## Ring Slip in Associative Reactions of Some Indenyl and Phenylcyclopentadienyl Iridium Complexes

Afroze Habib, \*<sup>,†</sup> Robin S. Tanke,<sup>†</sup> Elizabeth M. Holt,<sup>‡</sup> and Robert H. Crabtree<sup>†</sup>

Sterling Chemistry Laboratory, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, and Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Received August 9, 1988

The complex ion  $[(\eta^5-\text{Ind})\text{IrHL}_2]^+$  (Ind = indenyl, L = PPh<sub>3</sub>) undergoes substitution with t-BuNC, CO, and PMe<sub>3</sub>, while the Cp analogue (Cp = cyclopentadienyl) is inert. The phenylcyclopentadienyl complex  $[(\eta^5-PhC_5H_4)IrHL_2]^+$  undergoes rapid substitution with PMe<sub>3</sub> but not with t-BuNC or CO. Slipped  $\eta^3$  and  $\eta^1$  intermediates are proposed in these reactions, and several examples of such complexes are detected by NMR at low temperatures. Deprotonation with n-BuLi takes place only for  $[(\eta^5.\text{Ind})\text{IrHL}_2]^+$  and  $[(\eta^5.\text{Ind})\text{IrHL}_2]^+$  $PhC_{5}H_{4})IrHL_{2}^{+}$ , but not the Cp analogue. The reactions of the deprotonated complex  $[(\eta^{5}-Ind)IrL_{2}]$  with a number of electrophiles are also investigated and the resulting cations  $[(\eta^5-Ind)IrXL_2]^+$  (X = Me, Et,  $CH_2Ph$ , Cl, I) characterized. The ethyl complex loses ethylene at 60 °C by  $\beta$ -elimination, but only in donor solvents, which may attack associatively in the first step of the reaction. In nondonor solvents, the  $\beta$ -elimination is induced by UV photolysis, which may induce ring slip. Allyl bromide reacts with  $[(\eta^5 -$ Ind)IrL<sub>2</sub>] to give  $[(\eta^5-\text{Ind})\text{Ir}(\eta^3-\text{allyl})\text{L}]^+$ , via  $[(\eta^5-\text{Ind})\text{Ir}(\eta^1-\text{allyl})\text{L}_2]^+$  as an observed but unisolated intermediate. The structure of the chloro complex  $[(\eta^5-\text{Ind})\text{IrC}(\text{L}_2)]$  was determined by X-ray methods (space group  $P\bar{I}$ ; a = 11.314 (4) Å, b = 14.469 (5) Å, c = 13.021 (2) Å,  $\alpha = 87.05$  (2)°,  $\beta = 100.25$  (2)°,  $\gamma = 68.43$  (2)°; V = 1934.8 (10) Å<sup>3</sup>; mol wt = 954.2, Z = 2; F(000) = 944;  $\rho_{calcd} = 1.638$  g cm<sup>-3</sup>; R = 0.04 for 6379 reflections). Hydrogenation of  $[(\eta^5-Ind)IrHL_2]^+$  with Rh/C gives the tetrahydroindenyl complex.

An indenyl complex such as 1 generally substitutes at a higher rate than the corresponding cyclopentadienyl.<sup>1</sup> This "indenyl effect" has been ascribed to the stabilization of a slipped  $\eta^3$  intermediate (2) by recovery of the full aromatic stabilization in the benzo ring of the slipped indenyl group (eq 1).



Stable, isolable  $\eta^3$ -indenyl and  $\eta^3$ -Cp complexes are still rare. Werner<sup>2</sup> reported the first case of substitution inducing a slip reaction for Cp by employing Pd, a metal that does not form particularly stable  $\eta^5$ -Cp complexes. Other cases are known, for both Cp and indenyl groups.<sup>3,4</sup>

## **Results and Discussion**

We have reported<sup>5</sup> a simple route to  $[(\eta^5-Ind)IrHL_2]^+$ (3, Ind = indenyl;  $L = PPh_3$ ) by a C-H activation sequence from indene and  $[IrH_2(solv)_2L_2]^+$  (solv = Me<sub>2</sub>CO), and in this paper we compare the reactions of 3 with those of the corresponding cyclopentadienyl [CpIrHL<sub>2</sub>]<sup>+</sup> (4).

