C-C Bond Cleavage in Hydrocarbons by Iridium Complexes

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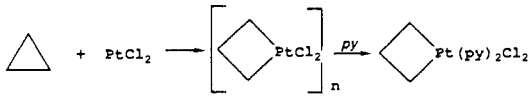
Abstract: A variety of transformations involving C-C bond cleavage in iridium complexes is described. 1,1-Dimethylcyclopentane reacts with $[IrH_2(Me_2CO)_2L_2]SbF_6$ (L = $(p\text{-}FC_6H_4)_3P$, **1**) to give first $[(5,5\text{-}C_5H_4Me_2)IrL_2]SbF_6$ (**2**) and then $[(MeC_5H_4)IrMeL_2]SbF_6$ (**3**). The corresponding 5,5-dimethylcyclopentadiene gives 1,2- and 1,3-diethylcyclopentadienyl complexes by a route that involves alkyl migration from ring to metal and back. 4,4-Dimethylcyclopentene also reacts to give **3** but the 3,3-isomer follows a different path to give $[(MeC_5H_4)IrHL_2]SbF_6$. Crystal structures of two diene complexes of type **2** are reported and mechanisms for the reactions observed are proposed.

Our interest in the organometallic chemistry of alkanes[1] has led us to explore approaches to alkane C-C bond cleavage reactions with transition-metal complexes. Although C-H bond cleavage is now well-known, C-C bond cleavage is still very rare. The first example dates from 1955 when Tipper[2] reported that $PtCl_2$ gave a cyclopropane complex. The platinacyclobutane structure was first suggested by Chatt.[3]

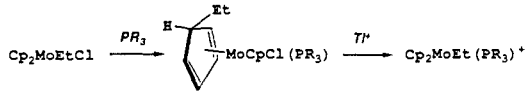


All the examples described since that time[1] have also involved strained alkanes. Two types of reaction have been observed. The electrophilic type (eq 2) tends to be found in Ag^+-catalyzed rearrangements of strained hydrocarbons, while Rh(I)-catalyzed rearrangements are generally believed to go via oxidative addition (eq 3).[1]

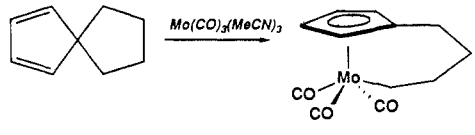
$$Ag^+ + C\text{-}C \rightarrow Ag\text{-}C + C^+ \quad (2)$$

$$Rh + C\text{-}C \rightarrow C\text{-}Rh\text{-}C \quad (3)$$

Although C-C cleavage reactions are much rarer than those involving C-H bonds, a number of examples are known of C-C bond cleavage in ligands. Maitlis[4] showed how a pentamethylcyclopentadienyl complex could be obtained from hexamethyl(deware benzene), and Green[5] observed a most interesting reversible rearrangement to and from a C_5 ring.



Eilbracht[6] has described many examples of similar cleavage reactions for a wide variety of dienes.



Other ligands have also shown C-C cleavage chemistry, for example, metalacycles,[7] lanthanide alkyls,[8] and cyclobutylmethyl groups.[9] In a series of very interesting investigations, Suggs[10] has cleaved a variety of C-C bonds in 8-substituted quinolines.

Both thermodynamic and kinetic factors appear to be responsible for the rarity of C-C bond cleavage. Special factors are usually involved when this reaction is observed. In the case of cyclopropane, ring strain is involved. In the Green-Eilbracht reaction, the aromatization of the cyclopentadienyl ring can be invoked. In contrast to the case of C-H activation, where no very great kinetic barrier is believed to stand in the way of the reaction, the barrier for C-C activation is probably much greater. This is suggested by the common occurrence of stable polyalkyls, e.g., WMe_6, $PtMe_3I$, and metallacycles, in contrast to the comparative rarity of alkyl hydrides. Given that thermodynamic factors should normally favor reductive elimination, and the fact that it is not usually observed, microscopic reversibility arguments suggest that there will usually be a substantial kinetic barrier to C-C activation.[1] In view of these unfavorable kinetic and thermodynamic factors, successful routes to C-C bond activation by d-block transition-metal complexes may require the use of indirect routes that avoid the "frontal assault" of direct C-C bond breaking as the first step.

Results and Discussion

We describe in this paper three related reaction types involving C-C bond cleavage in hydrocarbons. One involves alkanes, another dienes, and the third alkenes. We have previously shown that complexes of the $[IrH_2S_2L_2]A$ type (**1**: S = Me_2CO; L = PR_3; A = noncoordinating anion) can dehydrogenate cyclopentanes to cyclopentadienes.[13] Our entry into this work was to ask what would happen to 1,1-dimethylcyclopentane under the alkane dehydrogenation conditions. We imagined that a dimethyldiene complex of type **2** might be formed and that this might undergo the Green-Eilbracht[5,6] reaction to give a product of type **3**. This proved to be possible, and we discuss this reaction sequence first. Following up this work led us to two further and quite unexpected rearrangements involving C-C bond cleavage.

Neat 1,1-dimethylpentane reacts with $[IrH_2(Me_2CO)_2\{(p\text{-}FC_6H_4)_3P\}_2]SbF_6$ (**1**) at 150 °C over 8 h to give the 5,5-dimethylcyclopentadiene complex **2** in 50% yield. Also present in

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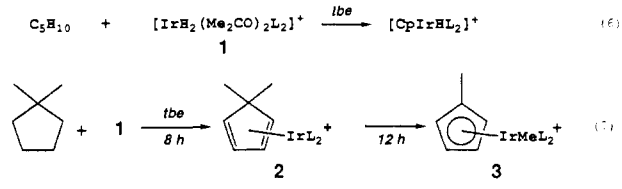
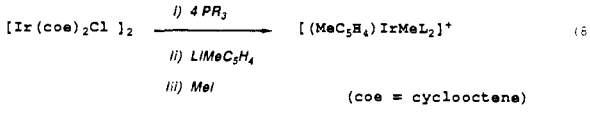
this reaction mixture is *tert*-butylethylene (tbe) which, as in our previous work,[13] acts as hydrogen acceptor. The identity of **2**



followed from the spectral data and by independent synthesis from 5,5-dimethylcyclopentadiene and **1** (neat, 85 °C, 2 h). In particular two methyl singlets are seen at δ 0.82 and 1.62 which we were able to identify with the *endo*- and *exo*-methyls, respectively (see below). The corresponding ^{13}C NMR resonances occur at δ 24.6 and 37.1, and for both $^1J(^{13}C, H)$ is 127 Hz.[14]

