. This allows the alkane-derived alkyl hydride complex to become coordinatively unsaturated so that it can β-eliminate.

k_H/k_D for thermal cyclohexane dehydrogenation by **4a** was 4.4 (±0.1), although interpretation of this result is not straightforward in a catalytic system in which several steps involving C–H and M–H bonds may have comparable transition-state energies.

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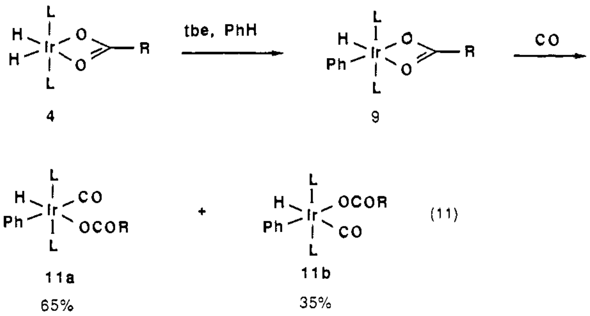
Values for the photochemical system (**4b**, cyclohexane) were 5.1 (±0.1) (in the presence of tbe, 50 mol equiv) and 7.7 (±0.1) (in the absence of tbe). Crossover was *not* observed (<3%) in the alkenes from C_6H_{12}/C_6D_{12} mixture (by GC/MS of the final alkene dibromides), again consistent with the mechanism proposed. Since D_2 exchanges readily with the Ir–H groups of **4a**, the lack of crossover suggests that **4** does not liberate free H_2 or D_2. The observations are consistent, with the elements of H_2 or D_2 being transferred to tbe by a hydrogenation reaction.

The exact nature of the reactive species is unknown; we have suggested the $Ir(\eta^1\text{-}OCOCF_3)L_2$ form because $[Ir(\eta^2\text{-}O_2CCF_3)L_2]$ might be expected to be a relatively unreactive square-planar Ir(I) species. In the PCy_3 case, two L groups might not easily be able to become cis. In spite of many attempts, we have not been able to synthesize $[Ir(\eta^2\text{-}O_2CCF_3)L_2]$ by the standard methods; the Rh analogue has been reported, however.[24]

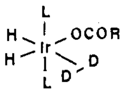
The fact that the rates of dehydrogenation (Table II) correlate with the stability of the product alkene suggests that the rate-determining step may be β-elimination from the intermediate alkyl hydride and not C–H activation, which is known[3a] to be slower for cyclooctane than hexane, at least for $Cp^*Ir(PMe_3)$.

Reactions of 9. In the hope of functionalizing benzene, we treated **9** with CO at room temperature. A mixture of the two carbonyls shown in eq 11 was formed. Interestingly, **11a** is the major product even though the phenyl group is normally considered to have a lower trans effect than H.[25] These gave no benzaldehyde on heating under CO.



The reacrtion of I_2 with **9** gave only C_6H_6 like Janowicz and Bergman[3a] saw for $Cp^*Ir(PMe_3)(Ph)(H)$.

D_2 reacts rapidly with **4a** to give **4a**-*d* and then **4a**-d_2. The most reasonable mechanism would involve the dihydrogen dihydride **12** analogous to known species that are known to undergo exchange



12

rapidly.[26] In support of this mechanism, the hydride triplet of **4a** broadens in the presence of H_2 and sharpens with an N_2 purge. Furthermore, **4a**, **4a**-*d*, and **4a**-d_2 have distinct ^{31}P resonances, with an isotope shift of −0.127 ppm per bound D.

9 loses arene on heating with first-order kinetics at 65 (±2) °C ($k = 1.1\ (\pm 0.1) \times 10^{-4}\ s^{-1}$) to give an equilibrium mixture of **9** and the orthometalated species **8**. A typical plot is shown in Figure 3. Expressing the concentrations in terms of mole fractions leads to a K_{eq} of 3.64 (±0.05) in favor of the phenyl hydride ($\Delta G^\circ = -0.87$ kcal/mol). Jones and Feher[3c] have found that benzene is lost from $Cp^*Rh(PMe_3)(Ph)(H)$ with a rate of $1.06 \times 10^{-4}\ s^{-1}$ at 60 °C and that an equilibrium between the oxidative addition product and the cyclometalated form is found for $Cp^*Rh(PMe_2CH_2Ph)(Ph)(H)$ but that the cyclometalated form is favored, as is reasonable for the more stable 5-membered ring formed in the Rh case. The phenyl hydride, d^0 **9**, gives >95% d^0 C_6H_6 on treatment with D_2. This may be a ligand-induced reductive elimination but must be very rapid to avoid substnatial D incorporation.