We will report several reaction sequences in which incoming ligands cause  $\eta^5$  to  $\eta^3$  to  $\eta^1$  rearrangements of the indenyl group, even followed in some cases by loss of indene. In no case did the Cp complex 4 give an analogous reaction. In addition we have found that PhCp also shows a substantial acceleration of substitution chemistry relative to Cp itself.

**Reaction of**  $[(\eta^5-Ind)IrHL_2]A$  (3) with CO.  $[(\eta^5-Ind)IrHL_2]A$  (3) with CO. Ind)IrHL<sub>2</sub>]A (L = PPh<sub>3</sub>, A = SbF<sub>6</sub>, 3) slowly reacts with CO (1 atm) at 25 °C over 2-4 days in CH<sub>2</sub>Cl<sub>2</sub> to give free indene and the known<sup>6a</sup>  $[Ir(CO)_3L_2]BF_4$ . No intermediates could be detected by NMR. No reaction takes place with the cyclopentadienyl analogue 4 under the same conditions.

This difference in reactivity might be a manifestation of the indenyl effect as described above, but we need to exclude the possibility that differences in steric effect and donor/acceptor character of Ind and Cp are the cause. To do this we studied the tetrahydroindenyl analogue 5 and the phenylcyclopentadienyl analogue 6. We consider the tetrahydroindenyl ligand in 5 to be at least as large as the indenyl in steric bulk but comparable to Cp in donor/ acceptor properties (and, if anything, more donor). On the other hand 6 should have donor/acceptor properties closer to those of the indenyl ligand than to those of Cp. Because the cyclopentadienyl complex 4 does not react under any conditions, we are unable to exclude the possibility that it does not react for thermodynamic rather than kinetic reasons.

Preparation of 5 and 6. The tetrahydroindenyl complex 5 was prepared by hydrogenation of the indenyl complex 3 with Rh/C; this type of reaction has not previously been reported. The indenyl benzo group was selectively hydrogenated in preference to the PPh<sub>3</sub> groups, perhaps as a consequence of the dienoid character of this ring implied by the canonical form shown for 3 in eq 2. The tetrahydroindenyl ligand completely resists hydrogenolysis from the metal.  $[(PhC_5H_4)IrHL_2]SbF_6$  (6) was

(2) Werner, H.; Kuhn, A.; Burschka, C. Chem. Ber. 1980, 113, 2291.
(3) Casey, C. P.; Jones, W. D. J. Am. Chem. Soc. 1980, 102, 6154.
(4) (a) Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andrianov, V. G.; Struckov, Yu, T.; Andrae, S.; Ustynyuk, Yu, A.; Malyugina, S. G. J. Organomet. Chem. 1978, 158, 189-99. (b) Merola, J. S.; gina, S. G. Organomet. Chem. 1978, 136, 139-99. (b) Microla, J. S.;
Kacmarcik, R. T.; Engen, D. V. J. Am. Chem. Soc. 1986, 108, 329. (c)
Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. J. Am. Chem. Soc. 1986, 108, 2460. (d) Merola, J. S., personal communication, 1986. (e) Kowala, C.; Wunderlich, J. A. Acta Crystallogr., Sect. B 1976, B32, 820. Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.;
Benjeke, V.; Neugebauer, D. J. Organomet. Chem. 1978, 145, 329. (f)
Casey, C. P.; O'Connor, J. M. Organometallics 1985, 4, 384.

(5) Crabtree, R. H.; Parnell, C. P. Organometallics 1984, 3, 1727-31. (6) (a) Church, M. J.; Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. J. Chem. Soc., A 1970, 2909, 3000. (b) The notation H(1) or C(1) represents the standard numbering for the indenyl group as shown in eq 3; the crystallographic section uses the numbering shown in Figure 1 and is reported with the notation C1, C2, ...

<sup>&</sup>lt;sup>†</sup>Yale University.

<sup>&</sup>lt;sup>‡</sup>Oklahoma State University.