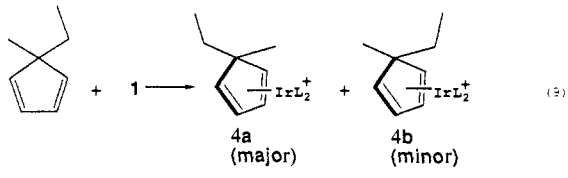
This complex can be converted into the methyliridium complex **3** by the Green–Eilbracht reaction. This occurs if the reaction mixture from the 1,1-dimethylcyclopentane reaction is heated at 150 °C for 20 h or if pure microcrystalline **2** is heated in vacuo at 145 °C for 18 h. In each case, the conversion of **2** to **3** is essentially quantitative, but the overall yield from the alkane is only ca. 50% because of the poorer yield of the first step. This combination of our alkane dehydrogenation chemistry with the Green–Eilbracht reaction seems to be the first example of a C–C bond-breaking sequence starting from an unstrained alkane.

The identity of complex **3** followed from its spectral data and independent synthesis by the route shown in eq 8. The Ir–Me



group appears as a triplet at δ 1.45 in the ^1H NMR ($^3J(P,H)$ = 5.5 Hz) and at δ −27.7 in the ^{13}C NMR ($^2J(P,C)$ = 5.5 Hz), and the MeC_5H_4 group resonates at δ 1.83 (^1H) and 15.5 (^{13}C). In an off-resonance-decoupled spectrum additional quartet splitting was detected in the resonances we assigned to Ir–*Me* as expected for a CH_3 group. No hydride resonances were observed in the crude reaction mixture from the pyrolysis of **2**; in particular $[(MeCp)IrHL_2]^+$, prepared by independent synthesis from methylcyclopentene and **1** (80 °C, 4 h), was absent (<1%).

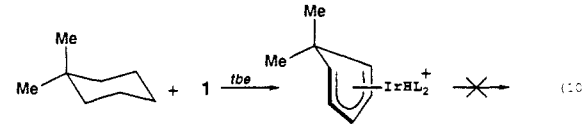
We were interested to see whether it is the *endo*-alkyl group that is cleaved, and so we looked at 1-methyl-1-ethylcyclopentadiene, which gives a mixture of diene complexes on reaction with **1** at 85 °C for 2 h. Two isomers, **4a** and **4b**, were present in a 3:1 ratio. The overlapping pattern of the ^1H NMR resonances



of these species was resolved only at 500 MHz. The resonance positions were not informative because the exo and endo groups are both shifted relative to the free diene, one upfield and the other downfield. We were able to carry out an NOE experiment in which the methyl singlet of each isomer was irradiated while the phosphine aromatic proton ortho to phosphorus was observed. The characteristic enhancement of the aromatic resonance only for the major isomer shows this isomer has the *endo*-methyl group and that the endo group is the one with the high field coordination shift. This stereochemistry was also confirmed crystallographically (see below). The major isomer, purified by recrystallization, gave on heating (150 °C, 46 h) only the ethylcyclopentadienyl iridium methyl in essentially quantitative yield, showing that the endo group had been selectively cleaved. The product was identified from its Ir–*Me* resonance at δ 1.33 in the ^1H NMR, which showed coupling to phosphorus ($J(P,H)$ = 5.3 Hz) confirming that the methyl is directly bound to the metal. These values can be compared with the corresponding values of δ 1.33 and 5.3 Hz for the closely related complex $[CpIrMe(PR_3)_2]^+$ prepared by the method of eq 8. The quartet pattern and triplet pattern of the ethyl group ($J(H,H)$ = 7.6 Hz) are not coupled to phosphorus, showing that the ethyl group has remained on the cyclopentadienyl ring.

The minor isomer **4b** was never obtained pure, and so its pyrolysis products were only observed as byproducts in the pyrolysis of the 3:1 mixture of **4a** and **4b**. The nature of these products will be discussed in a later section.

Aromatization of 1,1-dimethylcyclohexane to toluene and methane would be particularly interesting both in itself and because it might go catalytically. Toluene might dissociate from the metal to regenerate the active catalyst; in contrast, we have seen that a cyclopentadienyl group does not dissociate. Unfortunately, as can be seen from eq 12, only the first step of the reaction goes.



This is because **5**, in contrast with **2**, is an 18e rather than a 16e compound and so no further sites on the metal are available for C–H or C–C bond breaking to take place. On heating in vacuo, **5** only decomposed at 150 °C after 5 h and then only to 3,3- and 4,4-dimethylcyclohexenes (53:47, 95%) and a trace of toluene (~0.01%) along with unidentifiable metal-containing products.

This illustrates the requirement for multiple coordinative unsaturation to be available to aromatize gem-disubstituted cycloalkanes. The 12e "IrL_2" fragment is successful for cyclopentanes, but a 10e metal catalyst fragment would be required for the cyclohexane case. We have not yet devised a suitable system to do this.

Complex **5** was independently prepared from 3,3-dimethylcyclohexene and **1** (85 °C, 2 h) and was identified from its spectral properties (see Experimental Section). We also prepared $[(toluene)IrL_2]SbF_6$ from **1**, toluene, and tbe at 85 °C for 2 h. Pyrolysis of this compound liberated toluene on decomposition but only after 15 h at 150 °C. Complex **5** was also subjected to a number of different reagents and conditions (e.g., 254-nm light, Br_2, O_2) without giving significant amounts of C–C cleavage products.

