show ^{1}H NMR averaging of hydride resonances separated by 2200 Hz.

Discussion

The work reported here shows that the polyolefin cyclooctatetraene has the capacity to trap the phototransient $ReH_5(PMe_2Ph)_2$ to give several hydrogen-transfer products, each of which is isomeric with simple adducts of the $ReH_5(PMe_2Ph)_2$ and C_8H_8. The formation of the η^4-diene intermediate from photogenerated ReH_5P_2 and C_8H_8 involves the transfer of two hydrogens from the metal to the coordinated olefin. Transfer of a third hydrogen to the cyclooctatriene ring in **1** yields final product **2**, the product of net transfer of three hydrogens from the phototransient ReH_5P_2 to C_8H_8. Coordinative saturation is maintained by forming one additional Re–C bond for every hydrogen transferred. The possibility that these Re-to-C hydrogen transfers are intramolecular is supported by deuterium label studies which show that all three transfers occur to the endo side of the bound C_8 ring.

Rhenium η^4-diene complexes analogous to **1** can be produced from transient $ReH_5(PMe_2Ph)_2$ (available either by photolysis of $ReH_5(PMe_2Ph)_3$ or by heating $ReH_7(PMe_2Ph)_2$) and 1,5-cyclooctadiene. The significant difference here is that the diene, once it is hydrogenated, is displaced by excess diene to give a trihydride complex lacking the hydrogenated fragment; metal–carbon bonds are broken when operating with diene substrates in a manner distinct from the case for cyclooctatetraene (eq 1). The results reported here also show a selectivity for the third hydrogen transfer (from **1** to **2**) to occur at a terminus of the polyolefin system, so as to maintain a conjugated π-olefin system in the product.

Both $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$[8] and $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$ show remarkable differences for the chemical shifts of their two nonequivalent hydrides (−3 and −13 ppm). This effect is absent in compounds **1** and **3**. Each pentadienyl complex has a structure with one hydride "under" the open end of the pentadienyl π-cloud and the other hydride under the central carbon of the π-cloud. Since $(\eta^5\text{-}C_5H_5)ReH_2(PMe_2Ph)_2$, with no open end to its π-cloud, has only an upfield hydride chemical shift (−11.5 ppm),[2] we suggest that the −3 ppm chemical shift be associated with the hydrogen lying in the mirror plane at the open end of the pentadienyl π-system (H34 in Figure 1). Every π-orbital of the pentadienyl has either a node or a minimum in its electron density in this mirror plane, an effect perhaps responsible for the unusual chemical shift.

In contrast to $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$, $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$ is fluxional at 34 °C.[8] Upon cooling to −40 °C, two hydride environments are frozen out in $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$; the hydride chemical shifts, δ −3.1 and −12.7, correspond closely to those reported here for the $\eta^5\text{-}C_8H_{11}$ complex. The larger ring analogue thus has the higher activation energy for ring rotation, a feature which appears to be due to the larger distance between the termini of the dienyl unit of the rings, coupled with the nodal properties of the open pentadienyl system.[10] $HZr(\eta^5\text{-}C_8H_{11})(Me_2PCH_2CH_2PMe_2)_2$ is similarly rigid.[11]

Stereochemical rigidity appears to be a characteristic, if unusual, property of several of the polyhydride rhenium complexes reported here, since $(\eta^4\text{-}C_8H_{10})ReH_3(PMe_2Ph)_2$ does not experience facile rotation of the cyclooctatriene moiety (to equivalence the two phosphorus nuclei), and both this and also $(\eta^4\text{-}1,5\text{-}COD)ReH_3(PMe_2Ph)_2$ show no facile scrambling of the three hydride nuclei. Stereochemical rigidity among seven-coordinate complexes, and also among trihydride species, is uncommon.

Supplementary Material Available: Tables of observed and calculated structure factors, hydrogen positional and thermal parameters, and anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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Arene and Cyclohexadienyl Complexes as Intermediates in the Selective Catalytic Dehydrogenation of Cyclohexenes to Arenes

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A catalytic aromatization of cyclohexene to benzene is described by using $[IrH_2(Me_2CO)_2L_2]SbF_6$ (L = PPh_3) as catalyst in refluxing 1,2-$C_2H_4Cl_2$. *tert*-Butylethylene (tbe) acts as hydrogen acceptor; in the absence of tbe, 2 equiv of cyclohexane are formed per mole of benzene. A mechanism is suggested based on the isolation of the proposed intermediates $[Ir(\eta^5\text{-}C_6H_7)HL_2]SbF_6$ and $[Ir(\eta^6\text{-}C_6H_6)L_2]SbF_6$. Some reactions of these complexes are discussed.

