Organometallics 1984, *3*, 1727-1731

58-8; DCPD, 91523-73-8; Me_6Sn_2, 661-69-8; Na, 7440-23-5; $CH_3CH(OH)(CH_2)_3CH{=}CH_2$, 24395-10-6; $(C_6H_{11})_2P(O)OH$, 832-39-3; $(C_6H_{11})_2PCl$, 16523-54-9; $CH_3CHBr(CH_2)_7CH{=}CH_2$, 91523-74-9; $CH_3C(O)(CH_2)_7CH{=}CH_2$, 36219-73-5; $I(CH_2)_4CH{=}CH_2$, 18922-04-8; $CH_3CH(OH)(CH_2)_7CH{=}CH_2$, 91523-75-0; (*R*)-$CH_3(CH_2)_5CH(CH_3)SnMe_3$, 79055-01-9; (*S*)-$CH_3(CH_2)_5CH(CH_3)SnMe_3$, 79054-99-2; 5-chloro-2-pentanone ethylene ketal, 5978-08-5.

Haptotropic Rearrangements and C–H Bond Activation in Indan, Indenyl, and Naphthalene Complexes of Iridium

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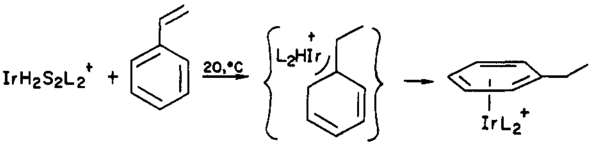
2-Vinylnaphthalene reacts with $[IrH_2(Me_2CO)_2L_2]A$ (**1**, L = PPh_3, A = SbF_6) to give $[Ir(NpEt)L_2]A$ (**3**, NpEt = 2-ethylnaphthalene). Below 10 °C the kinetic product has the metal bound to the ring bearing the ethyl group. Above 10 °C a 50:50 mixture of haptomers is formed in each of which the metal is bound to a different ring. Indene reacts with **1** at 25 °C to give $[Ir(\eta^6\text{-indan})L_2]A$ (**4**), but at 80 °C, **4** dehydrogenates to give $[Ir(\eta^5\text{-indenyl})HL_{32}]A$ (**5**). Indan reacts with **1** and *tert*-butylethylene (tbe) at 90 °C to give first **4** and then **5**, an example of arene precoordination facilitating CH activation on the side chain. **3**, **4**, and **5** as well as the related $[Ir(\eta^5\text{-}C_6H_7)HL_2]A$ all react with tbe and cyclopentane at 100 °C to give $[IrCpHL_2]A$, all examples of alkane C–H activation. The conformation of the idenyl ring in **5**, deduced from NMR measurements, puts H trans to the fused benzene ring, contradicting the expectation based on steric effects. A rationalization is proposed that also embraces other literature examples. **5** has largely 18-electron character with an η^5-indenyl and is chemically rather inert, but **3** has largely 16-electron character with an η^4-NpEt ligand and is chemically very reactive. ^{13}C NMR was used to determine the hapticity of the carbocyclic ligands.

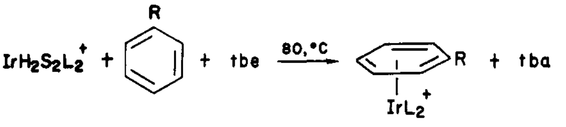
In looking for ways to generate multiple active sites on metal complexes, we have made extensive use of $[IrH_2(Me_2CO)_2(PPh_3)_2]A$ (**1**, A = noncoordinating anion). Both the hydrogen and the acetone can be lost to give a highly reactive system that can even dehydrogenate alkanes.[1] Unfortunately, the range of phosphorus ligands for which these acetone complexes are stable is limited, as is the range of metal systems forming acetone complexes. We therefore sought to free ourselves of this limitation by moving to removable ligands other than acetone and H. We were attracted to the idea of using η^6-arene complexes, which generate three two-electron sites if the arene were lost. The corresponding η^5-cyclohexadienyl and η^4-diene complexes were also studied for completeness. We wished to test these ideas in a known system, one we knew would be active for alkane dehydrogenation if the arene were liberated. We therefore began our studies on some bis(triphenylphosphine)iridium complexes related to **1**.