C–C Bond Breaking in *gem*-Dialkyldienes. We have seen above how an *endo*-methyl group can be cleaved from coordinated dimethylcyclopentadiene and methylethylcyclopentadiene ligands in **2** and **4a**, respectively. For completeness we studied the *gem*-diethylcyclopentadiene complex **6** and were surprised to find a new reaction pathway. The products are a ca. 1:1 mixture of two iridium hydrides **7a** and **7b**. At first we thought that C–C cleavage had taken place and that the iridium ethyl had β-eliminated to give $[Ir(EtC_5H_4)HL_2]^+$. Independent synthesis of this compound (by the method of eq 8 but with EtC_5H_4Li and quenching with H_3O^+ instead of MeI) showed that the product was very similar but not identical with either **7a** or **7b** (NMR). Our second idea was that cyclometalation had taken place. The ^{31}P NMR showed that two phosphorus nuclei were indeed present in the mixture of **7a** and **7b** but that their chemical shifts were trivially different and neither had the right shift for one of them to be a part of a 4-membered cyclometalated ring.[15]

The correct formulations are the ones shown in eq 11. As predicted on these structures, the off-resonance-decoupled ^{13}C NMR spectrum of the mixture shows two types of ethyl group are present, two types of quaternary Cp carbon, and four different Cp *C*H groups in a 2:2:1:1 ratio. The CH_2 protons of the ethyl groups are diastereotopic in the ^1H NMR spectrum, and the ^1H

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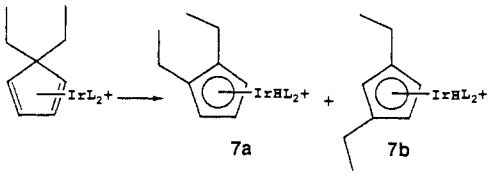
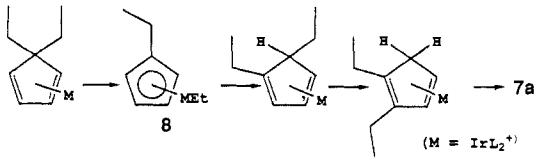


(11)

decoupled ^{31}P NMR spectrum showed that each of the two phosphorus resonances was split into a doublet, indicating that the iridium bears a single H in each case.

How does this transformation go? We verified that the free diethyldiene itself was stable to the reaction conditions, so the metal is playing a role. The simplest proposal is that C–C bond cleavage occurs as before, but that the ethyl group can migrate back to a different carbon atom of the Cp group. The *exo*-hydrogen now has to migrate to another carbon atom to expose an *endo*-hydrogen to attack by the metal, which gives the final product. This migration might occur by a standard 1,5-electrocyclic rearrangement in the bound ligand, or the diene may have to dissociate.



(12)

This mechanism predicts that an intermediate in the process is $[(EtC_5H_4)IrEtL_2]^+$. This is very easy to test. We made the closely related $[CpIrEtL_2]^+$ by the general method of eq 8 and heated it under the conditions of eq 11. We were very pleased to find that the rearrangement occurs smoothly to give the ethylcyclopentadienyl hydride, which can be independently synthesized from 1-ethylcyclopentene and **1** (80 °C, 2 h). The

$$[CpIrEtL_2]^+ \longrightarrow [(EtC_5H_4)IrHL_2]^+ \quad (13)$$

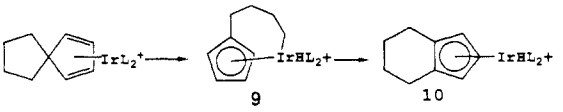
thermodynamic driving force for reaction 13 must arise from an Ir–H and a C–C bond having a higher net bond dissociation energy than an Ir–C and a C–H bond; this is not surprising.

Kinetically, it is perhaps more surprising that the alkyl does not β-eliminate before it transfers to the Cp ring. Green has observed alkyl transfer rather than β-elimination at ambient temperature, but we are observing it here at 140 °C over 4 d. The $CpIrL_2R^+$ system must be very robust and not dissociate L or Cp; otherwise the β-elimination would certainly have occurred at once.

On pyrolysis, the minor isomer of $[(5,5\text{-}MeEtC_5H_4)IrL_2]^+$ having the ethyl group endo at the metal (**4b**) gave spectrally similar products to **7a** and **7b**. This suggests that the ethyl group also migrates to the metal and back to the ring in this case too. The key feature in allowing for migration back to the ring must be the Ir–Et group, not any substitution pattern of the Cp ring.

The next question that arises is why the ethyl group in **8** transfers to the Cp ring ultimately to give **7a** and **7b**, while the methyl group in $(MeC_5H_4)IrMeL_2^+$ (**3**) does not do so. We verified that pyrolysis of **3** for extended periods at elevated temperature (180 °C) only led to decomposition, not to the formation of the 1,2 and 1,3 isomers of $[(Me_2C_5H_3)IrHL_2]^+$. All we can suggest is that the Ir–C bond strength may be a little higher for Ir–Me than for Ir–Et. This might be sufficient to raise the transition state for the sequence of eq 12 above that for decomposition.

We tried to trap the presumed ethyliridium intermediate **8** but without success. We did manage to observe an analogous intermediate in the case of spiro[4.4]nona-1,3-diene. In this case we imagined that the initial C–C cleavage product would not be able to undergo back migration of the alkyl group to the Cp ring, because the cyclic product could not easily adopt the conformation required. In this conformation the Cp ring must rotate approximately 70° so that the next carbon in the ring is opposite the alkyl–iridium bond. In the pyrolysis of the spirononene complex we saw essentially only the C–C cleaved product **9** and only a very little of an iridium hydride having the same ^1H NMR resonances as the known complex **10**, which would be the result of back migration. While **9** could be fully characterized, we were not able



(14)

to obtain more than a few precent of **10** by this route, so it does not constitute a good preparation. **10** can be readily prepared from **1** and 1,2,3,4,5,6-hexahydroindene, however. Unfortunately, **9** transforms only very slowly into **10** at 150 °C. We were therefore not able to obtain more than a few percent of **10** before the material decomposed.

These reactions constitute an interesting counterpoint to Green's results shown in eq 4. There, the alkyl migrated from the metal to the ring and back. Here, the migration is from the ring to the metal and back.