Several methods are available for the homogeneous transition-metal-catalyzed aromatization of *cyclohexadienes*,[1] but there is no satisfactory method for the corresponding cyclohexenes. In view of the ability of $[IrH_2S_2L_2]A$ (**1**, S = Me_2CO, L = PPh_3, A = BF_4 or SbF_6) to stoichiometrically dehydrogenate alkenes and alkanes,[2] including, very recently, cyclohexane to benzene,[3] we wondered if this complex might catalyze the aromatization of cyclohexenes. This paper describes a successful ho-

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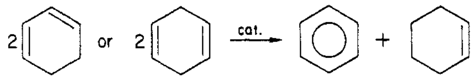
mogeneous catalyst system based on 1.

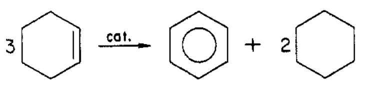
Several catalytic systems are known for diene disproportionation (eq 1). Lyons[4] use of Vaska's complex was



(1)

the first reported case and many have been discovered since.[5] The metal appears to dehydrogenate the diene and pass the resulting hydrogen to a second molecule of diene to give the olefin. Since the diene acts as its own hydrogen acceptor, a mole of olefin is produced along with the desired arene, making the process inefficient from a synthetic point of view.

Only two cases are known in which dehydrogenation of cyclohexene, as opposed to the diene, has been achieved. Wilkinson et al.[6] obtained cyclohexane and benzene (eq 2) with Ru(styrene)$_2$(PPh$_3$)$_2$. Here, even larger amounts

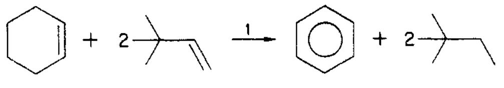


(2)

of substrate are wasted than in eq 1, 2 mol of the cyclohexane byproduct are formed per mole of benzene. Trost et al.[7] also studied Pd(OCOCF$_3$)$_2$ as a catalyst for reactions of type 2. They were the first to employ an auxiliary hydrogen acceptor, maleic anhydride, to attempt to drive the reaction toward the desired product. This was not completely successful, for even at 5% mol ratio catalyst loading and at 60 °C, no more than 75% conversion of 4-*tert*-butylcyclohexene and 25% yield of *t*-BuPh were obtained. In addition, metallic palladium is deposited and so the homogeneity of the catalyst was questioned. Pd/C also catalyzes reaction 2 heterogeneously.[8] IrH$_5$(PPh$_3$)$_2$ has been reported to disproportionate terminal alkenes to diene complexes and alkanes, although only inefficiently.[9]

Results and Discussion

We aimed to develop a system in which an essentially quantitative aromatization of cyclohexene (eq 3) could be obtained under mild conditions with a homogeneous catalyst. We report here on such a system, based on 1 as catalyst, and describe the isolation of some related complexes.



(3)

In our initial work we studied the disproportionation reaction of eq 2 as a prelude to the aromatization of eq 3. **1a** (S = Me$_2$CO; L = PPh$_3$; A = BF$_4$) is known[2] to convert cyclopentene to [IrHCpL$_2$]BF$_4$ and cyclopentane. Clearly, the η^5-C$_5$H$_5$ ligand is unlikely to dissociate from the "catalyst" but we felt the corresponding arene might well do so. Indeed, we now find the disproportionation of eq 2 is catalyzed by **1a** at 80 °C in 1,2-dichloroethane (DCE) in 12–24 h. The most efficient catalyst we found was **1b** (S = Me$_2$CO; L = P(p-FC$_6$H$_4$)$_3$; A = SbF$_6$) for which the rate was three turnovers/h with a substrate catalyst ratio of 100:1. For comparison, **1a** gave one turnover/h under analogous conditions.[6]

Table I. Rates of Cyclohexene Disproportionation and Aromatization (turnover/h)

	rates	
cat. precursor	disproportnatn (eq 2)	aromatizatn (eq 3)
[Ir(cod){P(p-FC$_6$H$_4$)$_3$}$_2$]$^+$	3.0	5.1
[Ir(cod)(PPh$_3$)$_2$]$^+$	1.0	1.7
[Ir(cod){P(p-MeC$_6$H$_4$)$_3$}$_2$]$^+$	0.95	
[Ir(cod)(dpe)]$^+$	0.07	
[Ir(cod)(PCy$_3$)(py)]$^+$	0.07	

The reaction went to completion if uninterrupted, but the catalysts are deactivated when the substrate is exhausted. This deactivation arises from reaction with the DCE to give [L$_2$HIr(μ-Cl)$_3$IrL$_2$H]A[3] and the related compound [L$_2$HIr(μ-Cl)$_2$(μ-H)IrL$_2$H]A,[10] neither of which is active in catalysis. The substrate protects the catalyst from deactivation, and it only takes place when this protection is removed.