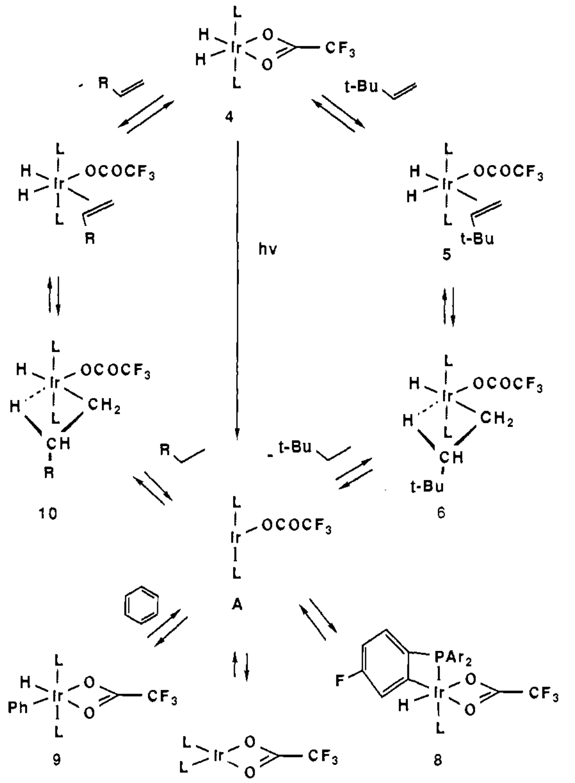


Figure 2. Proposed mechanism for the catalytic thermal dehydrogenation of alkanes with **4a**. In the photochemical reaction, the catalyst is the closely related complex **4b** and the proposed cycle is very similar except that irradiation expels H_2 from **4b** to give the reactive intermediate **A**, for which the structure shown here is speculative.

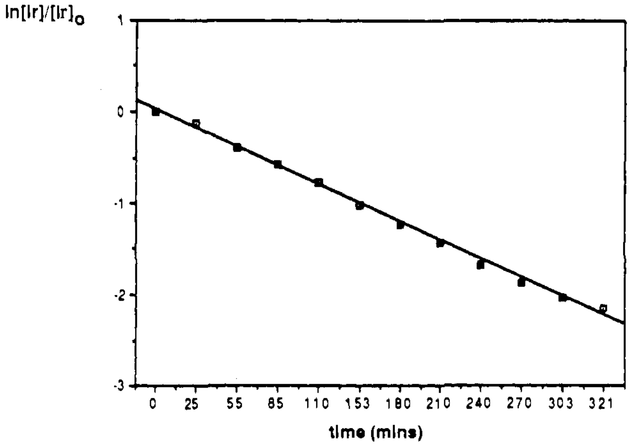


Figure 3. Typical rate plot for the reductive elimination of benzene from **9**.

In the past, cyclometalation has been viewed (at least by ourselves) as an obstacle to alkane C–H activation. We now see that cyclometalation is compatible with alkane C–H activation, as long as it is reversible. P–C cleavage in the phosphine, however, remains an irreversible deactivation reaction.

Experimental Section

Syntheses were performed under purified N_2 or Ar by standard Schlenk techniques. NMR spectra were obtained on Bruker WM500, HX490, and WM250 or a JEOL FX90Q instrument and IR spectra on a Nicolet 5-SX FT-IR. Photolyses were carried out in a Rayonet Series

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RMR-500 photochemical reactor with four 8-W 254-nm lamps. Reagents were obtained from Strem Chemical Co. and Aldrich Chemical Co. Solvents were dried and purified by standard techniques.