<sup>(1) (</sup>a) Cramer, R.; Seiwell, L. P. J. Organomet. Chem. 1975, 92, 245. (b) Basolo, F.; Schuster, H. G. J. Am. Chem. Soc. 1966, 88, 1657. Rerek, M. E.; Basolo, F. Organometallics 1983, 2, 372. (c) Rest, A. J.; Whitwell, Li, Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. J. Chem. Soc., Chem. Commun. 1984, 624. (d) Yang, G. K.; Bergman, R. G. Organometallics 1985, 4, 129. (e) Hart-Davis, A. J.; Mawby, R. J. J. Chem. Soc. A 1969, 2403.

$$\frac{Ph/C}{H_2} \xrightarrow{Ph/C} IrHL_2^+$$
(2)

prepared from  $[IrH_2(acetone)_2L_2]^+$  and  $PhC_5H_5$  at 90 °C for 1 day; cyclopentene and indene give similar reactions.<sup>5,7</sup> Neither 5 nor 6 reacts with CO under any of the conditions used above, even the presence of UV light (medium-pressure Hg lamp, Pyrex filter).

**Reaction of**  $[(\eta^5 \cdot Ind)IrHL_2]A$  (3) with Isonitrile. The reaction with 3 with 1.5 equiv of t-BuNC is very rapid at room temperature to give free indene and an unstable iridium species which shows both terminal and bridging t-BuNC groups by IR ( $\nu(NC)$  2152.3 (s), 2059.5 (sh), 1584.6 (m), and 1568.3 (w) cm<sup>-1</sup>). Unfortunately, we were never able to characterize this product because it failed to give crystals of sufficient quality and tended to decompose on standing. Analytical data suggest the formulation  $[Ir_2L_4(t-BuNC)_3]^{2+}$ , and it may be  $[L_2Ir(\mu-RNC)_2IrL_2^{-1}(CNR)]^{2+}$ . Once again, 4–6 do not react with t-BuNC under these conditions.

At 200 K, the first intermediate detectable by NMR appears in a few minutes (eq 3). It contains a hydride, as shown by the triplet hydride resonance at  $\delta$  -14.2 (J(P,H) = 9 Hz). A peak due to a single coordinated t-BuNC at  $\delta$  0.58 is also present. The proton resonances of the intermediate can be readily identified because they rise and fall together on warming from 200 to 270 K or on standing at a fixed temperature. Cooling does not cause a reversal of the spectral changes. After 20 min at 260 K, the resonances of the intermediate dominate the spectrum.

Integration of these resonances show an indenyl:hydride:t-BuNC ratio of 1:1:1, corresponding to the stoichiometry  $[(\eta^3-Ind)IrL_2(t-BuNC)H]^+$  (7). This assignment of an  $\eta^3$  structure is based on an assumed 18e configuration for 7 and on the resonance positions<sup>6b</sup> observed for the  $\eta^3$ -indenyl group itself (H(2),  $\delta$  8.5; H(1) and H(3),  $\delta$  4.41), which, as we shall see, differ from those characteristic for the  $\eta^1$ - and  $\eta^5$ -binding modes. In slipping to  $\eta^3$ , the indenvi H(2) protons tend to move ca. 2 ppm to lower field from the  $\delta$  5–7 typical for the  $\eta^1$ - and  $\eta^5$ -binding modes.<sup>4b</sup> For the  $\eta^5$  complex 3, H(2) resonates at  $\delta$  6.59 and, for the  $\eta^3$ complex 7, resonates at  $\delta$  8.5, so the  $\eta^5$  to  $\eta^3$  slip shift is +1.91 ppm in this case. The stereochemistry could not be determined, but the L groups may well be trans as in the majority of related octahedral Ir(III) bis(phosphine) complexes.7,8