Starting with 1-methylcyclohexene, but in CH$_2$Cl$_2$ at 80 °C (sealed tube), gave very similar results: toluene and methylcyclohexane were formed. If the less stable isomeric olefins methylenecyclohexane or 4-methylcyclohexene were employed, initial isomerization to 1-methylcyclohexene took place. Isomerization is therefore faster than dehydrogenation, as might be expected.

The aromatic stabilization appeared to be required for success. No free dienes were ever observed, nor did monoenes such as 2,3-dimethyl-1-butene and -2-butene ever give disproportionation to diene and alkane.

The reaction could be carried out in acetone or in neat cyclohexene, but in these cases it was much slower. Dichloromethane (DCM) was a satisfactory solvent in sealed tube experiments at 80 °C. Other catalyst precursors such as [(cod)IrL$_2$]BF$_4$ (cod = 1,5-cyclooctadiene) gave essentially the same result, except that an equivalent of cyclooctane was also formed. The cod evidently acts as a hydrogen acceptor during the initial catalytic cycles. The rates observed (in mol of arene produced/mol of Ir/h) are shown in Table I. Perhaps the electron-withdrawing ligand (p-FC$_6$H$_4$)$_3$P may work well because it allows easier release of the coordinated arene from the metal, a step which could reasonably be regarded as turnover (rate) limiting (see below).

[IrH$_2$(MeCN)$_2$L$_2$]BF$_4$[11] proved to be a catalyst for eq 2 with a rate comparable to that of the acetone complex. In contrast with the acetone complex, however, the unchanged acetonitrile complex, instead of [Ir$_2$H$_2$Cl$_3$L$_4$]BF$_4$, could be isolated at the end of the reaction. The acetonitrile complex was also recovered unchanged from reflux in pure DCE, showing that the MeCN ligands protect the catalyst from reaction with the DCE solvent, even in the absence of olefin.

***tert*-Butylethylene as Hydrogen Acceptor.** We used *tert*-butylethylene (tbe) as hydrogen acceptor in our alkane activation studies, and it was reasonable to try it in an attempt to divert the reaction of eq 2 from cyclohexane formation to give arene alone (eq 3). This proved to be straightforward. If a little more than the stoichiometric quantity of tbe is added to the reaction mixture (2.5 molar

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Table II. NMR Spectra Data[a]

complex[b]	Ir–H	ring protons[c]	other
$[IrH(C_6H_7)(PPh_3)_2]A$	−17.81 t (19.5)	5.2, 4.0, and 1.45, complex	
$[IrH(C_6H_7)(PMePh_2)_2]A$	−17.51 t (21)	5.5, 4.2, 3.8, 2.2, and 1.5, complex	
$[IrH(C_6H_7)(P(C_6H_4F)_3)_2]A$	−17.77 t (21)	5.2, 4.0, 3.7, 2.2, and 1.4, complex	
$[IrH(C_6H_4Me\text{-}i\text{-}Pr)(PPh_3)_2]A$	−20.97 dd (18.5, 25)	5.2, 4.5, and 1.9, complex	1.49, c, CH_3CH 2.4, s, Me, 2.9, c,CH
$[Ir(C_6H_6)(PPh_3)_2]A$		6.08[d]	
$[Ir(PhMe)(PPh_3)_2]A$		5.6 d (4), 1- and 5-H 5.8[e] t (6), 2- and 4-H	2.4, s, Me
$[Ir(PhEt)(PPh_3)_2]A$[f]		5.0, d (6), *o*-H 5.4, dd (6,8), *m*-H 6, 9, dd (6,8), *p*-H	 1.3 t (8), Me 2.6, q (8), CH_2
$[IrH(C_6H_8)(PPh_3)_2]$	−14.48 t (19.5)	1.5–5.2, complex	

[a] In acetone-d_6 at 25 °C; resonances reported as position (δ), multiplicity (coupling const, Hz). [b] A = SbF_6. [c] Other than PPh_3 groups. We were not able to assign the resonances in every case. [d] δ 5.90 in CD_2Cl_2. ^{13}C NMR (−20 °C, CD_2Cl_2): 95.6 ppm. [e] 3-H obscured by PPh_3 resonance. [f] From ref 13 for comparison.

equiv {theoretical 2.0} tbe/cyclohexene), the reaction can be followed to completion. The products are benzene (99%), cyclohexane (1%), and *tert*-butylethane (99% of theory in each case). This means that the catalyst shows a ca. 100:1 selectivity for transfer of hydrogen to tbe rather than to cyclohexene. This example shows the unusually high degree of selectivity for this catalyst, which is also a feature of the hydrogenation activity of the related catalyst $[Ir(cod)(PCy_3)(py)]BF_4$.[10,12] At 120 °C, 1-methylcyclohexene gave toluene (98%) and methylcyclohexane (2%). The lower selectivity is probably due to the fact that we were forced to heat the mixture to higher temperatures (sealed tube) to get adequate rates.