Purification of Alkanes.[27] The alkanes were stirred over successive portions of concentrated H_2SO_4 until no further coloration developed in the acid layer. The alkane was separated, washed with H_2O and then four times with saturated $NaHCO_3$, then dried over anhydrous $MgSO_4$, and passed through a column of neutral Al_2O_3. Spinning-band distillation gives a pure and rigorously alkene-free product.

Dihydridobis(acetone)bis[tris(*p*-fluorophenyl)phosphine]iridium(III) Hexafluoroantimonate (3). $[Ir(cod)\{(p\text{-}FC_6H_4)_3P\}_2](SbF_6)$[4] (0.50 g, 0.43 mmol) in acetone (7 mL) was cooled to 0 °C. The solution was then vigorously stirred under H_2 (1 atm) for 30 min. With a maintained hydrogen atmosphere, the complex **1a** was precipitated as a cream-colored solid by the addition of Et_2O (70 mL) and pentane (20 mL). After the solid was filtered and washed with pentane (3 × 5 mL), it was dissolved in CH_2Cl_2/acetone (5 mL/0.5 mL) and the resultant mixture stirred under H_2 for 5 min. Precipitation with Et_2O/pentane (30 mL/15 mL) afforded **3** as a flocculant white solid, 418 mg (90%). Anal. Calcd for $C_{42}H_{38}O_2P_2F_{12}SbIr$: C, 42.80; H, 3.22. Found: C, 42.78; H, 3.05. ^1H NMR (acetone-d_6): δ −27.6 (t, J_{PH} = 16 Hz, Ir–H), 1.86 (s, acetone), 7.28 (t, phenyl ortho to F), 7.61 (c, phenyl ortho to P). The analogous tri-*p*-tolylphosphine complex was prepared in a similar manner. ^1H NMR (acetone-d_6): δ −27.9 (t, 16.0 Hz, Ir–H), 1.78 (s, acetone), 2.39 (s, *p-Me*Ar), 7.29–7.35 (c, phenyl). Anal. Calcd for $C_{48}H_{56}P_2O_2F_6SbIr$: C, 49.94; H, 4.85. Found: C, 50.20; H, 4.80.

Dihydrido(η^2-trifluoroacetato)bis[tris(*p*-fluorophenyl)phosphine]iridium(III) (4a). To $[IrH_2(acetone)_2\{(p\text{-}FC_6H_4)_3P\}_2](SbF_6)$ (**3**; 0.4 g, 0.34 mmol) in dry THF (10 mL) was added NaO_2CCF_3 (0.231 g, 1.7 mmol), and the mixture was stirred for 2 h. After the solvent was removed in vacuo, the residue was taken up in C_6H_6 (10 mL) and the solution filtered through dry Celite to remove the insoluble inorganic salts. The colorless benzene filtrate was then concentrated to ca. 2 mL, and heptane (8 mL) was added to precipitate **4a** as a colorless solid (0.24 g, 75%), which was recrystallized from benzene/heptane[28] or CH_2Cl_2/heptane (2 mL/8 mL). Generally, precipitation of **4a** was facilitated by concentrating the solution to ca. 5 mL following the addition of heptane. The product **4a** was filtered, washed with cold heptane (−20 °C, 2 × 2 mL), and dried in vacuo. IR: 1647 and 1610 cm^{-1} (s, ν_{as}). ^1H NMR: δ −30.3 (t, 16.6 Hz, Ir–H), 6.74 and 7.10 (c, Ar). ^{31}P NMR: δ +22.1. Anal. Calcd for $C_{38}H_{26}H_9O_2P_2Ir$: C, 48.56; H, 2.79. Found: C, 48.58; H, 3.21. The compound was monomeric by vapor pressure lowering measurements in CH_2Cl_2 (MW Calcd 939, found 900 ± 50).

The dideuteride **4a**-d_2 was prepared as follows. A C_6H_6 (5 mL) solution of **4a** (0.2 g, 0.21 mmol) was stirred under D_2 (1 atm) for 20 min. The solvent was then removed in vacuo to give **4a**-d_2 in quantitative yield. This complex was recrystallized as described for **4a**. ^2H NMR (C_6H_6): δ −30.1 (Ir–D). We were not able to obtain MS data, owing to decomposition.