Results and Discussion

Arene Complexes. We showed recently that styrene reacts with the acetone complex **1** to give $[(\eta^6\text{-PhEt})IrL_2]A$ (eq 1, L = PPh_3)[2] and that a variety of arenes (e.g., C_6H_6, PhMe) react with **1** and tbe (tbe = *tert*-butylethylene) to give $[(\eta^6\text{-ArH})IrL_2]A$ (**2**, ArH = arene) in a more general synthesis of the same type of complex (eq 2).[3]



(1)



(2)

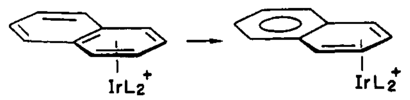
S = Me_2CO, L = PPh , tbe = t - BuCH ═ CH , tba = t-BuEt

When these were heated with cyclopentane and tbe in a sealed tube at 110 °C for 18 h, we observed mostly free arene but only 5% of the alkane dehydrogenation product $[IrHCpL_2]A$ (eq 3 and 4). This suggested that the same reactive system that can be formed directly from **1** is also formed from **2**, but less effectively. This shows that the general principle seems to hold but that simple η^6-arene complexes might not be the best choice of labile ligands.

$$IrH_2S_2L_2^+ + 3tbe + C_5H_{10} \rightarrow IrCpHL_2^+ + 3tba + 2S \tag{3}$$

$$Ir(ArH)L_2^+ + C_5H_{10} + 2tbe \rightarrow IrCpHL_2^+ + 2tba + ArH \tag{4}$$

Naphthalene Complexes. We wondered whether naphthalene might be a more suitable leaving group, because the first act of arene departure may be an η^6 to η^4 rearrangement of the arene. In the case of naphthalene, this could be aided by the recovery of benzenoid character in the uncomplexed ring (eq 5).



(5)

For the synthesis of a suitable complex, we first tried the action of 2-vinylnaphthalene with **1**. As expected from our experience with styrene (see eq 1), we did indeed obtain the desired $[Ir(NpEt)L_2]A$ (**3**, NpEt = 2-ethylnaphthalene) but as a mixture of isomers, the iridium being

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[1] Crabtree, R. H.; Demou P. C.; Eden, D.; Mihelcic J. M.; Parnell, C.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994.

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

[3] Crabtree, R. H.; Parnell, C. P. *Organometallics*, in press.

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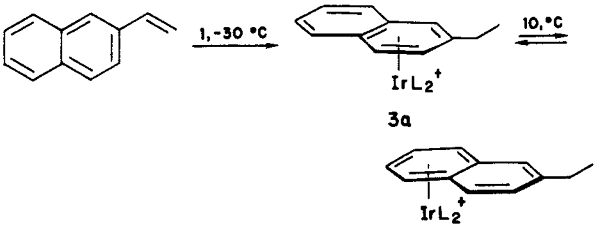
Table I. NMR Data for the New Complexes

	^{13}C[a]			^{1}H[a]		
complex	δ[b]	Δδ[c]	assignt[d]	δ[e]	intg[f]	assignt[d]
3a	113.2 (s)	−28.4	2	7.74 (t, 6.9)	1	5, 8
	90.2 (d)	−40	1, 3-4	7.72 (t, 6.9)	1	
	86.9 (d)			6.93 (d, 7.1)	2	6, 7
	83.0 (d)			5.49 (d, 6.5)	1	1
	125.3 (s)	−8	9-10	5.06 (d, 6.5)	1	
	125.7 (s)			4.42 (s)	1	
	124.4 (d)	−2.3	5-8	2.96 (c)	1	11′
	123.9 (d)			2.70 (c)	1	11″
	16.3 (q)	+0.8	12	1.36 (t, 7)	3	12
	27.7 (t)	−1.3	11			
3b	146.8 (s)	+5.2	2	7.63 (7)	1	4
	125.1 (d)	−3.1	1, 3-4	7.10 (7)	1	3
	122.7 (d)			6.80 (s)	1	1
	122.5 (d)			6.44 (dd, 5, 5.2)	1	5, 8
	122.6 (s)	−10.3	9-10	6.30 (dd, 5, 5.2)	1	
	90.9 (d)	−38.5	5-8	4.75 (t, 5.7)	2	6, 7
	89.3 (d)			2.71 (q)	2	11
	86.6 (d)			1.33 (t)	3	12
	85.3 (d)					
4	122.2 (s)	−21.8	8-9	6.26 (dd, 4.4, 2.7)	2	4, 7
	95.8 (d)	−31.5	4-7	4.94 (dd, 4.4, 2.7)	2	5, 6
	91.5 (d)			2.45 (c)	4	1, 3
	31.0 (t)	−1.9	1, 3	2.1 (c)	2	2
	26.0 (t)	+0.7	2			
5	114.9 (s)	−29.1	8-9	7.33 (c)[g]	2	4, 7
	122.3 (d)	+0.9		6.58 (c)	1	2
	129.9 (d)		4-7	5.78 (dd, 3, 6.2)	2	5, 6
	92.7 (d)		2	5.24 (t, 3)	2	1, 3
	75.8 (dt)		1, 3	−19.10 (t, 23.5)	1	Ir-*H*