As might be expected, the rates of arene formation via eq 3 are faster (nearly two fold) than via eq 2, since tbe is evidently a better hydrogen acceptor than is cyclohexene.

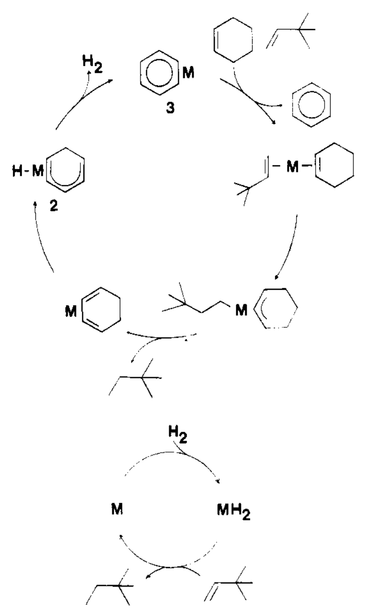
Surprisingly, tbe had no effect on the disproportionation of cyclohexene with $Ru(styrene)_2(PPh_3)_2$; cyclohexane was still formed as before. The mechanism of the disproportionation may differ in the ruthenium case, or tbe may be a poor H acceptor because it is too bulky to bind well to the smaller Ru atom.

Mechanism

The most straightforward mechanism that can be proposed for the disproportionation of eq 2 and the aromatization of eq 3 is shown in Scheme I. Two cycles are shown. In one, cyclohexene is dehydrogenated to arene. In the second, part of the resulting H_2 is transferred to the hydrogen acceptor (which is cyclohexene in eq 2 and tbe in eq 3). The exact order of the hydrogen transfers is conjectural, as is the nature of the rate-determining step; this may be loss of arene from the catalyst. This is suggested by the increase of rate on moving to tbe as hydrogen acceptor (which may help displace the arene) and the decrease in rate on moving to the substituted olefin 1-methylcyclohexene (since 3 is more stable kinetically in the case of toluene).

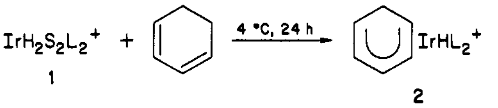
In this cycle, we propose the intermediacy of the cyclohexadienyl hydride 2 and the arene complex 3. If this mechanism is valid, these complexes should also act as catalysts. We therefore tried to isolate them. This proved to be unexpectedly difficult. Reaction of cyclohexene with **1a,b** at 25 °C always led to a mixture of 2 and 3. In spite of much effort, neither 2 nor 3 could be isolated pure from this mixture, either by chromatography or crystallization. Nor were attempts successful to convert all the 2 present to 3, because 3 began to decompose in solution at the elevated temperatures required (60 °C).

Scheme I. The Catalytic Cycles Proposed for Cyclohexene Aromatization[a]



[a] The upper cycle shows the dehydrogenation reaction (M = IrL_2^+) and the lower shows, in broad outline only, the hydrogenation cycle. The latter seems to be required because although tbe can participate directly in the first dehydrogenation steps as shown in the upper cycle, the loss of the second equivalent of H_2 probably does not involve tbe directly, because the hydrogen acceptor is unlikely to react with the 18-electron cyclohexadienyl hydride species 2.