Other mechanisms were also considered. A sigmatropic shift of the *exo*-alkyl group in eq 7 seems unlikely because pyrolysis of **4a** gives the product of migration of the *endo*-methyl, not the *exo*-ethyl. Homolytic Ir–C bond cleavage in eq 11 and 13 is unlikely because crossover products were not observed in the pyrolysis of an intimate mixture of the diethyldiene and the spirononadiene complexes. β-Elimination of the ethyl group on iridium, before transfer to the ring, might be taking place, but we would have expected to see crossover at 140 °C by alkene dissociation if this were happening.

This work suggests that the cyclopentadienyl ligand may not always be innocent but may sometimes rearrange by alkyl transfer to the ring. This creates coordinative unsaturation at the metal and can give rise to further chemistry. This possibility has therefore always to be taken into account in interpreting the results of experiments on cyclopentadienyl metal alkyls.

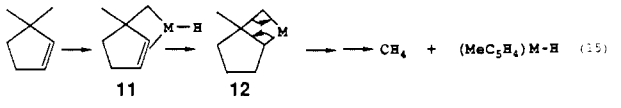
C–C Bond Cleavage in Dimethylcycloalkenes. We next looked at the 3,3- and 4,4-dimethylcyclopentenes and obtained an unexpected and interesting result. These two alkenes do not give the same products with **1**. The 3,3-isomer gives as the first detectable product at 80 °C (neat, 1 h) $[(MeC_5H_4)IrH(PR_3)_2]SbF_6$, while the 4,4-isomer gives the dimethyldiene complex $[Ir(Me_2C_5H_4)(PR_3)_2]SbF_6$ (**2**) under the same conditions. There is no difficulty in understanding the formation of the diene complex from the 4,4-isomer. Dehydrogenation of the cyclopentene to the cyclopentadiene can occur by a normal sequence of C–H activation reactions. The diene product can then undergo the "normal" C–C cleavage, but only at higher temperature (150 °C) to give the same methylcyclopentadienyl iridium methyl that we saw in eq 7. The 3,3-alkene, on the other hand, behaves in a very different way. First, C–C cleavage seems to occur at a much lower temperature (80 °C) than in eq 7 (150 °C), and the product is the iridium hydride not the methyl. We took exceptional care to see that our sample of the 3,3-isomer was pure and not significantly contaminated by the 4,4-isomer or, much more to the point, methylcyclopentenes. The latter could go directly to the observed product by standard C–H bond-breaking chemistry. We would have been able to detect 0.1% of any methylcyclopentene in the 3,3-isomer by GC, and a 50% yield of $[Ir(MeC_5H_4)HL_2]SbF_6$ was observed with as little as 10 mol equiv of 3,3-dimethylcyclopentene. Presumably the methyl group is cleaved off as methane, but we were never able to detect this product in the gases above the reaction mixtures. Our analytical method was not good enough to detect the expected amounts when we analyzed a synthetic mixture containing the appropriate amount of CH_4, which had been heated to 80 °C for 1 h. We found no isomerization of the unreacted 3,3-isomer under these conditions (80 °C); in particular no 4,4-isomer nor methylcyclopentenes were formed. Similarly, we were unable to detect isomerization of the unreacted 4,4-isomer.

Changing the structure of the alkene led to suppression of the C–C cleavage chemistry and to the formation of the "normal" products. For example, both 3,3-and 4,4-dimethylcyclohexene gave the dimethylcyclohexadienyl iridium hydride, previously observed from the cycloalkane. Similarly, both [4.4] spiro-2-nonene and 3-nonene gave the normal spirononadiene complex.

Table I. Crystal Data for **4a** and **6**

	4a	**6**
formula	$IrSbP_2F_{12}C_{44}H_{36}$	$IrSbP_2F_{12}C_{45}H_{38}$
mol wt	1168.7	1182.7
a, Å	11.094 (3)	11.187 (6)
b, Å	16.130 (4)	16.080 (7)
c, Å	24.309 (10)	24.496 (12)
β, deg	93.98 (3)	94.40 (4)
V, Å^3	4339.7 (25)	4390.9 (36)
F(000)	2264	2296
μ(Mo K), cm^{-1}	38.32	37.88
λ(Mo K), Å	0.71069	0.71069
D_{calcd}, g cm^{-3}o	1.788	1.789
Z	4	4
obsd. reflcns	3701	4602
R, %	6.3	6.0
space group	$P2_1/n$	$P2_1/n$

The most reasonable mechanism for the anomalous 3,3-dimethylcyclopentene reaction is shown in eq 15. After coordination of the C-C group, C-C bond activation might take place directly, but this seems most unlikely in view of the results reported in the earlier part of this paper. Instead C-H activation might take place at the *endo*-methyl of the *gem*-dimethyl group, an example of distal C-H activation.[16] This would lead to an iridium hydride complex **11** in which a hydride insertion could yield the metalacyclic product **12**. A metathesis-like[17] cleavage of this ring would lead directly to the observed products. A similar mechanism has been proposed for the isomerization of neopentane to 2-methylbutane over a heterogeneous Pt catalyst. The corresponding cyclohexane,



which does not react in the same way, may have a different conformation, one in which the *endo*-methyl group is further removed from the metal. Similarly, the corresponding C-H bond in the spirononene might also be conformationally inaccessible, held rigidly as it is by the second ring, and unable to rotate as is the case for the methyl analogue. This reaction seems to be specific to 3,3-dimethylcyclopentene and so may not have general importance. For this reason we did not continue our studies on it.

Crystal Structures of 4a and 6. We were interested in confirming the bond connectivity for **4a** and **6** and in finding out whether there are any unusual structural features in the dialkyldiene complexes and chose the ethyl methyl (**4a**) and diethyldiene (**6**) complexes for detailed crystallographic study. Unfortunately, neither low-temperature nor neutron data are available, and the *R* factors were rather high, so we were not able to locate the hydrogens. The X-ray as opposed to the analytical samples were unsolvated; the SbF_6^- ions were ordered, because the SbF angles and distances were normal, but the anisotropic thermal parameters were rather high for the F atoms (82-561).