Analogous Complexes. The analogous acetato complex was prepared in a manner identical with that described above for **4a** except that the corresponding quantity of NaO_2CCH_3 was used in the place of sodium trifluoroacetate. The isolated yield of product was 0.25 g (82%). Anal. Calcd for $C_{39.75}H_{33}F_9O_2P_2Ir$: C, 52.41; H, 3.65. Found: C, 52.04; H, 3.44. Heptane (0.25 mol/mol of **2b**) was observed by ^1H NMR. IR: 1528 and 1452 cm^{-1} (s, ν_{as} and ν_s). ^1H NMR: δ −28.6 (t, 16 Hz, Ir–H), 1.09 (s, CH_3), 6.76 and 7.52 (c, Ar).

$[IrH_2\{(p\text{-}MeC_6H_4)_3P\}_2(\eta^2\text{-}O_2CCF_3)]$ was prepared by a procedure identical with that described above for **4a** except that a corresponding amount of $[IrH_2(acetone)_2[(p\text{-}MeC_6H_4)_3P]_2](SbF_6)$ was used as the starting iridium complex, 0.23 g (75%). ^1H NMR: δ, −30.14 (t, 16 Hz, Ir–H), 1.99 (s, Ar*Me*), 6.98 and 7.71 (c, Ar).

Dihydrido(η^2-trifluoroacetato)bis(tricyclohexylphosphine)iridium(III). A mixture of $[Ir(cod)Cl]_2$ (0.30 g, 0.45 mmol) and AgO_2CCF_3 (0.31 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 concentrated to ca. 10 mL, and PCy_3 (0.50 g, 1.8 mmol) was then added. After the resulting orange solution was stirred for 5 min, it was vigorously stirred under H_2 (1 atm) for 1 h during which time the solution turned colorless. The addition of heptane (10 mL) precipitated **4b** as a white solid, which was filtered, washed with heptane (2 × 3 mL), and dried in vacuo; yield 0.66 g (84%). The compound can be recrystallized from CH_2Cl_2/heptane or benzene/heptane.[28] Anal. Calcd for $C_{38}H_{68}F_3O_2P_2Ir$: C, 52.57; H, 7.89; F, 6.57. Found: C, 52.74; H, 7.60; F, 6.63. ^1H NMR: δ −33.3 (t, 14.8 Hz, Ir–H), 1.25–2.1 (c, Cy). ^{31}P NMR: δ +32.6. IR: 1619 and 1440 cm^{-1} (ν_{as} and ν_s).

Hydridophenyl(η^2-trifluoroacetato)bis[tris(*p*-fluorophenyl)phosphine]iridium(III) (9). $[IrH_2[(p\text{-}FC_6H_4)_3P]_2(\eta^2\text{-}O_2CCF_3)]$ (**4a**; 0.50 g, 0.53 mmol) and 3,3-dimethyl-1-butene (tbe; 0.20 mL, 1.6 mmol) were heated in C_6H_6 (7 mL) to 65 °C for 3 h. After the solution was cooled, heptane (10 mL) was added, and the solution was concentrated to ca. 5 mL during which time the product precipitated as a colorless solid, which was then filtered, washed with cold heptane (−20 °C, 2 × 2 mL), and dried in vacuo; yield 0.382 g (71%). This compound is recrystallized from a warm benzene/heptane (65 °C, 2 mL/6 mL) solution cooled to 4 °C. ^1H NMR (CD_2Cl_2): δ −28.9 (t, 16.0 Hz, Ir–H), 6.19 (dd, J_{HH} = 7.75 Hz, *m*-H of Ph), 6.34 (t, 7.2 Hz, *p*-H), 6.60 (br d, 8.75 Hz, *o*-H), 7.02 (t, phosphine to F), 7.35 (m, phosphine ortho to P). $^1H\{^{31}P\}$ NMR (C_6D_6): δ +17.15. IR (CD_2Cl_2): 1682 and 1639 cm^{-1} ($\nu_{as}(CO_2)$). Anal. Calcd for $C_{44}H_{30}F_9O_2P_2Ir\cdot{}^1/_8C_6H_6$: C, 52.91; H, 3.05. Found: C, 52.88; H, 3.27. The benzene of crystallization was observed and quantified ($^1/_8$ mol of C_6H_6/mol of **9**) by ^1H NMR.