The method we finally adopted for 2 involves manipulations at 4 °C or below, because solutions tend to decompose to 3 above this temperature. The isolated solid



(4)

2 was stable, however. In the first version of the method, 1 was stirred with 1,3- or 1,4-*cyclohexadiene* at 4 °C (cold room) for 24 h, followed by isolation with Et_2O. *Cyclohexene* only gave mixtures of compunds by this method. In a modification of this procedure, $[Ir(cod)L_2]SbF_6$ could be briefly hydrogenated in the presence of cyclohexadiene at 0 °C and then stirred under N_2 for 24 h at 4 °C as before. The brief exposure to H_2 is necessary to remove

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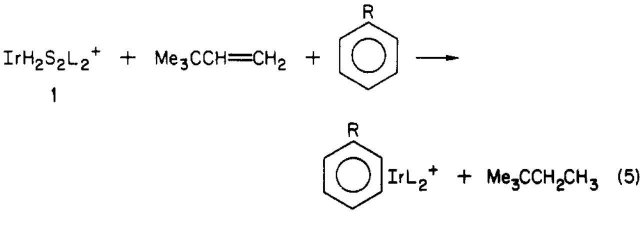
[12] Suggs, J. W.; Cox, S. D.; Crabtree, R. H.; Quirk, J. M. *Tetrahedron Lett.* 1981, *22*, 303.

the cod by hydrogenating it to cycloctane, but longer exposure would risk hydrogenating all the diene. This would give cyclohexene, which does not lead to **2** at 4 °C.

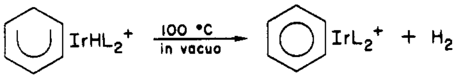
The identity of the new complexes **2** followed from microanalytical and spectral data (Table II). IR spectroscopy revealed the presence of the unperturbed SbF_6 anion, and microanalysis showed only one was present per metal. ^1H NMR spectroscopy showed a triplet at δ ca. −17 to 18 (according to the nature of the phosphine involved, see Table II). The coupling to phosphorus was ca. 20 Hz, as expected for the structure **2**. Finally, five resonances are observed in the range δ 1.4–5.5 in the same pattern in all the complexes. Two resonances at δ ca. 1.5 and ca. 2.2 are assigned to the aliphatic CH_2 protons in the 6-position. The former is tentatively assigned to the endo proton because it suffers a diagmagnetic shift which could be due to the proximity of the metal. Three resonances at δ ca. 5.4, ca. 4.1, and ca. 3.7 in the intensity ratio 2:2:1 are observed. This suggests that the resonance at δ 3.7 should be assigned to the 3-H and the resonances at δ 4.1 and 5.4 be assigned to the 1,2,4- and 5-H. As expected, **2** is a catalyst for the reactions of eq 2 and 3 and gives systems with essentially the same rate as is found for the corresponding complexes $[(cod)IrL_2]BF_4$.

A mixture of α- and γ-terpinene (the 1,3- and 1,4-cyclohexadienes corresponding to *p*-isopropyltoluene) gave only cyclohexadienyl complexes of type **2**, but at least two of the six possible isomers of the product were obtained and separation proved impossible.

Arene Complexes. Two general methods were successful for obtaining the corresponding arene complexes of type **3**. For the special case of ethylbenzene, **3** can also be obtained from the reaction of styrene with **1**,[13] but this method cannot be applied to the cases of benzene and toluene. We now report a general method for these arenes, in which a suspension of **1** in the arene of interest is refluxed with an equivalent of tbe for 6 h. The role of the tbe is to remove the hydrides from **1** to make way for the arene. Precipitation of the complex with Et_2O and recrystallization from CH_2Cl_2/Et_2O gave the complexes **3** in 80% yield. Alternatively, the complexes **2** can be converted to **3** by heating to 100 °C in a dynamic vacuum without solvent. Under these conditions, H_2 is lost and **3** is formed essentially quantitatively. We were surprised that the arene was not lost under these conditions, because the reaction presumably goes via the η_4-C_6H_6 complex $[Ir(\eta^4\text{-}C_6H_6)H_2L_2]SbF_6$; alternatively, loss of L may occur instead.



1 **3**



(6)

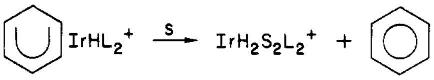
2 **3**

The new complexes were characterised by microanalysis and from spectral data. In particular, the complexes are 1:1 salts (IR and microanalysis) and the benzene complexes show a sharp peak near δ 6.1 in the ^1H NMR. This we assign to the C_6H_6 ligand. The resonance is ca. 1.3 ppm upfield from that of free benzene. The toluene complexes show the C_6H_4Me resonance at δ 2.4 very little perturbed from the position in free toluene, and the ortho and meta hydrogens near δ 5.6 and 5.8, respectively. The para hydrogen is apparently obscured by the PPh_3 resonances. The assignments are made easier in this case by the close analogy with the well-studied $[Ir(C_6H_5Et)L_2]BF_4$ case in which full decoupling studies[13] allowed unambiguous assignments to be made. We confirmed that the known ethylbenzene complex was indeed formed from **1** and ethylbenzene by the method mentioned above. We have discussed the spectra and structure of the ethylbenzene complex in more detail elsewhere.[13]

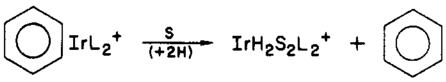
The benzene of type **3** are catalysts for reaction 3 in refluxing DCE, as expected on the hypothesis that **3** is an intermediate in our original catalytic cycle. Rates are essentially the same as observed for **1**; there is no induction period, so **3** decomposes fast enough to be a true intermediate.