[a] Conditions: for 3, BF_4 salts in CD_2Cl_2 at −20 °C; for 4-5, BF_4 salts in CD_2Cl_2 at 20 °C. Resonances due to PPh_3 (^1H, δ 7.2-7.8; ^{13}C, δ 128-134) are not listed. [b] Chemical shift (ppm) relative to Me_4Si and multiplicity (s = singlet, d = doublet) from gated decoupled spectra. [c] Coordination shift from ethylnaphthalene (3), indan (4), or indene (5). [d] See text for numbering scheme. [e] Chemical shift (ppm) relative to Me_4Si multiplicity and coupling const (Hz). [f] Integration. [g] Resonances assigned to the ortho hydrogens of the PPh_3 groups were observed in the range δ 6.87-6.95 and to the meta and para hydrogens at δ 7.23-7.42. For comparison, $[IrCpHL_2]^+$ has PPh_3 resonances at δ 7.27-7.48.

bonded to the alkylated ring as well as to the other one (eq 6). The reaction mixture was monitored by ^1H NMR on warming from −80 °C. At −30 °C, reaction was observed to give only one isomer **3a**, which underwent a haptotropic rearrangement only on warming to +10 °C, when the 50:50 mixture of haptomers **3a** and **3b** was established within minutes. The reason only one isomer is observed initially is that, as we have previously shown,[2] these reactions proceed via an intermediate η^3-benzyl species of the type shown in parentheses in eq 1. This intermediate naturally leads to **3a**, which subsequently rearranges to **3b** (eq 6).



3a

3b

(6)

This rearrangement is intramolecular since no trace of the excess vinylnaphthalene is ever incorporated into the products nor did the complex exchange with free naphthalene.

Dr. Michelle Mellea[4] in our group has observed similar behavior with 4-phenylstyrene. Here, the metal initially becomes coordinated to the ethyl substituted ring, and brief heating to 40 °C is required to effect the haptotropic rearrangement to give a 50:50 isomeric mixture. In this biphenyl system the isomerization seems to be slightly more difficult than in the fused-ring naphthalene system mentioned above.

These rearrangements are relatively unusual examples of haptotropism.[5,6] Albright and Hoffmann et al.[5] have concluded from a theoretical study that such rearrangements will tend to have a high activation energy, at least for $Cr(CO)_3$ and isolobal fragments, and that the least motion pathway is symmetry forbidden so a circuitous route is preferred. Experimentally,[6] such rearrangements are generally very slow ($t(1/2)$ > 30 min) at 25 °C, in contrast to what we see here. Intramolecular haptotropism in a biphenyl system seems never to have been previously observed. Our results suggest that the IrL_2^+ fragment may be particularly apt for haptotropism. Apart from the characteristic ease of 16-electron/18-electron rearrangements in this system, we can suggest no cogent reason.

3 seems to be more reactive than other arene complexes of the same type. It reacted with cyclopentene and cyclooctene even in refluxing CH_2Cl_2 (40 °C) to give $[IrHCpL_2]A$ and $[Ir(cod)L_2]A$ quantitatively. Reflux in acetone gave $[IrH_2(Me_2CO)_2(PPh_3)_2]A$. This reaction will be discussed in detail elsewhere.[3]

The naphthalene complex proved to be a poor precursor for alkane activation reactions, however. Only ca. 5% of $IrCpHL_2^+$ was formed from cyclopentane under our

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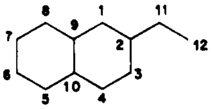
(4) Mellea, M. F. Ph.D. Thesis, Yale University, 1984.

(5) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

(6) (a) Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1978**, 142. (b) Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko, Y. F.; Roznyatovsky, V. A.; Luzikov, Y. N.; Ustynyuk, Y. A. *J. Organomet. Chem.* **1980**, *202*, 279. (c) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654. (d) Kundig, E. P.; Timms, P. L. *Ibid.* **1980**, 881. (e) Treichel, P. M.; Fivvizzani, K. B.; Haller K. J. *Organometallics* **1982**, *1*, 931.