The deuterio analogue $[Ir(C_6D_5)(D)[(p\text{-}FC_6H_4)_3P]_2(\eta^2\text{-}O_2CCF_3)]$ (**9**-d_6) was prepared in an analogous manner at 50 °C for 2 h with C_6D_6 as solvent. ^2H NMR (C_6H_6): δ −28.7 (br, Ir–D), 6.24, 6.37, and 6.81 (br, Ir–C_6D_5). $^1H\{^{31}P\}$ NMR (C_6D_6): δ +17.29. The initial rates of formation of **9** and **9**-d_6 in a competitive experiment were determined by ^{31}P NMR at 25 °C (202.1 MHz) and gave k_H/k_D = 4.5. The kinetics of the reductive elimination from **9** were determined by ^1H NMR in C_6D_6 at 65 °C over 3 half-lives.

The cyclometalated species, **8** was never obtained as a solid in a pure state but was identified from its spectral properties. ^1H NMR (CD_2Cl_2): δ −27.6 (dd, J_{HP} = 20, 15 Hz), 6–7.5 (c, Ar). ^{31}P NMR (CH_2Cl_2): δ +17.1 and −44.3 (d, $J_{PP'}$ = 368 Hz).

Thermal Alkane Dehydrogenations. All thermal alkane dehydrogenation reactions were performed in resealable glass vessels (capacity 10–15 mL) equipped with Kontes or Ace glass Teflon stopcocks and made of triple-thickness Pyrex glass. The reaction mixtures were stirred with small Teflon-coated stirbars. Temperatures were maintained to within ±2 °C with a fully equilibrated GE silicone oil bath.

(i) Proton Sponge Reactions. In a typical experiment, the reactor was charged with $[IrH_2(acetone)_2[(p\text{-}FC_6H_4)_3P]_2](SbF_6)$ (**3**; 20.0 mg, 0.017 mmol), tbe (0.11 mL, 8.5 mmol), 1,8-bis(dimethylamino)naphthalene (4.0 mg, 0.0187 mmol), and degassed cyclooctane (2 mL). The solution was degassed with three freeze–pump–thaw cycles, and the reactor was heated to 150 °C for 24 h and then cooled to room temperature. The orange-yellow solution was then distilled in vacuo, and the volatiles were analyzed as described in ref 12. The involatile products were analyzed spectroscopically.

(ii) Reactions Involving 4. In a typical procedure, $[IrH_2[(p\text{-}FC_6H_4)_3P]_2(\eta^2\text{-}O_2CCF_3)]$ (**4a**; 10.0 mg, 0.0106 mmol), the (0.07 mL, 0.53 mmol), and degassed cyclooctane (1.5 mL) were placed in the reactor, and the solution was degassed as above. The highest activities were obtained when the reactor was filled with an Ar atmosphere prior to heating. The reaction was then run, and the products were analyzed as above. A homogeneous yellow solution formed after 5 min and persisted throughout.

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

Photochemical Alkane Dehydrogenations. All photochemical experiments were carried out in quartz glass Schlenk tubes (capacity 20–50 mL) equipped with high vacuum Teflon stopcocks. The reactions were stirred with small Teflon-coated stirbars. The photolyses were performed at 25 °C (air cooling) by a Rayonet Series photoreaction with four 254-nm (or 350-nm) UV lamps.

In a typical run, $[IrH_2(PCy_3)_2(\eta^2\text{-}O_2CCF_3)]$ (**4b**; 10.0 mg, 0.0115 mmol) and degassed cyclooctane (1.5 mL) were placed in the reactor and degassed as before, and the reactor was filled with Ar. After 7 days of photolysis at 254 nm, the resulting colorless homogeneous solution was distilled, and the volatiles were analyzed as above. The involatile organometallic fraction was analyzed spectroscopically and was found to consist largely (up to 70%) of starting complex **4b**.