Reactions of $[(C_6H_7)IrH(PPh_3)_2]SbF_6$ (2) and $[(C_6H_6)Ir(PPh_3)_2]SbF_6$ (3). Both the cyclohexadienyl complex **2** and the benzene complex **3** react with cyclooctene or cyclopentane in refluxing DCE to give $[Ir(cod)L_2]SbF_6$ and $[Ir(\eta^5\text{-}C_5H_5)HL_2]SbF_6$, as does $[IrH_2S_2L_2]SbF_6$ itself. Reaction was also observed with the corresponding alkanes in the presence of tbe. These reactions will be discussed elsewhere[14] in the context of our other alkane activation studies.

Both complexes react with acetone, methanol, or acetonitrile at reflux for 12 h to give $[IrH_2S_2L_2]^+$ (**1**, S = solvent). In the case of **2** the presence of hydrides in the product **1** is unexceptional, but in the case of **3** insufficient hydrogen is initially present as hydride to account for the presence of two hydrogens in the product. The origin of this extra hydrogen was shown in the case of acetone to be the solvent (see eq 7 and 8). The organic products of this reaction were present in too small an amount to allow their detection or characterization. Traces of reducing agents in the solvent (e.g., *i*-PrOH) may also be involved.



(7)



(8)

A number of other reactions were briefly surveyed. Photolysis of **2** or **3** in CH_2Cl_2 gave $[HL_2Ir(\mu\text{-}Cl)_3IrHL_2]SbF_6$. Unexpectedly, photolysis (350 nm) of **2** did not lead to **3**. Photolysis of **2** or **3** in acetone gave $[IrH_2S_2L_2]^+$. In the case of **3** we used $(CD_3)_2CO$ and found that $[IrD_2S_2L_2]^+$ (S = $(CD_3)_2CO$) was formed. The extra hydrogen in the product therefore arises from the solvent. Concurrent photolysis did not affect the rate of the aromatization reactions (eq 2 and 3).

LiBEt$_3$H reacts with the cyclohexadienyl complex in CH_2Cl_2 at 0 °C to give a new neutral diene complex, $[IrH(C_6H_8)L_2]$ (eq 9). The reaction is reversed with $HSbF_6$.

(9)

The ^1H NMR spectrum shows a triplet at δ −14.5. Related complexes such as $[IrH(cod)L_2]$ give a similar triplet.[15]

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[13] Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913.

[14] Crabtree, R. H.; Parnell, C. P. *Organometallics* 1984, *3*, 1727.

Resonances at δ 1.5–5.5 are assigned to the coordinated diene.

Conclusion

We have shown that homogeneous catalytic disproportionation of cyclohexene is effected by a number of catalyst precursors capable of giving the IrL_2^+ fragment. Selective catalytic aromatization is possible when tbe is added as hydrogen acceptor. $[IrH(\eta^5\text{-}C_6H_7)L_2]^+$ and $[Ir(\eta^6\text{-}C_6H_6)L_2]^+$ appear to be intermediates in the catalytic cycle. These complexes were prepared and some of their reactions studied.

Experimental Section

Ammonium chloroiridate was a generous gift of Johnson Matthey Inc. Ligands were purchased from Aldrich Chemical Co. and distilled before use. NMR spectra were recorded on a Bruker 270 MHz instrument or on a JEOL FX-90Q, and IR spectra were recorded on a Nicolet 7000 instrument. Starting materials were prepared by published routes.[16] In the case of 1 the SbF_6 salt was used in all these experiments; its synthesis is described in ref 14. Reactions were carried out under N_2. Et_2O and C_6H_6 were distilled from Na/Ph_2CO. Me_2CO was dried over 4 Å molecular sieves. The chlorinated solvents were distilled from CaH_2.