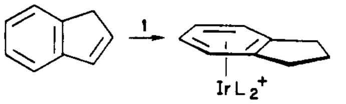
standard conditions (see Experimental Section).

The identification of the two haptomers **3a** and **3b** followed from their ^{1}H and ^{13}C NMR spectra (Table I). The resonances for **3a** were easily distinguished from those for **3b** by observing the spectrum of pure **3a** at 0 °C. In the cases of **3a** and **3b**, the ^{13}C NMR spectrum was studied both with ^{1}H decoupling and with off-resonance gated decoupling (to reveal the number of protons to which each carbon was attached). The CH_2CH_3 resonances were little shifted from the corresponding resonances of free NpEt, as expected.[2] The ring carbons fell into two groups. One group showed a strong high-field shift, easily detected as these fall in an otherwise empty region of the spectrum. By analogy with the similar shifts,[2] we found for $[(\eta^2\text{-PhEt})IrL_2]A$, these were assigned to ring carbons in the bound ring. The second group fell in a position little shifted from their position in free NpEt, but these were sometimes obscured by the intense PPh_3 resonances that occur in the same region, so we cannot be certain about their number and identification. Among the shifted group, **3a** shows one singlet and three doublets, indicating that these carbons are carbons 1–4 of the NpEt group (see diagram I for our numbering scheme). In contrast, **3b** shows four shifted doublets, indicating that iridium is bound to carbons 5–8. The ^{1}H NMR (Table I) is similar in that one group of aromatic CH resonances is shifted and can be identified with certainty and the other group is little shifted and partially obscured by PPh_3 resonances. The picture that emerges from a study of the shifted group is consistent with what we saw above: **3a** has three protons and **3b** has four. In confirmation of these assignments, the $CH_3CH'H''$ group in **3a**, but not in **3b**, shows the separate resonances for the diastereotopic hydrogens H′ and H″. This is expected whenever there is no plane of symmetry that contains the C_2-C_{11} bond. In principle, both **3a** and **3b** should show this effect but in **3a** the IrL_2^+ group is close to the ethyl group, thus breaking the local symmetry more effectively than in the case of **3b** where the IrL_2^+ group is on the distant ring.



Both **3a** and **3b** can be regarded as η^6-arene complexes, as shown in eq 4. However, a notable feature of Ir(I) chemistry is its preference for the 16-electron configuration. Equation 5 shows how an 18-electron η^6 complex could become a 16-electron η^4 species by a lateral movement of the IrL_2^+ fragment. This would be favored for naphthalene because the uncomplexed ring can now become fully benzenoid, as mentioned above. This might be accomplished by a bending of the naphthalene at carbons 1 and 4 to remove the free benzenoid ring from coordination to the metal. Such a structure would also be consistent both with the deep wine red color of **3** (since, empirically, 16-electron $Ir(PPh_3)_2$-containing complexes are red or purple and 18-electron ones are often colorless to yellow) and with the high reactivity of the complex. In connection with this idea, it is interesting to note that for **3a** that the unequivocally metal-bonded carbons show ^{13}C NMR coordination shifts of −28 to −40 ppm and the unequivocally nonbonded ring carbons shifts of −2.3 ppm but carbons 9 and 10 an intermediate shift of 8 ppm. This intermediate shift would be consistent with the long Ir–C distances and low Ir–C bond order for C9 and C10 as expected for an η^4 structure. This method for determining hapticity may well be generally applicable. A few other examples of η^4-naphthalene complexes are known,[7] but ^{13}C NMR data are not available.

Indene Complexes. The results obtained with naphthalene encouraged us to look at the closely related case of indene. Since it can be regarded as a special case of a substituted styrene, it is not surprising that indene reacts with 1 (40 °C, 6 h) according to eq 7 in a way analogous

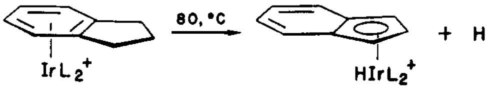


(7)

4

to the reaction with styrene (eq 1) and with vinylnaphthalene (eq 4).