Detection of H_2. After a typical photolysis reaction was performed as above, the evolved fractions were passed into a vessel containing $[Ir(cod)(PPh_3)_2](SbF_6)$ (20.0 mg, 0.0188 mmol) in acetone-d_6 (1 mL) at 0 °C over 1 h with a stream of argon. After the solution was stirred for 1 h, it turned colorless, and formation of $[IrH_2(acetone\text{-}d_6)_2(PPh_3)_2](SbF_6)$ and coa was observed by ^1H NMR. The amount found was equivalent to 4.90 mol of H_2/mol of **4b** and corresponded to the ca. 5 mol of alkene formed.

NMR Observation of Substitution Products from 4. (i) With CO. $[IrH_2[(p\text{-}FC_6H_4)_3P]_2(\eta^2\text{-}O_2CCF_3)]$ (**4a**; 20.0 mg, 0.021 mmol) was placed in an NMR tube under Ar. Degassed C_6D_6 (or CD_2Cl_2) (0.5 mL) was

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[27] We thank H. Felkin for communicating his finding that alkenes are produced by pyrolysis of an as yet unidentified species present after the H_2SO_4 treatment, unless removed by Al_2O_3 before distillation.

[28] All compounds needed for alkane activation were recrystallized for benzene/heptane to ensure no halocarbons were present in the sample.

then added, CO (1 atm) was bubbled through the solution for 5 min, and the resulting solution was analyzed by ^1H and ^{31}P NMR and IR spectroscopy as shown in Table III.

(ii) **With PMe_3.** To a solution of **4a** as above was added PMe_3 (2.16 μL, 0.021 mmol). Quantitative conversion to the PMe_3 adduct was observed.

(iii) **With MeCN.** To **4a** (40.0 mg, 0.042 mmol) in C_6D_6 (0.5 mL) in an NMR tube was added MeCN (2.2 μL, 0.042 mmol). Quantitative conversion to the MeCN adduct was observed.

(iv) **With Alkenes.** Low-temperature ^1H NMR experiments were carried out on a Bruker WM 250 (250-MHz) instrument with a probe precooled to 193 K (−80 °C). The temperature was maintained to within ±1 °C. In a typical experiment, $[IrH_2[(p\text{-}FC_6H_4)_3P]_2(\eta^2\text{-}O_2CCF_3)]$ (**4a**; 12.2 mg, 0.013 mmol) dissolved in CD_2Cl_2 at −80 °C (0.5 mL) was placed in an NMR tube under Ar, and *tert*-butylethylene (8.3 μL, 0.065 mmol) was then added at −80 °C. The ^1H NMR data indicated that an equilibrium between **4a** and the tbe adduct **5** had been established (Table IV). K_{eq} was determined by integration, or for more strongly binding olefins, which gave ≈100% of **5**, the equilibrium between cyclooctene and the olefin was studied.

(v) **With D_2.** To a solution of **4a** as in i above was added D_2. Early in the conversion, the mixed species $[IrHD(O_2CCF_3)L_2]$ was observed, but the final product was **4a**-d_2 (^1H, ^2H, and ^{31}P NMR; see text).

NMR Observation of Reactions of 9. (i) **With CO.** CO (1 atm) was bubbled through a solution of **9** (15 mg, 0.015 mmol) in CD_2Cl_2 (0.5 mL) to give **11a** and **11b**. ^1H NMR (resonances for **11a** given first; **11a**:**11b** intensity ratio 2:1): δ −20.15 (t, 14.5 Hz), −6.03 (t, 16 Hz), 7.02 and 7.14 (t, aryl CH ortho to F), 7.31 and 7.51 (c, aryl CH ortho to P). IR: 2038 and 2012 cm^{-1} (s, CO).

(ii) **With I_2.** Free C_6H_6 was observed when excess I_2 was added to a solution of **9** identical with that used above. The organometallic products were not characterized.

(iii) **With H_2 and D_2.** A solution of **9** as above was treated with H_2 (1 atm, 5 min), and free C_6H_6 was observed in the ^1H NMR. When D_2 was used, the C_6H_6 formed contained no D (GC/MS).