Cyclohexene Disproportionation and Aromatization. These reactions were performed in a resealable 20-mL glass tube immersed in an oil bath at 80 °C (method A) or in refluxing 1,2-dichloroethane (DCE) at 80 °C under N_2 (method B). In each case $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (75 mg, 0.07 mmol) and cyclohexene (0.71 mL, 7.0 mmol) were dissolved in CH_2Cl_2 (method A) or DCE (method A or B). In the case of the aromatization reactions *tert*-butylethylene (tbe, 2.0 mL, 15.5 mmol) was also added. On heating the reaction mixtures became orange. After 24 h at 80 °C the reaction mixture was distilled in vacuo into a cold trap and studied by GC (5% Carbowax 20M on Anachrom 80/100, 6 ft column), which showed, in order of elution, cyclohexane, cyclohexene, benzene, and DCE. In cases where the cyclohexane was all consumed, $[Ir_2H_2Cl_3(PPh_3)_4]SbF_6$ was recovered in ca. 80% yield from the involatile residues, by extraction with CH_2Cl_2 and recrystallization from CH_2Cl_2/Et_2O.

1-Methylcyclohexene was studied in CH_2Cl_2 by method A at 120 °C, in which case GC analysis showed, in order of elution, methylcyclohexane, CH_2Cl_2, 1-methylcyclohexene, and toluene.

No dienes were formed in any of these reactions. We verified that they would have been separated by GC from the other products if they had been formed. In cases where tbe was present, *tert*-butylethane was also detected in the volatiles in the amount expected on the basis of eq 3.

We also verified the report[6] that $RuH_4(PPh_3)_3$ also catalyzes reaction 2 but we found that tbe had no effect on the products.

(η^5-Cyclohexadienyl)hydroidobis(triphenylphosphine)iridium(III) Hexafluoroantimoniate (2). Method A. $[Ir(cod)(PPh_3)_2]SbF_6$ (500 mg, 0.47 mmol) and cyclohexadiene (either 1,3 or 1,4, 4 mL) were dissolved in CH_2Cl_2 (30 mL, 0 °C) and H_2 passed through the solution at 0 °C for 20 min. The solution was then swept with argon and the mixture stirred at 4 °C for 24 h. Slow addition of Et_2O gave the cream product which was filtered and recrystallized from CH_2Cl_2/Et_2O. Yield: 420 mg (86%). **Method B.** $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (500 mg, 0.467 mmol) and cyclohexadiene (4 mL) were dissolved in CH_2Cl_2 (30 mL) and stirred for 24 h at 4 °C. Workup as above gave 415 mg (85%) of product. Anal. Calcd for $C_{42}H_{38}P_2SbF_6Ir$: C, 48.84; H, 3.71; P, 6.00. Found: C, 48.73; H, 4.02; P, 5.84. Two analogous complexes were also prepared and were identified from their spectra (Table II) and microanalyses. The $PMePh_2$ complex was prepared by method A in 80% yield. Anal. Calcd for $C_{32}H_{34}P_2F_6SbIr$: C, 42.30; H, 3.77. Found: C, 42.59; H, 3.42. The $(p\text{-}FC_6H_4)_3P$ complex was prepared in 80% yield by method B. Anal. Calcd for $C_{42}H_{32}F_{12}P_2IrSb$: C, 44.22; H, 2.82. Found: C, 44.51; H, 2.60.

(η^6-Benzene)bis(triphenylphosphine)iridium(I) Hexafluoroantimoniate (3). $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (300 mg, 0.28 mmol) and tbe (36 μL, 0.28 mmol) were refluxed in benzene (25 mL) for 6 h. To the resulting cooled orange solution was added Et_2O to give an orange solid, which was filtered and recrystallized from CH_2Cl_2/Et_2O to give 243 mg yield (84%). Anal. Calcd for $C_{42}H_{36}P_2IrSbF_6\cdot{}^3/_4CH_2Cl_2$: C, 46.91; H, 3.45; P, 5.66; F, 10.41. Found: C, 46.85; H, 3.67; P, 5.57; F, 10.86.[17] **Analogous Complexes.** Subjected to the reaction described above, indan gave the known[14] indan complex in 50% yield. Toluene give a complex in 85% yield which has a ^1H NMR spectrum identical with that of the known[18] toluene complex. Ethylbenzene gave the known[13] ethylbenzene complex in 75% yield. All these products were orange crystalline solids.

Reaction of Complex 2. A. With Olefins. 2 (100 mg, 0.097 mmol) and cyclopentene or cyclooctene (2 mL) were refluxed in $C_2H_4Cl_2$ (10 mL) for 4 h. The products isolated by addition of Et_2O and recrystallized from CH_2Cl_2/Et_2O were $[Ir(\eta^5\text{-}C_5H_5)HL_2]SbF_6$ (82%) and $[Ir(cod)L_2]SbF_6$ (80%), identified by their characteristic ^1H NMR spectra.[2,11] **B. With Solvents.** 2 (100 mg, 0.097 mmol) was heated in refluxing acetone, MeCN, or MeOH (10 mL) for 6 h. White solids, precipitated in 80–90% yield with Et_2O and recrystallized from CH_2Cl_2/Et_2O, were identified by their characteristic[11,16] NMR spectra as $[IrH_2S_2L_2]SbF_6$ (S = Me_2CO, MeCN, or MeOH). Reaction with CH_2Cl_2 only took place on photolysis (350 nm, 25 °C) after 12 h. $[Ir_2H_2Cl_3L_4]SbF_6$[14] was found as the sole identifiable product in ca. 60% yield.