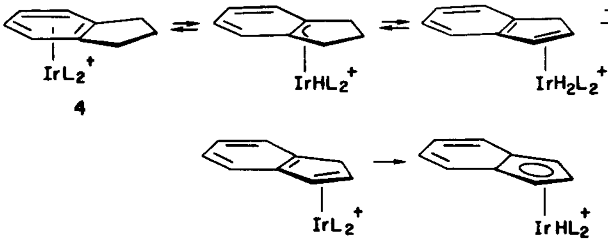
The structural assignment for 4 followed from the ^{1}H and ^{13}C NMR spectra. The four aromatic protons suffer the usual high-field shift on complexation, and the saturated ring appears in the form of two broad resonances at δ 2.45 (benzylic CH_2) and 2.1 (homobenzylic CH_2), the former slightly shifted (−0.5 ppm) from the position in free indan. The carbon resonances behave similarly. The aromatic carbons show a high-field coordination shift, but the aliphatic CH_2's show negligible shift (from free indan). If the indan complex 4 is refluxed in $C_2H_4Cl_2$ with or without tbe as the hydrogen acceptor, the cream-colored $[IrH(indenyl)L_2]A$ (**5**) is formed after 4 h. In view of the



(8)

4 5

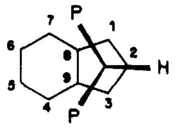
stoichiometry of the reaction, H_2 must be released, although we have not been able to verify this experimentally. Since added cyclopentene did not intercept the $IrHL_2^+$ fragment to give $IrCpHL_2^+$, we assume the reaction is intramolecular. The most reasonable mechanism is shown below (eq 9). It will be seen that the proposed intermediates are an η^3-benzyl complex of the type proposed in reactions 1 and 7, a diene dihydride, and a diene complex, all of which have precedent.[1] The first step in eq 9 is probably not rate determining, because the proposed η^3-benzyl complex is the same one that must be involved in reaction 7 (cf. eq 1), where it rearranges to 4. Although the relevant thermodynamic data are not available to be sure, the fact that reaction 9 goes from left to right suggests that the metal–arene bond dissociation energy may be lower than that for M–Cp. The same pattern also appears in literature data.[6e]



(9)

4 5

The Structure of 5 and the Orientation of the Indenyl Group. The structure of **5** was assigned on the basis of the ^{1}H and ^{13}C NMR spectra. For example, the ^{13}C NMR showed three resonances in positions that could be assigned to carbons bound to Ir. The quaternary carbons resonate at δ 114.87 and a resonance at δ 92.67 was assigned to C1 and C3 and at δ 75.82 to C2. C4–7 resonate at frequencies that differ little from those found in free indan. Only C1 and C3 show a virtually coupled triplet due to coupling to phosphorus ($^2J(P, C)$ = 6 Hz). This would be best explained if the rotamer of the type shown below were preferred; only in this rotamer are C1 and C3 trans to phosphorus. Twelve protons of the PPh_3 groups also show a ca. 0.4 ppm diamagnetic shift compared to $[IrCpHL_2]^+$. This is also consistent with the proposed structure since the 12 ortho protons of the PPh_3 groups would all be expected to spend some time in the region of space normal to the plane of the C4–C9 ring of the indenyl group, in which a strong diamagnetic shift is to be expected due to the aromatic ring current. Related observations have been made by Faller.[8a] Very recently, Faller has confirmed this conformational preference for **5** by X-ray crystallography, a result which will appear separately.[8b] This conformation contradicts the usual steric effect argument by which the bulky C4–C9 aromatic ring of the indenyl group might be expected to position itself opposite the PPh_3 groups, not next to them as is found. We propose that the high trans effect ligand, H in this case, will always tend to orient the indenyl ring so the C8–C9 are trans to that ligand. The most reasonable explanation is, we believe, that the H will lengthen the Ir–C8 and Ir–C9 bonds (a ca. 8.5% lengthening is found[8] crystallographically) by the usual trans effect and allow C8 and C9 to contribute more fully to the aromatic stabilization of the C4–C9 ring. This is preferable to orienting the H trans to C1–C3 because in this case the loss in Ir–C bonding would not be compensated by a gain in aromatic stability of C4–C9. These ideas tend to be confirmed by comparison with known structures of indenyl complexes, for example, $(\eta^5\text{-Ind})(\eta^3\text{-Ind})W(CO)_2$,[9a] $(\eta^5\text{-Ind})Cr(CO)_2(NO)$,[9b] and $(\eta^5\text{-Ind})Mo(PMe_3)_2(MeC{\equiv}CMe)$,[9c,d] where the higher trans effect ligands CO, NO, and PR_3, respectively, are trans to the fused ring. $(\eta^5\text{-Ind})Rh(PMe_3)_2H^+$ is known[9e] and probably has the same type of structure.