The complexes both crystallized from CH_2Cl_2/Et_2O in the space group $P2_1/n$ with very similar unit cell parameters and structures. The crystal data are given in Table I, the positional parameters in Table II, and the significant distances in Table III. Structure factors (Table 1) and further positional and thermal parameters (Tables 2 and 3) and further distances and angles (Table 4) appear in the supplementary data. Figure 1 shows the structure for **4a**. The structure of **6** is very similar except that the *endo*-methyl group is replaced by an ethyl group. The structure of **4a** confirms the *endo*-methyl conformation determined by NOE measurements. The chief point of interest in both structures is the close approach of the C(1)-C(6) bond to the iridium (see Table III). Surprisingly the interaction appears to be greater for the more bulky ethyl group in **6**. This suggests that we are not dealing with a repulsive interaction but that the more electron rich ethyl group may be

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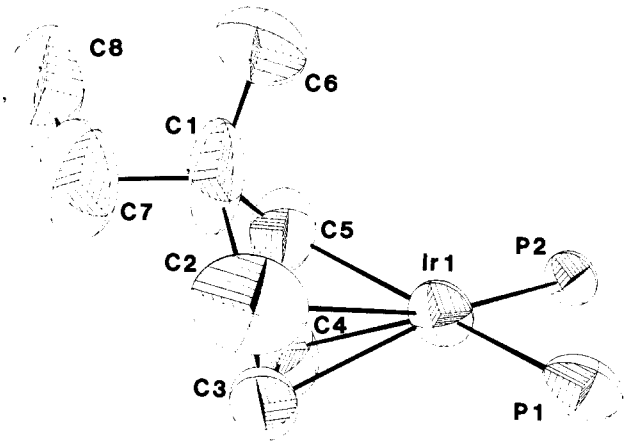

Figure 1. The structure of the *endo*-methyl isomer **4a** of the 1-ethyl-1-methyl diene complex. The structure of the 1,1-diethyl complex 6 is essentially the same except for the extra methylene group.

binding more efficiently to the metal. In both complexes the fold angle of the C_5 ring is 27.5° (this is the angle between the C(1)C(2)C(5) and the C(2)C(3)C(4)C(5) planes). There seems to be no reason why the ligand should not be able to fold further away from the metal, again suggesting that the interaction between the endo group and the metal may be attractive. In complex **6** Ir-C(1) is 2.71 Å and Ir-C(6) is 3.29 Å. The sum of the appropriate van der Waals radii is 3.65 Å and that of the covalent radii is 2.1 Å.

We need to consider the possibility that the C-H bonds (rather than the C-C bonds) of the system are binding significantly to the metal. Using the arguments we made in our studies of agostic C-H bonds in a closely related Ir system, we can say that in neither structure are the C-H bonds interacting very strongly with the metal. In the ethyl case, these hydrogens can be approximately located by assuming C(6) is tetrahedral, and our standard measure of strength of the interaction, r_{bp}, can be calculated as 1.64 Å for the CH bond closest to the metal. This represents little more than a van der Waals contact, which would give an r_{bp} of ca. 1.7 Å. In the case of **4a**, the hydrogen positions could not be calculated, but they cannot be very much closer to the metal than seems to be the case for **6**. Consistent with this conclusion, the ^{13}C NMR showed no perturbation of the values of ^1J(C,H) for the endo groups in each case. The final characterization of an agostic C-C bond in **4a** and **6** will require further work on related compounds. We hope in the future to look at 18-electron complexes of the diethyldiene ligand to see what happens when there is no possibility of an agostic C-C bond.

Conclusion

We have seen a surprisingly diverse series of C-C bond-breaking reactions in alkanes, alkenes, and dienes. Unstrained alkanes undergo C-C bond breaking by dehydrogenation followed by alkyl migration. In the alkene case a metathesis-like rearrangement may have been responsible for C-C cleavage. In the diene case a C-C cleavage/formation sequence led to overall rearrangement of the substituents of the diene, which implies that the cyclopentadienyl group is not always an innocent bystander in metal alkyl chemistry.

Experimental Section

NMR spectra were obtained on a Bruker 250 MHz instrument and IR spectra on a Nicolet 7000 instrument. Ligands were obtained from Aldrich Co., or elsewhere as noted.

Reaction of the Hydrocarbons with $IrH_2(Me_2CO)_2\{P(p\text{-}FC_6H_4)_3\}_2SbF_6$. Method A: Alkanes. The reactions were carried out in a 5 mL glass vial closed by a Teflon tap. To this vessel was added **1** (100 mg, 0.11 mmol) and 1,1-dimethylcyclopentane (0.4 mL, labeled 99.993% pure by the American Petroleum Institute, Carnegie Mellon University; no impurities were detected by GC). *tert*-Butylethylene (100 μL, 0.77 mmol) was added and the reaction mixture was freed from air by freeze-thaw cycling. The mixture was sealed in vacuo and heated to 150 °C for 8 h to give the 5,5-dimethylcyclopentadiene complex **2** (50%) and the methyl-

Table II. The Positional and Thermal[a] Parameters for the Chemically Significant Atoms[b] in **4a** and **6**