At higher temperatures, a second intermediate with a triplet hydride resonance at  $\delta$  -10.8 (J(P,H) = 11 Hz) is seen, but it never contributes more than 20% to the total integrated intensity of Ir-H peaks. The most resonable structure is  $[(\eta^{1}\text{-Ind})\text{IrL}_{2}(t\text{-BuNC})_{2}\text{H}]^{+}$  (8) on the basis of the fact that the analogous ( $\eta^{5}\text{-Ind}$ )IrMeL<sub>2</sub><sup>+</sup> gives a well-characterized  $\eta^{1}\text{-Ind}$  derivative with t-BuNC (see below), which has a similar NMR spectrum. In particular, H(3) appears at  $\delta$  3.98 for 8, close to the value of  $\delta$  4.0 in the fully characterized methyl analogue but different from the values of  $\delta$  5.2–5.8 found for  $\eta^{5}\text{-Ind}$  groups. The cis disposition of H and  $\eta^{1}\text{-Ind}$  groups is probable on the basis of the value of  $\delta$  (Ir-H) which is appropriate<sup>7b</sup> for H trans to t-BuNC but not H trans to ( $\eta^{1}\text{-Ind}$ ) and by analogy with the structures of a large number of derivatives<sup>7,8</sup> of the type

 $[IrX_2L_2(PPh_3)_2]^+$  (X = 1e ligand; L = 2e ligand). On further warming, resonances for free indene grow in.

The probable sequence of events, shown in eq 3, illustrates the progressive displacement of the  $\eta^5$ -Ind group via the intermediate  $\eta^3$  and  $\eta^1$  stages.



**Reaction of**  $[(\eta^5-\text{Ind})\text{IrMeL}_2]A$  (9a) with Isonitrile. We studied the analogous methyl  $[(\eta^5-\text{Ind})\text{IrMeL}_2]^+$  (9a) because reductive elimination reactions that form sp<sup>3</sup>-sp<sup>3</sup> C-C bonds tend to be slow, and so the intermediate  $\eta^1$ -Ind form should now be stable.

The corresponding  $\eta^1$ -Ind complex  $[(\eta^1$ -Ind)IrMe(t-BuNC)\_2L\_2]^+ (10), formed by reaction with t-BuNC over 6 h, was indeed stable enough to isolate in ca. 90% yield and could be fully characterized. The stereochemistry shown in eq 4 is strongly indicated by the inequivalence of the t-BuNC groups (<sup>1</sup>H NMR  $\delta$  1.31 and 0.89) and by analogy with other cis,cis,trans-[IrX\_2L\_2(PPh\_3)\_2]^+ complexes.<sup>7,8</sup>

The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts (see Experimental Section) indicate that an  $\eta^1$  structure is adopted. In particular H(1) and H(3) and C(1) and C(3) show distinct resonances, as expected for an  $\eta^1$  structure but in contrast to the single resonance observed for the  $\eta^3$  and  $\eta^5$  forms. The C(1) and C(2) resonances are close to those of free indene, as is expected because these are not bound to the metal. C(3), which is the only one attached to the metal, shows a 60 ppm coordination shift from C(3) in free indene. Similarly, C(4-7) appear as four distinct resonances in the region 122.7-125.25 ppm because of the lack of symmetry.

By following the reaction of the methyl complex with 1 mol of t-BuNC (<sup>1</sup>H NMR), resonances were seen strongly resembling those of the  $\eta^3$ -Ind species observed in the case of the hydride. In particular, this  $\eta^3$ -Ind species shows a resonance at  $\delta$  8.58 in a region ( $\delta$  7–9) characteristic for the H(2) proton of an  $\eta^3$ -Ind structure and a triplet methyl resonance at  $\delta$  0.18, showing that the two PPh<sub>3</sub> ligands are still attached to the metal. The  $\eta^3$ -form was relatively unstable and was never present in more than small amounts, and so it cannot be identified as 11a with certainty. The pure, isolated  $\eta^1$  complex 10, described above, showed no trace of 11a in the <sup>1</sup>H NMR, suggesting that dissociation of t-BuNC did not occur to any substantial extent, but a small amount of a different  $\eta^3$ -complex 11b was observed. The appearance of H(2) at  $\delta$  8.38 and the appearance of a doublet Ir–Me resonance at  $\delta$  0.23 are both consistent with the formulation shown, but the equilibrium mixture contains no more than 15% of 11b and we were not able to isolate and fully characterize it. The sequence 11a to 10 to 11b would constitute an associative substitution by isonitrile on an  $\eta^3$ -indenyl complex via an  $\eta^1$ intermediate.