The ^1H NMR spectrum of **5** confirms the structure. A triplet at δ −19.5 has a similar chemical shift and coupling constant to those of the IrH resonance in the closely related complex $[IrHCpL_2]A$. A peak at δ 6.58, integrating for one proton, was found to be coupled to the ^{13}C peak at δ 92.67, and a peak, integrating for two protons, at δ 5.24 correlated with the carbon resonance at δ 75.82. This allowed the unambiguous assignment of C1–3 and H1–3 and shows that the Ir is bound to the five-membered ring.

The Chemistry of 4 and 5. Neither **4** nor **5** had activity for alkane activation nor would they react with a number of other reagents. **4** always reacted to give **5**, and **5** was inert to the common reagents we tried. For instance, it failed to react with alkenes or HCl in refluxing $C_2H_4Cl_2$, light at 360 nm, CO at 25 °C, and acetone at reflux. PMe_3 gave some phosphine exchange, but slowly, and no pure product was isolated. Neither complex reacted with tbe in alkanes. This was a disappointment because we had hoped that $\eta^5 \rightleftharpoons \eta^3$ ring slippage would occur in the case of **5** leading to the formation of a reactive 16-electron intermediate. This contrasts strikingly with the high reactivity of the naphthalene complexes of type **3**, for which the η^4 structure was suggested above. The bridgehead carbons (C9 and C10 for **3** and C8 and C9 for **5**) that showed a low coordination shift (−8 ppm) in the case of the naphthalene complex **3** show an unambiguously metal-bonded shift (−29 ppm) for **5**. An η^5 structure is indicated, as is consistent with the cream color observed for **5**. This suggests (Figure 1) that the attaintment of benzenoid character in the uncomplexed ring is an insufficient driving force to make **5** adopt the η^3 structure, whereas it is sufficient to make **3** adopt the η^4 structure. We cannot yet say whether this difference is determined by the nature of the metal site or of the carbocyclic ligands. Perhaps the main determining factor is the preference of Ir(III) for 18-electron and of Ir(I) for 16-electron configurations. The naphthalene ligand does have an influence because benzene is η^6 in $Ir(C_6H_6)L_2^+$.[2,3] If **5** is best described as having an η^5-Ind ligand, the benzo ring should have dienoid character. To test this idea, we attempted a Diels–Alder reaction with dimethyl acetylenedicarboxylate. No reaction was observed, nor are any reported in the literature; the reason may be the high degree of crowding that would be present in the adduct.

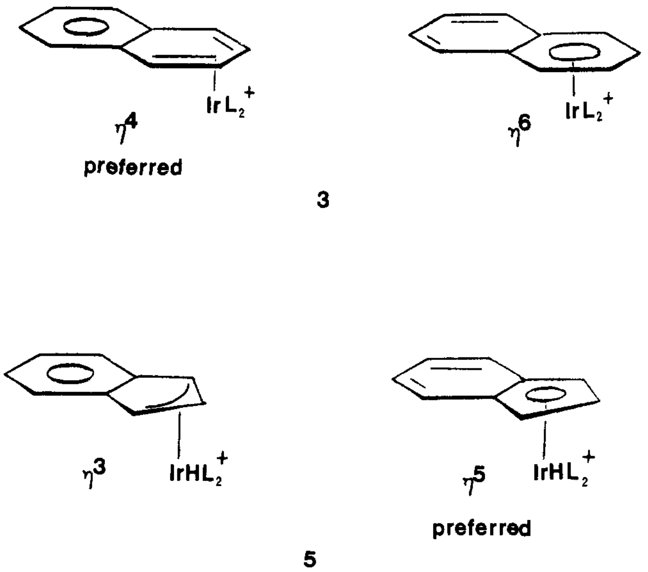
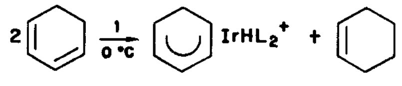


Figure 1. Possible structures for the complexes **3** and **5** and the probable preferred forms in each case as deduced from the experimental evidence (see text). The 2-ethyl group in **3** is not shown for greater clarity. Attainment of benzenoid character in the uncomplexed ring appears to be a sufficient driving force to make **3** largely η^4 but not to make **5** η^3.