	ATOM	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
4a	Ir1	0.6068 (1)	0.3108 (1)	0.3847 (0)	53 (0)	52 (0)	43 (0)	−10 (0)	−11 (0)	−6 (0)
	Sb1	0.0673 (2)	0.3648 (1)	0.2958 (1)	72 (1)	92 (1)	74 (1)	1 (1)	23 (0)	13 (1)
	P1	0.5575 (4)	0.1999 (3)	0.3287 (2)	43 (2)	41 (3)	36 (2)	−6 (2)	1 (2)	−2 (2)
	P2	0.6809 (5)	0.2440 (4)	0.4642 (2)	43 (3)	66 (3)	42 (3)	−14 (2)	−2 (2)	−3 (2)
	F1	−0.0799 (21)	0.3386 (15)	0.3132 (12)	155 (19)	170 (22)	310 (31)	−48 (16)	106 (20)	0 (21)
	F2	0.2172 (16)	0.3986 (14)	0.2801 (8)	101 (12)	217 (22)	135 (15)	−37 (13)	31 (11)	−27 (14)
	F3	0.0877 (17)	2.637 (11)	0.2607 (9)	148 (15)	91 (13)	200 (19)	−4 (11)	36 (14)	−10 (13)
	F4	0.0514 (20)	0.4615 (14)	0.3277 (11)	161 (19)	168 (21)	291 (29)	−21 (16)	102 (19)	116 (20)
	F5	0.0151 (22)	0.4085 (14)	0.2319 (9)	208 (23)	177 (21)	170 (21)	8 (18)	−47 (17)	59 (17)
	F6	0.1261 (41)	0.3109 (23)	0.3555 (13)	561 (64)	293 (40)	212 (29)	187 (43)	−70 (35)	99 (28)
	C1	0.4827 (29)	0.4621 (15)	0.3811 (13)	137 (26)	36 (14)	132 (24)	2 (16)	−68 (21)	−21 (15)
	C2	0.5184 (27)	0.4118 (15)	0.3346 (12)	95 (21)	58 (16)	118 (23)	2 (15)	−30 (17)	−20 (15)
	C3	0.6402 (29)	0.4081 (16)	0.3302 (12)	118 (23)	72 (18)	89 (21)	−21 (17)	−16 (18)	35 (15)
	C4	0.6975 (21)	0.4272 (14)	0.3831 (11)	63 (17)	57 (14)	110 (19)	−8 (12)	−38 (14)	16 (13)
	C5	0.6077 (24)	0.4404 (20)	0.4141 (10)	107 (19)	153 (26)	49 (16)	−9 (18)	−15 (13)	11 (17)
	C6	0.3691 (22)	0.4371 (18)	0.4071 (12)	55 (16)	94 (20)	131 (25)	−13 (15)	−3 (15)	30 (18)
	C7	0.4849 (32)	0.5513 (19)	0.3661 (15)	153 (31)	77 (21)	167 (33)	−13 (21)	−56 (26)	−52 (22)
	C8	0.3788 (37)	0.5787 (21)	0.3225 (18)	180 (38)	82 (24)	205 (41)	21 (24)	−26 (32)	−3 (25)
6	Ir1	0.6195 (1)	0.3006 (0)	0.3817 (0)	39 (0)	40 (0)	37 (0)	−2 (0)	−1 (0)	−4 (0)
	Sb1	0.0771 (1)	0.3563 (1)	0.2969 (1)	52 (0)	75 (0)	65 (0)	0 (0)	13 (0)	8 (0)
	P1	0.5669 (3)	0.1878 (3)	0.3276 (2)	32 (2)	40 (2)	45 (2)	0 (1)	8 (1)	−9 (1)
	P2	0.6900 (3)	0.2361 (3)	0.4615 (2)	31 (2)	60 (2)	37 (2)	−2 (1)	2 (1)	0 (2)
	F1	0.0618 (13)	0.3194 (11)	0.3224 (7)	109 (11)	173 (16)	205 (16)	−79 (11)	84 (11)	−27 (13)
	F2	0.2203 (12)	0.3940 (11)	0.2729 (6)	82 (9)	176 (16)	147 (13)	−43 (9)	−42 (8)	−13 (11)
	F3	0.0966 (14)	0.2584 (10)	0.2621 (8)	115 (11)	102 (11)	251 (20)	5 (9)	38 (12)	−45 (12)
	F4	0.0608 (16)	0.4507 (12)	0.3300 (10)	147 (15)	138 (15)	318 (27)	−22 (12)	117 (16)	−84 (17)
	F5	0.0068 (15)	0.3906 (13)	0.2333 (7)	130 (13)	225 (21)	141 (14)	−21 (13)	−24 (11)	57 (14)
	F6	0.1561 (18)	0.3198 (16)	0.3590 (8)	171 (17)	297 (28)	163 (16)	−78 (18)	−55 (13)	122 (18)
	C1	0.5145 (14)	0.4527 (10)	0.3724 (7)	46 (9)	44 (9)	50 (10)	−4 (7)	−6 (7)	−7 (7)
	C2	0.5499 (16)	0.4017 (11)	0.3257 (7)	74 (12)	54 (10)	40 (10)	−7 (9)	−14 (8)	0 (7)
	C3	0.6708 (15)	0.3935 (10)	0.3264 (7)	51 (10	49 (10)	48 (10)	2 (7)	14 (.8)	4 (7)
	C4	0.7146 (17)	0.4144 (11)	0.3784 (7)	78 (12)	49 (11)	48 (11)	−18 (9)	2 (9)	−1 (8)
	C5	0.6213 (14)	0.4313 (11)	0.4089 (7)	38 (9)	63 (11)	67 (11)	−2 (8)	4 (8)	−2 (9)
	C6	0.3937 (16)	0.4288 (11)	0.3942 (7)	63 (12)	58 (11)	61 (11)	29 (9)	−24 (9)	−7 (8)
	C7	0.5122 (21)	0.5475 (12)	0.3586 (8)	112 (17)	49 (12)	76 (13)	16 (11)	−25 (12)	−11 (10)
	C8	0.4054 (25)	0.5746 (15)	0.3169 (10)	138 (23)	80 (17)	99 (18)	22 (16)	−7 (16)	10 (14)
	C9	0.3595 (19)	0.4708 (14)	0.4474 (9)	91 (15)	88 (16)	90 (16)	26 (12)	26 (12)	−31 (13)
	H61	0.3298	0.4401	0.3651						
	H62	0.3936	0.3675	0.4000						
	H71	0.5116	0.5800	0.3927						
	H72	0.5908	0.5621	0.3432						

[a] Anisotropic thermal parameters in the following form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^{*2} + 2U_{23}klb^*c^*)] \times 10^4$. [b] For the other atoms, see supplementary material.