**Reaction of**  $[(\eta^5-\text{Ind})\text{IrHL}_2]A$  (3) with PMe<sub>3</sub>. 3 reacts with PMe<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature over 24 h to give as thermodynamic product *trans*- $[(\eta^1-\text{Ind})\text{IrH}-(\text{PMe}_3)_4]A$  (12), which can be isolated and fully characterized. The new complex 12 shows a quintet Ir-H reso-

<sup>(7)</sup> Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. J. Am. Chem. Soc. 1982, 104, 107-11. 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, 6994-7001.

<sup>1982, 104, 6994-7001.
(8)</sup> Shapley, J. R.; Schrock, R. R.; Osborn, J. A. J. Am. Chem. Soc.
1969, 91, 2816.



nance at  $\delta$  -21.6 (<sup>1</sup>J(P,H<sub>cis</sub>) = 14.5 Hz) appropriate<sup>7,8</sup> for H trans to a carbon ligand and cis to four equivalent PMe<sub>3</sub> groups. During the early stages of the reaction (2–12 h), the cis isomer 13 was detected by <sup>1</sup>H NMR. The Ir-H resonance for 13 at  $\delta$  -11.82, a chemical shift appropriate for H trans to a phosphine, appears as a doublet (<sup>2</sup>J-(P,H<sub>trans</sub>) = 149 Hz) of quartets (<sup>2</sup>J(P,H<sub>cis</sub>) = 18.9 Hz), showing that the Ir-H is trans to one and cis to three phosphorus nuclei, as expected on the basis of the proposed structure.



In contrast to the case of the isonitrile complexes, the  $\eta^{1}$ -indenyl hydrides 12 and 13 show no tendency to eliminate indene. This type of behavior has been observed previously for complexes of the type cis-[Ir(PMe<sub>3</sub>)<sub>4</sub>(X)H]<sup>+</sup> (X = alkyl) and ascribed to the failure of PMe<sub>3</sub> to dissociate to give a reactive 16e intermediate.<sup>9</sup>

A Phenylcyclopentadienyl Effect? The cyclopentadienyl and tetrahydroindenyl complexes 4 and 5 were inert to PMe<sub>3</sub> under conditions in which the indenyl complex 3 reacts. The phenylcyclopentadienyl complex 6 also reacts to give the  $\eta^1$ -PhCp complex shown in eq 6. Steric effects may be responsible for the phenyl group appearing at the 3-position of the C<sub>5</sub> ring in the product. The Ir-H resonance appears at  $\delta$  -21.56, a shift appropriate for H trans to a C-donor ligand, and shows a quintet splitting ( $J(P,H_{cis}) = 14.7$  Hz) analogous to that observed for the indenyl analogue 12.



This suggests that the phenyl substituent also accelerates substitution reactions of Cp complexes, although not to the extent observed for the indenyl group because 6 did not react rapidly with CO or t-BuNC. The sensitivity to the nature of the nucleophile suggests that the substitution of 6 is an associative process. Ring slippage is induced by PMe<sub>3</sub> attack. If slip occurred independently of attack by the nucleophile, there would be no reason why the small and strongly ligating CO and t-BuNC ligands should not trap the 16e  $\eta^3$ -Ind intermediate just as efficiently as would PMe<sub>3</sub>. It will be interesting to see how general this phenylcyclopentadienyl effect will be.

The phenyl group probably favors ring slippage because the C=C group liberated from the metal in an  $\eta^5$  to  $\eta^3$  slip process is stabilized by conjugation with the aromatic ring.

**Deprotonation Reactions.**  $[CpIrHL_2]^+$  (4) and  $[IndIrHL_2]$  (3) were strikingly different in their proton acidity as shown by eq 7 and 8. While 3 slowly deprotonates with NEt<sub>3</sub>, 4 resists *n*-BuLi and even *t*-BuLi/TMEDA. This was confirmed by showing that only 3 and not 4 was deprotonated when a mixture of the two compounds was treated with *n*-BuLi. This great difference might be thermodynamic in origin, but the annelation of a benzo ring onto 4 to make 3 does not seem sufficient to alter the  $pK_a$  of the Ir-H proton by over 25 pK units.

$$CpIrHL_{2}^{+} \xrightarrow{BuLi/TMEDA} \text{ no reaction}$$
(7)

$$IndIrHL_2^+ \xrightarrow{\text{NEt}_3} IndIrL_2 \tag{8}$$

The resistance to deprotonation shown by 4 must therefore be in kinetic origin. Slip may be important in deprotonation. The slipped 16e species may be more kinetically labile, or the pathway of eq 9 may operate. As expected on the slip argument, the PhCp analogue 6 is deprotonated even by NEt<sub>3</sub> or *n*-BuLi, but the tetrahydroindenyl complex 5 resists *n*-BuLi.