Arene Precoordination in C–H Activation. Jones et al.[10] have emphasized the role of precoordination of an arene as a preliminary step for C–H activation reactions in arenes. This would account for the kinetically higher reactivity of arenes that has generally been observed. For this reason we looked at the reaction of neat indan with **1** and tbe. At 90 °C for 6 h essentially on the η^6-indan complex **4** was observed. Only after 16 h were substantial amounts of indenyl complex **5** formed. At 105 °C for 44 h essentially only **5** was formed. **4** appears to be an intermediate, since the purified complex fails to react with cyclopentene (as do the benzene complex **2** or the naphthalene complex **3**) but rather gives only **5** on heating. This therefore seems to be a good example of arene precoordination, in which the intermediate has considerable stability.

Cyclohexadienyl Complexes. We have described elsewhere[3] the synthesis of $[Ir(\eta^5\text{-}C_6H_7)HL_2]A$ (**6**) from **1** and cyclohexadiene (eq 10). This complex was also



6 (10)

studied as a precursor to the alkane activation system. It gave the most satisfactory results of any of complexes **2**–**7**. For example, in a typical run with cyclopentane and tbe, after 24 h at 110 °C only ca. 5% of starting material remained and $[Ir(C_6H_6)L_2]A$ (40%) and $[IrCpHL_2]A$ (35%) were formed. We also looked at $[Ir(C_6H_6)L_2]A$ itself in the alkane reaction, but it was never as effective, as was mentioned above. Possibly, the first step in the reaction of **6** is an η^5 to η^3 ring slippage. The 16-electron product can now cleave the endo CH bond of the cyclohexadienyl to give an η^4-benzene complex. Perhaps this loses benzene to give $[IrH_2L_2]^+$, which is responsible for the subsequent chemistry. Certainly, heating **6** in acetone rapidly gives $[IrH_2(Me_2CO)_2L_2]^+$ quantitatively as would be expected on these ideas. **1** itself remains as the best precursor we have studied, giving an 82% yield of $[IrCpHL_2]^+$ under comparable conditions.[11]

Diene Complexes. Following the procedure of Moore, Morris, et al.,[12] we synthesized $[IrH_2(CH_2{=}CMe{-}CMe{=}CH_2)L_2]A$ (**7**) from 2,3-dimethylbutadiene and **1**. Although these authors did not report isolating the complex, we found it could be obtained as cream-colored microcrystals. Reflux in $C_2H_4Cl_2$ with cyclopentene gave $[IrHCpL_2]A$ quantitatively, and heating with cyclopentane and tbe led to the formation of the same cyclopentadienyl complex in 20% yield. The complex **7** was therefore a moderately satisfactory precursor to the alkane activation system.

Hexafluoroantimonate Salts. Many of the salts reported in this paper were isolated with the SbF_6 counterion. This was a great improvement on the BF_4 and PF_6 salts we have previously studied. The antimonates were easier to crystallize, appeared to be more stable, and had a slightly lesser tendency to contain the ubiquitous CH_2Cl_2 of crystallization that is often found with the borate and phosphate salts.

Conclusion

We have synthesized a number of complexes in order to see how effectively they generate the IrL_2^+ fragment for alkane dehydrogenation experiments. We find the order of effectiveness to be $[IrH_2(Me_2CO)_2L_2]^+ > [Ir(\eta^5\text{-}C_6H_7)HL_2]^+ \approx [Ir(2,3\text{-dimethylbutadiene})H_2L_2]^+ > [Ir(\eta^6\text{-}C_6H_6)L_2]^+ \approx [Ir(\eta^5\text{-indenyl})HL_2]^+$. We have observed a very facile haptotropic rearrangements in a $[Ir(NpEt)L_2]^+$ (**3**) and were able to observe one haptomer directly by NMR. In $[Ir(\eta^5\text{-indenyl})HL_2]^+$ (**5**) the indenyl is oriented by the trans effect of the hydride. While **5** has largely 18-electron character with an η^5-ligand and is chemically relatively inert, **3** has largely 16-electron character with an η^4 ligand and is chemically very reactive.

In the dehydrogenation of indan by **1** to give an indenyl complex, the η^6-indan complex **4** appears to be an intermediate. C–H activation processes in arenes may be generally kinetically facilitated by prior coordination to the ring.[10]

Experimental Section

(η^4-1,5-Cyclooctadiene)bis(triphenylphosphine)iridium(I) Hexafluoroantimonate. This was prepared by the method previously used for the hexafluorophosphate and tetrafluoroborate.[13] The red crystalline product was spectroscopically identical with the other salts.[13]