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Relative Reactivities and Mechanistic Aspects of the Reactions of Organic Halides with Alkali Metals in Alcohol Environments

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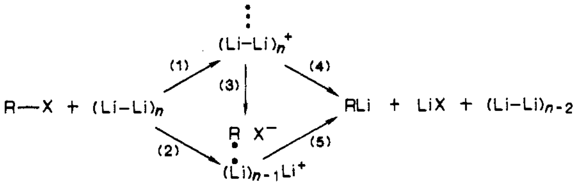
Abstract: The relative reactivities of organic halides over wide concentration ranges have been determined with limited amounts of lithium, sodium, and potassium in 2-ethoxyethanol (**1**) at 0 °C. Under these conditions the organometallics formed protonate to their hydrocarbons rather than undergo exchange, elimination, and simple or crossed coupling. In dilute solution in **1** the relative reactivities (r_1/r_2) of varied halides with lithium are essentially structure independent. However, as the concentrations of the halides increase, their relative reactivities become significantly different and depend on the total concentrations $\{C_T\ (M) = [R_1X] + [R_2X]\}$ of the organic halides. With lithium at increased halide concentrations (1) the reactivities are iodides > bromides > chlorides, (2) halides of lower molecular weight react more rapidly than their higher homologues, and (3) the reactivity orders of chlorides are (a) allyl > primary > secondary > tertiary > neopentyl, (b) 2-buten-1-yl > 1-buten-3-yl, (c) benzyl > phenyl, and (d) *p*-chlorotolyl > *o*-chlorotolyl > *m*-chlorotolyl. As examples, the relative reactivities of 1-chlorobutane/2-chloro-2-methylpropane (C_T = 5.83 M), 3-chloropropene/1-bromobutane (C_T = 4.60 M), bromobenzene/*p*-chlorotoluene (C_T = 4.37 M), and benzyl chloride/chlorobenzene (C_T = 4.02 M) are 6.71, 5.43, 24.1, and 22.1, respectively. Additions of aprotic solvents to 1-chlorobutane and 2-chloro-2-methylpropane in **1** decrease the relative reactivities of the halides. The effectiveness of cosolvents in lowering the relative reactivities of lithium with 1-chlorobutane and 2-chloro-2-methylbutane is tetrahydrofuran > dioxane ≅ 2-ethoxyethanol (**1**) > cyclohexene ≅ benzene. The relative reactivities of halides with sodium and with potassium in **1** at 0 °C are also total halide concentration (C_T) dependent. Under comparable concentrations the relative reactivity differences of halides are greater with lithium than sodium than potassium. The reactivities of halides under conditions of chemical control can be correlated with the ionization potentials of the alkali metals, and the kinetically controlling features of these systems are different from those with magnesium. The behavior of the alkali metals, the effects of concentration, and the roles of solvents on the reactivities of halides are discussed on the basis of (1) the active sites on the metal surfaces as modified by induction and (2) steric and electronic factors in the organic substrates. The kinetically controlled reactions of lithium with sp^3 halides may be interpreted to involve formation of lithio organohalide radical anions ($R^\bullet\text{–}X^-,Li^+$), electron transfer to the lithio radical anions on the metal surface, or unsymmetrical four-center carbanionic processes on the metal. In addition to incorporating an electron into the lowest unoccupied σ level of its C–X bond, an sp^2 halide offers the possibility for kinetically controlling electron transfer into the π system of its carbon–carbon double bond(s).

Varied organic halides react with alkali metals (Li, Na, and K) to yield alkali metal derivatives.[1] Although such organometallics are widely used, knowledge of their structures[2] and their mechanisms of formation is limited.[3] Of particular significance with respect to reaction mechanism is that lithium reacts with chiral 1-halo-2,2-diphenylcyclopropanes with major retention (68–85%) of stereochemistry and the stereospecificities of the conversions are related to the halide (Cl > Br > I) and to the sodium content and the particle size of the lithium.[3h-n,4] The reactions of lithium and halides have been discussed[3h,n] (Scheme I, processes 1–5) on the basis of transfer of a single electron to

Scheme I



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