Merola<sup>4b</sup> has previously synthesized 14 by the route shown in eq 10, and so the identity of the bright orange deprotonation product can be independently checked by comparison with authentic material. It is very air- and moisture-sensitive, even in the solid state. In particular, it readily abstracts protons from  $H_2O$  to re-form 5.

$$[\mathrm{Ir}(\mathrm{coe})_2\mathrm{Cl}]_2 \xrightarrow{\mathrm{Ll}[\mathrm{Ind}]} [(\mathrm{Ind})\mathrm{Ir}(\mathrm{coe})_2] \xrightarrow{\mathrm{L}} [(\mathrm{Ind})\mathrm{Ir}\mathrm{L}_2] \quad (10)$$
14

T / (T - 41

Merola identifies 14 as an  $\eta^5$ -Ind complex. We agree on the basis of the <sup>13</sup>C NMR resonance position for C(8,9) at  $\delta$  115.8. In free indan, this resonance appears at  $\delta$  144 close to the positions we observe for our  $\eta^1$ -Ind complexes ( $\delta$ 147.4 and 154) and that Merola observes for  $[(\eta^3$ -Ind)Ir-(PMe<sub>3</sub>)<sub>3</sub>] ( $\delta$  156.7).

**Reactions of**  $[(\eta^5-\text{Ind})\text{IrL}_2]$  (14) with H<sub>2</sub>. We were interested to find that 14 could be hydrogenated, with loss of indene. The reaction takes place with H<sub>2</sub> in THF over 2 h to precipitate IrH<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>, identified by its characteristic IR band at 1948 cm<sup>-1</sup>. The indenyl group is completely removed from the metal and appears as indene among the final products. In contrast  $[(\eta^5-\text{Ind})\text{IrHL}_2]^+$  (3) does not undergo hydrogenation in THF, even though  $[\text{IrH}_2(\text{THF})_2\text{L}_2]^+$ , the analogous cationic product, is known and stable. Probably 14 has a much higher tendency to slip to the 16e  $(\eta^3-\text{Ind})\text{IrL}_2$  form than does 3 because Ir(I) tends to prefer the 16e configuration, while Ir(III) tends to prefer an 18e form. It was for the Ir(I) complex 14 that

<sup>(9)</sup> Thorn, D. L.; Tulip, T. H. Organometallics 1982, 1, 1580-6.

Merola<sup>4b</sup> observed a PMe<sub>3</sub>-induced slip to give  $(\eta^3$ -Ind)-Ir(PMe<sub>3</sub>)<sub>3</sub>.

We decided to monitor the reaction of  $H_2$  with 14 in the much less coordinating solvent  $C_6D_6$  at 20 °C. A resonance at  $\delta$  -8.21 (t,  ${}^2J(P,H) = 13$  Hz) appeared and grew in intensity with time in step with resonances at  $\delta$  7.75 (H(2)) and 3.56 (H(1,3)). The most likely species to account for this spectrum is  $[(\eta^3-Ind)IrH_2L_2]$ , but we were never able to isolate it in a pure form for full characterization. Once again,  $IrH_5L_2$  is precipitated and indene formed but over 2 days rather than 2 h, as was the case in THF.