Dihydridobis(acetone)bis(triphenylphosphine)iridium(III) Hexafluoroantimonate. This complex was made by the method of ref 14 from $[Ir(cod)(PPh_3)_2]SbF_6$ in acetone under H_2. It was easier to isolate and handle than the previously reported salts and did not contain CH_2Cl_2 of crystallisation as found for the other salts. The ^1H NMR spectrum was identical with that previously reported.[14]

(η^6-2-Ethylnaphthalene)bis(triphenylphosphine)iridium(I) Hexafluoroantimonate (3). $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (200 mg, 0.187 mmol) in CH_2Cl_2 (10 mL) was stirred with 2-vinylnaphthalene for 5 min to give the solution the color of bordeaux wine. A deep red compound was precipitated with Et_2O, the solution filtered, and the precipitate recrystallized from CH_2Cl_2/Et_2O to give a 176 mg (85%) yield of a 50:50 mixture of the two isomers **3a** and **3b**. Anal. Found (Calcd) for $C_{48}H_{42}P_2SbF_6Ir\cdot{}^1/_4CH_2Cl_2$: C, 51.25 (51.29); H, 4.01 (3.79).[15]

Hydrido(η^5-indenyl)bis(triphenylphosphine)iridium(III) Hexafluoroantimonate (5). Method A. $[IrH_2(MeCO)_2(PPh_3)_2]SbF_6$ (200 mg, 0.187 mmol) was refluxed with indene in 1,2-dichloroethane (10 mL) for 12 h. The colorless product was isolated from the cooled solution with Et_2O and recrystallized with CH_2Cl_2/Et_2O to give a 177 mg (88%) yield.

Method B. $[Ir(\eta^6\text{-indan})(PPh_3)_2]SbF_6$ was refluxed in dichloroethane for 8 h. Workup as above gave a 191 mg (95%) yield. Anal. Found (Calcd) for $C_{45}H_{38}P_2IrF_6Sb\cdot CH_2Cl_2$: C, 48.14 (47.8); H, 3.63 (3.49); P, 5.63 (5.37).[15]

Observation of 4 as an Apparent Intermediate in the Dehydrogenation of Indan by 1. To indan (2 mL) in a resealable glass vial (5 mL) equipped with a Teflon stopcock (3 mm) was added $[IrH_2(Me_2CO)_2(PPh_3)_2]SbF_6$ (20 mg, 0.19 mmol) and *tert*-butylethylene (1.5 mg, 0.18 mmol), and the mixture was heated at 90 °C for 6 h. The volatiles were removed in vacuo, and the residue was studied by ^1H NMR. **4** was the major product (ca. 90%). Another vial heated for 18 h showed substantial amounts (ca. 50%) of **5** as well, and a vial heated at 105 °C for 44 h showed essentially (ca. 90%) only **5** as product.

Reaction of 2–7 with Cyclopentene. **2–7** (0.1 mmol) were separately refluxed with cyclopentene (2 mL) in CH_2Cl_2 (10 mL) for 4 h. The solutions were cooled and the volatiles removed in vacuo. $[IrH(\eta^5\text{-}C_5H_5)(PPh_3)_2]SbF_6$ was detected as essentially the only product (ca. 95%) in the case of **2–3** and **6–7**. In the cases of **4–5** only starting material was seen (or ca. 5% of **5** from **4** in the case of **4**).

Reactions of 2–7 with Cyclopentane. **2–7** were treated with *tert*-butylethylene and cyclopentane (3 mL) in refluxing $C_2H_4Cl_2$.[14] After 20 h at 100 °C, $[IrH(C_5H_5)(PPh_3)_2]SbF_6$ was detected (^1H NMR) in the following amounts among the organometallic products: **2**, 5%; **3**, 5%; **4**, 0%; **5**, 0%; **6**, 35%; **7**, 20%. The following were also detected: from **2**, starting material (40%); from **4**, **4** and **5** (45% each), from **5**, starting material quantitatively; from **6**, **2** (40%) and free benzene (60%).

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Registry No. **1**, 89509-77-3; **3a**, 91410-17-2; **3b**, 91410-19-4; **4**, 91410-21-8; **5**, 91410-23-0; **6**, 91410-24-1; **7**, 91410-25-2; $[IrH(\eta\text{-}C_5H_5)(PPh_3)_2]SbF_6$, 91410-26-3; $[Ir(cod)(PPh_3)_2]SbF_6$, 91410-27-4; cyclopentene, 142-29-0; cyclopentane, 287-92-3.

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(15) The appropriate amounts of CH_2Cl_2 were detected in the ^1H NMR of these complexes in acetone-d_6 solution.