Reactions of Complex 3. Complex 3 gave the same reactions as did complex 2 under the conditions described under the conditions of A and B above. Additional reactions were also attempted. **C. Arene Exchange.** 3 (100 mg, 0.097 mmol) was heated with toluene (10 mL) at 80 °C for 8 h. No identifiable products were observed. Similar results were obtained with PhEt, indan, 1-methylnaphthalene, and *o*-xylene.

Hydrido(η^4-cyclohexadiene)bis(triphenylphosphine)iridium(I). $[IrH(C_6H_7)(PPh_3)_2]SbF_6$ (250 mg, 0.242 mmol) in THF (10 mL) was cooled to 0 °C and $LiBEt_3H$ (0.3 mL of 1 M solution in THF, 0.3 mmol) added. The solution was warmed to room temperature and MeOH (0.2 mL) added. Removal of the solvents gave an oil that was crystallized from hot CH_2Cl_2. Anal. Calcd for $C_{42}H_{39}P_2Ir\cdot 0.33CH_2Cl_2$: C, 61.54; H, 4.84; P, 7.50. Found: C, 61.47; H, 4.87; P, 7.60.[17]

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Registry No. **2**, 91410-24-1; **3**, 94249-80-6; tbe, 558-37-2; $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$, 89509-77-3; $[Ir(cod)\{P(p\text{-}FC_6H_4)_3\}_2]^+$, 75192-66-4; $[Ir(cod)(PPh_3)_2]^+$, 47864-81-3; $[Ir(cod)\{P(p\text{-}MeC_6H_4)_3\}_2]^+$, 75192-61-9; $[Ir(cod)(dpe)]^+$, 47778-82-5; $[Ir(cod)(PCy_3)(py)]^+$, 64536-77-2; $[IrH(C_6H_7)(PMePh_2)_2]SbF_6$, 94249-82-8; $[IrH(C_6H_7)(P(C_6H_4F)_3)_2]SbF_6$, 94249-83-9; $[IrH(C_6H_5Me\text{-}i\text{-}Pr)(PPh_3)_2]SbF_6$, 94249-93-1; $[Ir(PhMe)(PPh_3)_2]SbF_6$, 94249-85-1; $[Ir(PhEt)(PPh_3)_2]SbF_6$, 94249-86-2; $[IrH(C_6H_8)(PPh_3)_2]$, 94249-87-3; $[Ir_2H_2Cl_3(PPh_3)_4]SbF_6$, 94249-89-5; $RuH_4(PPh_3)_3$, 31275-06-6; $[Ir(cod)(PPh_3)_2]SbF_6$, 91410-27-4; $[Ir(\eta^5\text{-}C_5H_5)H(PPh_3)_2]SbF_6$, 91410-26-3; $[IrH_2(MeCN)_2(PPh_3)_2]SbF_6$, 94345-85-4; $[IrH_2(MeOH)_2(PPh_3)_2]SbF_6$, 94480-16-7; $[IrH(\eta^4\text{-}C_6H_8)(PPh_3)_2]$, 94249-90-8; $LiBEt_3H$, 22560-16-3; $[Ir(cod)(PPh_2Me)_2]SbF_6$, 94249-91-9; $[IrH_2(Me_2CO)_2\{P(C_6H_4F)_3\}_2]SbF_6$, 89529-62-4; cyclohexene, 110-83-8; benzene, 71-43-2; cyclohexane, 110-82-7; 1-methylcyclohexene, 591-49-1; methylcyclohexane, 1335-86-0; toluene, 108-88-3; *tert*-butylethane, 590-35-2; 1,3-cyclohexadiene, 592-57-4; indan, 496-11-7; (η^6-indan)bis(triphenylphosphine)iridium(I) hexafluoroantimoniate, 91410-21-8; ethylbenzene, 100-41-4; cyclopentene, 142-29-0; cyclooctene, 931-88-4; 1,4-cyclohexadiene, 628-41-1; methanol, 67-56-1; acetonitrile, 75-05-8; acetone, 67-64-1; methylene chloride, 75-09-2.

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