Reactions of  $[(\eta^5\text{-Ind})\text{IrL}_2]$  (14) with Halocarbons To Give Alkyls. The nucleophilic species 14 reacts with MeI, EtI, or PhCH<sub>2</sub>Br to give the corresponding methyl, ethyl, or benzyl complexes  $[(\eta^5\text{-Ind})\text{IrRL}_2]^+$  (9), identified by spectral and analytical studies. There is a high-field shift (-0.76 ppm for R = Me) of the ortho protons of the PPh<sub>3</sub> groups ("ortho shift"). In the similar case of  $[(\eta^5\text{ Ind})\text{IrHL}_2]^+$ , we ascribed<sup>10</sup> the shift to the ring current of the indenyl benzo ring in a conformer of type 15, which



is adopted by 3 (R = H) and by 9a (R = Me), 9b (R = Et), and 9c (R = PhCH<sub>2</sub>). The reason we believe this conformer is adopted<sup>5,10</sup> is that the high trans effect of R leads to an increase in the Ir–C(8,9) distances (verified crystallographically<sup>10</sup> in the case of R = H), which in turn leads to a greater participation of the  $p_z$  orbitals on C(8,9) in the aromatic system of the benzo group, leading to a net stabilization of the slipped system.

Solvent-Induced  $\beta$ -Elimination in  $(\eta^5$ -Ind)IrEtL<sub>2</sub> (9b). The ethyl complex 9b is particularly interesting in that it undergoes solvent dependent  $\beta$ -elimination to give  $C_2H_4$  and  $[(\eta^5$ -Ind)IrHL<sub>2</sub>]<sup>+</sup> (3). The reverse reaction,



formation of **9b** from **3** and  $C_2H_4$  (1 atm, 25 °C), was not observed in any solvent, however, and is probably contrathermodynamic. Even at room temperature **9b**  $\beta$ -eliminates in THF over several minutes. On the other hand, the same complex is stable in  $C_6H_6$  or  $CH_2Cl_2$  at room temperature and even in refluxing 1,3- $C_2H_4Cl_2$  (80 °C) for several hours. In refluxing acetone (60 °C),  $\beta$ -elimination is observed. The most reasonable explanation is that associative substitution of THF or acetone can occur to give a solvated species  $[(\eta^3-\text{Ind})\text{IrRL}_2(\text{solv})]$ . If this loses the solvent, the 16e intermediate could  $\beta$ -eliminate or slip back to the  $\eta^5$  form.

 $\beta$ -Photoelimination in  $[(\eta^5\text{-Ind})\text{IrEtL}_2]^+$  (9b) and Reductive Photoelimination of Indene from  $[(\eta^5\text{-Ind})\text{IrHL}_2]^+$  (3). In noncoordinating solvents, such as CH<sub>2</sub>Cl<sub>2</sub>, **9b** is thermally stable presumably because no solvento species is formed. Interestingly photolysis (254 nm,  $4 \times 8$  W lamps, 30 h) smoothly induces  $\beta$ -elimination in noncoordinating solvents. We propose that illumination causes slip by promoting a metal  $d_{\pi}$  electron to an M-L( $\sigma^*$ ) level. The resulting 16e species can  $\beta$ -eliminate whatever the solvent.

 $[(\eta^5-\text{Ind})\text{IrHL}_2]^+$  (3) is formed after short exposure of 9b to illumination, but it is not the final product because 3 itself is photolabile under the reaction conditions and loses indene to give an unidentified product, 16. This reductive photoelimination of 3 may also be the result of a photoinduced slip to the  $\eta^1$  form. As we saw above, reductive elimination of an  $\eta^1$ -indenyl hydride is relatively rapid.

**Reaction of**  $[(\eta^5-Ind)IrL_2]$  (14) with Allyl Bromide. Allyl bromide gives an interesting intermediate in its reaction with 14. A species we assign as the  $\eta^1$ -allyl complex, 17, is formed first and then rearranges to an  $\eta^3$ -allyl, 18, as the final product. The structures of 17 and 18 follow



from their spectral data. In particular, the off-resonance <sup>1</sup>H-decoupled <sup>13</sup>C NMR spectrum of the final product 18 shows the characteristics resonances for  $\eta^3$ -allyl at  $\delta$  39.8 (triplet, C(1,3)) and 72.3 (doublet, C(2)). Peaks at  $\delta$  79.0 (d, C(1,3)), 89.8 (d, C(2)), and 123 (s, C(8,9)) characterize the  $\eta^5$ -Ind group. The presence of one PPh<sub>3</sub> group is shown by microanalysis and also by integration of the aromatic versus the allyl resonances in the <sup>1</sup>H NMR spectrum. The complex was also obtained in analytically pure form on a preparative scale.