Table III. Significant Interatomic Angles (deg) and Distances (Å) for **4a** and **6**

	4a	**6**
Ir–C1	2.80 (2)	2.71 (2)
Ir–C6	3.40 (3)	3.29 (2)
Ir–H61		2.81
Ir–H62		3.94
Ir–C2	2.22 (3)	2.23 (2)
Ir–C3	2.10 (3)	2.12 (2)
Ir–C4	2.13 (2)	2.12 (2)
Ir–C5	2.21 (3)	2.20 (2)
Ir–C9		4.38 (2)
Ir–P1	2.289 (5)	2.295 (4)
Ir–P2	2.312 (5)	2.297 (4)
C1–C2	1.47 (4)	1.48 (2)
C2–C3	1.36 (4)	1.36 (2)
C3–C4	1.43 (4)	1.37 (2)
C4–C5	1.31 (4)	1.36 (2)
C5–C1	1.59 (4)	1.48 (2)
C1–C6	1.50 (4)	1.54 (2)
C1–C7	1.48 (4)	1.56 (2)
P1–Ir1–P2	100.9 (2)	101.0 (2)
C5–C1–C6	117 (2)	115 (1)
C5–C1–C7	108 (2)	111 (1)
C2–C1–C6	117 (2)	115 (1)
C2–C1–C7	110 (3)	112 (1)
C2–C1–C5	90 (2)	95 (1)
C6–C1–C7	113 (2)	108 (1)
C1–C6–C9		118 (2)
C1–C7–C8	114 (3)	114 (2)

cyclopentadienyl iridium methyl complex **3** (5%). After 18 h at 150 °C, only **3** was observed (50%) in the products. The products were detected by their characteristic ^{1}H NMR resonances (see below). 1,1-Dimethylcyclohexane (Aldrich, absence of alkenes verified by GC) gave the dimethylcyclohexadienyl iridium hydride **5** in 65% yield after 24 h at 145 °C.

Method B: Alkenes. These reactions were carried out as above but in neat alkene without added tbe and at 85 °C for 2 h.

Method C: Arenes. This reaction was carried out in neat arene with the present as in method A.

Isolation of Products. In each method, the complexes were isolated by removing the volatiles in vacuo (these were also routinely analyzed by GC) and recrystallizing the residue from CH_2Cl_2/Et_2O.

Bis[tris(*p*-fluorophenyl)phosphine](5,5-Dialkylcyclopentadiene)iridium(I) Hexafluoroantimonates (2). All these complexes were deep red to purple in color. The dimethyl complex was best prepared from 5,5-dimethylcyclopentadiene[18] and **1** following method B; yield 95%. Anal. Calcd for $C_{43}H_{34}F_{12}P_2IrSb\cdot 2.5CH_2Cl_2$, Et_2O: C, 43.95; H, 3.42. Found: C, 44.10; H, 3.29. The solvents of crystallization were detected in the ^{1}H NMR spectrum. ^{1}H NMR (90 MHz, $(CD_3)_2CO$): δ 0.82 (s, endo Me), 1.62 (s, *exo*-CH_3), 4.2 and 5.6 (c, Cp), 7.08–7.96 (c, Ar). ^{13}C NMR (off-resonance decoupled): δ 24.6 and 37.1 (q, CH_3), 62.2 (s, Cp quaternary), 90.7 and 94.3 (d, Cp), 121.6, 132.2, 141.0, 169.7, (m, Ar). ^{31}P NMR: δ 15.1. The 5-ethyl-5-methylcyclopentadiene complex was prepared in the same way from the diene[18] (yield 80%). Two isomers were observed in a 3:1 ratio. The major (maj) isomer was the *endo*-methyl complex as shown by ^{1}H NMR NOE experiment. ^{1}H NMR: δ 0.56 (t, 7.4 Hz, CH_3CH_2 (maj)), 0.76 (s, Me (min)), 0.93, (t, 7.4, CH_3CH_2 (min)), 1.12 (q, 7.5, CH_3CH_2 (maj)), 1.59 (s, Me (maj)), 2.14

(18) Eilbracht, P. *Ann.* **1979**, 1890.

(q, 7.5, CH_3CH_2 (min)), 3.81 and 3.92 (c, Cp (maj and min)), 5.42 (c, Cp), 7.09–7.32 (c, Ar). The 5,5-diethylcyclopentadiene complex was similarly prepared in 75% yield from the diene.[18] Anal. Calcd for $C_{45}H_{38}F_{12}P_2IrSb\cdot 3CH_2Cl_2$, Et_2O: C, 43.87; H, 3.61. Found: C, 43.92; H, 3.29. ^1H NMR: δ 0.51 (t, 7, CH_3CH_2 (exo)), 0.9, (t, 7, CH_3CH_2 (endo)), 1.18 (q, 7, (exo)), 2.35 (q, 7, CH_2CH_2 (endo)), 4.13 and 5.71 (c, Cp), 7.13–7.79 (c, Ar). ^{31}P NMR: δ 15.1. The spiro[4.4]nonadiene complex was prepared similarly in 85% yield from the diene.[19] Anal. Calcd for $C_{45}H_{36}F_{12}P_2IrSb\cdot 2CH_2Cl_2$, Et_2O: C, 45.92; H, 3.54. Found: C, 45.51; H, 3.13. ^1H NMR: δ 1.35 (c, CH_2), 1.66 (c, CH_2 (exo)), 2.22 (c, CH_2 (endo)), 4.26 and 5.61 (c, Cp), 7.06–7.65 (c, Ar). ^{31}P NMR: δ 14.28. Endo and exo resonances were only rigorously identified for the methylethyl complex, but the analogy between the complexes appears to be good.

(Alkylcyclopentadienyl)bis[tris(*p*-fluorophenyl)phosphine]alkyliridium(III) Hexafluoroantimonates (3). All these complexes were off-white in color. $[(RC_5H_4)IrR'L_2]SbF_6$ where R = R′ = Me was also prepared by the general method A from the corresponding diene complex of type **2**.

Method D. The alkyl complexes of type **3** were best prepared by pyrolysis of the diene complexes of type **2** dry and in vacuo at 150 °C for 24 h in a sealed 5-mL glass vial. These transformations were quantitative and gave very pure products. They could be recrystallized from CH_2Cl_2/Et_2O.

Method E. This method was used merely to verify the identity of **3** (R = R′ = Me) by independent synthesis of one case. To $[Ir(cyclooctene)_2Cl]_2$ (126 mgs, 0.14 mmol) in THF (7 mL) at −78 °C was added tris(*p*-fluorophenyl)phosphine (179 mg, 0.57 mmol). After 10 min Na[C_5H_4Me] (0.28 mmol as a 2.2 M solution in THF) was added and the mixture was stirred for 12 h, keeping the outside of the vessel at −78 °C; it was then warmed to 0 °C. Excess iodomethane (1 mL) was added at 0 °C, and the mixture was stirred for 1 h. The solvents were removed, and the product was treated with [Na][SbF_6] (100 mg) in acetone (5 mL). After 5 min of stirring at 25 °C, the solvents were removed and the residue was washed with H_2O and removed in vacuo over 25 h. The residue was taken up in the minimum volume of CH_2Cl_2 and recrystallized by adding Et_2O/pentane. The yield was 50 mg (17%) of a product spectroscopically identical with that formed from the dimethyldiene complex of type **2**. It was not microanalyzed. Alternatively, Na[C_5H_5] and Na[EtC_5H_4] can be used as the nucleophile and EtI can be used as the electrophile to prepare related complexes in comparable yields (20–25%). This method was used for identification rather than synthesis.

The following products were best prepared by method D. For example **3**, R = R′ = Me. Anal. Calcd for $C_{43}H_{34}P_2F_{12}SbIr$: C, 44.73; H, 2.95. Found: C, 44.94; H, 2.80. ^1H NMR ($(CD_3)_2CO$): δ 1.45 (t, ^2J(P,H) = 5.5 Hz), IrMe), 1.83 (C_5H_4Me), 5.04 and 5.50 (c, C_5H_4Me), 6.95–7.48 (c, Ar). ^{31}P NMR (CD_2Cl_2): δ −12.2 (s). ^{13}C NMR (CD_2Cl_2, off-resonance decoupled): δ −27.7 (tq, Ir*Me*), 11.29 (q, $C_5H_4CH_3$), 66.0 and 88.4 (d, Cp), 112.1 (s, Cp), 116.5, 128.3, 136.2, 164.8 (d, Ar). **3** (R = Et, R′ = Me) was prepared by method C to 79% yield after recrystallization from CH_2Cl_2/cyclopentane. Anal. Calcd for $C_{44}H_{36}P_2F_{12}SbIr$: C, 45.31; H, 3.09. Found: C, 45.10, H, 3.00. ^1H NMR (CD_2Cl_2): δ 1.17 (t, 7.6, CH_2CH_3), 1.33, 5 (5.3, IR-Me), 2.1 (q, 7.6, CH_2CH_3), 5.52 and 5.24 (c, Cp), 7.05 (c, Ar). Complex **9** was prepared from the spirononadiene complex **2** by method C in 80% yield after recrystallization from CH_2Cl_2/hexanes. Anal. Calcd for $C_{45}H_{36}P_2F_{12}SbIr$: C, 45.86; H, 3.05. Found: C, 45.65; H, 2.95. ^1H NMR ($(CD_3)_2CO$: δ 2.4–2.8 (c, $(CH_2)_4$), 4.83 and 5.77 (c, Cp), 7.25 (c, Ar).

Pyrolysis of (5,5-Diethylcyclopentadiene)bis[tris(*p*-fluorophenyl)phosphine]iridium(I) Hexafluoroantimonate (6). The title complex was subjected to the conditions of method D. An inseparable mixture of two compounds was formed. These were identified as 1,2- and 1,3-isomers of $[(Et_2C_5H_3)IrL_2H]SbF_6$ by NMR spectroscopy. ^1H NMR (CD_2Cl_2): δ 7.1 (c, Ar), 4.98, 4.75, 4.30 (c, Cp), −14.7 and −15 (t, 15, Ir–H). ^{31}P NMR (acetone): δ +5.3 and +4.33. ^{13}C NMR (CD_2Cl_2, off-resonance decoupled, multiplicity in parentheses; two peaks are usually observed for each type of carbon because two isomers **7a** and **7b** are present): δ 15.7 and 17.0 (q, Me), 18.8 and 20.9 (CH_2), 84.1, 85.2, 86.9, and 92.7 (d, Cp), 110.6 (s, Cp 4°).

(η^5-Ethylcyclopentadienyl)hydridobis[tris(*p*-fluorophenyl)phosphine]iridium(III) Hexafluoroantimonate. $[CpIrEtL_2]SbF_6$ was prepared by method E in 8% yield and heated dry by method D to give the title complex in 75% yield after recrystallization from CH_2Cl_2/Et_2O. ^1H NMR (CD_2Cl_2): δ −14.6 (t, 29.2, IrH), 1.17 (t, 7.9, CH_3), 2.22 (c, CH_2), 4.48, 5.32 (c, Cp), 7.2 (c, Ar). The same product was formed from 1-ethylcyclopentene and **1** by method B in 90% yield.

Crystallography. Crystals of $IrSbP_2F_{12}C_{44}H_{36}$ (**4a**) and $IrSbP_2F_{12}C_{45}H_{38}$ (6) were sealed in a capillary and mounted on a Synthex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures with molybdenum radiation (λ = 0.71069 Å). Data (9298 points for each complex) were collected at room temperature with a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections, and for the intensities of these reflections showing less than 8% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background but not absorption effects. After removal of redundent and space group forbidden data, 3701 reflections (**4a**), 4602 (6), were considered observed [$I > 3.0\sigma(I)$]. The structure was solved for heavy-atom positions by direct methods with MULTAN80.[20] Successive least-squares/difference Fourier cycles allowed location of the remainder of the non-hydrogen atoms. Refinement of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. Hydrogen positional parameters with the exception of those associated with C6 and C8 (**4a**) and C8 and C9 (6) were calculated assuming normal geometry and a C–H distance of 0.97 Å. Repeated attempts to locate hydrogens associated with the methyl carbons in a difference Fourier synthesis were unsuccessful. Hydrogen atoms were included in the final cycles of refinement with isotropic thermal parameters of U = 0.03. All parameters associated with hydrogen atoms were held invariant. The final cycle of refinement [function minimized $(|F_o| - |F_c|)^2$ led to a final agreement factor R = 6.3% (**4a**) and 6.0% (6) [$R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$]. Anomalous dispersion corrections were made for Ir and Sb. Scattering factors were taken from Cromer and Mann.[21] Unit weights were used throughout.

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Supplementary Material Available: Tables of full thermal and positional data and further distances and angles for **4a** and **6** (7 pages); table of structure factors (49 pages). Ordering information is given on any current masthead page.

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