The intermediate 17 is closely related to 9a-c and like them shows a high-field ortho shift in the PPh<sub>3</sub> group and resonance positions for the  $\eta^5$ -Ind group comparable to those of 18. We were not able to obtain a pure sample of 17 because it was always contaminated with its rearrangement product 18, but integration of the aromatic versus the allylic protons in the <sup>1</sup>H NMR spectrum together with 18e rule considerations strongly suggests the structure shown in eq 12. The rearrangement of 17 to 18 is likely to go via an associative attack of the allyl C==C group on the metal with slip of the idenyl group.

**Reaction of**  $[(\eta^5-\text{Ind})\text{IrL}_2]$  (14) with Halogens. Only Cl<sub>2</sub> and I<sub>2</sub> were studied in detail. Both attack 14 electrophilically to give the halo cations that can be isolated as BF<sub>4</sub><sup>-</sup> salts.

The chloro species 19a is particularly interesting in relation to our suggestion<sup>5,10</sup> that it is the differential trans influence of the ligands of the piano-stool "legs" which decides the conformation of the "seat" in complexes of the type  $[(\eta^5-Ind)ML_3]$ . A high trans influence ligand will prefer to be trans to the ring junction carbons, C(8) and C(9), because if these carbons partially disengage from the metal (as M–(C(8)) and M–(C(9)) become longer under the trans influence of the high trans influence ligand), the p orbitals on C(8) and C(9) are stabilized by increased delocalization with the benzo ring. In the case of 19a, the

<sup>(10)</sup> Faller, J. W.; Crabtree, R. H.; Habib, A. Organometallics 1985, 4, 529-35.

Table I. Crystallographic Data for [(Ind)IrCl(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>

(154)	
 formula	IrClP <sub>2</sub> 3C <sub>45</sub> H <sub>37</sub> BF <sub>4</sub>
MW	954.2
a, Å	11.314 (4)
b, Å	14.469 (5)
c, Å	13.021 (2)
$\alpha$ , deg	87.05 (2)
$\beta$ , deg	100.25 (2)
$\gamma$ , deg	68.43 (2)
V, Å <sup>3</sup>	1934.8 (10)
F(000)	944
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	36.39
λ(Μο Κα), Å	0.71069
$\rho_{\rm calcd}, {\rm g \ cm^{-3}}$	1.638
Z	2
obsd reflctns	6379
R	0.04
space group	$P\bar{1}$

Table II. Selected Bond Angles (deg) and Distances (Å) for

		198	
Ir-C1	2.181 (10)	Ir–C9	2.430 (8)
Ir–C2	2.163 (10)	Ir-P11	2.344 (2)
Ir–C3	2.212 (7)	Ir–P12	2.275(2)
Ir-C4	2.428 (7)	Ir-Cl	2.388 (3)
Cl-Ir-P11 Cl-Ir-P12	90.05 (8) 89.02 (8)	P11-Ir-P12	101.93 (6)

trans effects of Cl and PPh3 are much more nearly equal than are those of H and  $PPh_3$  (3) or alkyl and  $PPh_3$  (9). Several conformers might therefore be similar in energy for 19a, in contrast to the high stability of conformer 15 for 3 and 9. The <sup>1</sup>H NMR spectrum of 19a at 300 K shows a very weak ortho-shifted peak at  $\delta$  6.9 most plausibly assigned to conformer 15. The intensity of this peak shows that only ca. 10% of the material is in this form, but at 180 K this has risen to ca. 30%. We would have liked to be able to observe the bond distances in conformer 15 of complex 19a directly, so that we could gather evidence concerning our trans influence model. An X-ray structural study of 19a (Tables I-III and Figure 1) shows that the molecule adopts the conformer shown in Figure 1, not one of type 15, in the solid state. The data do show that our assignment of the structure is correct, however.

For the iodo analogue 19b the <sup>1</sup>H NMR showed no evidence for an ortho shift, and the conformer shown is the most likely solution form, as expected for the lower trans effect I ligand.



Crystal Structure of  $[(Ind)IrClL_2]^+$  (19a). Figure 1 shows the structure of the  $[(Ind)IrClL_2]^+$  cation of 19a. The crystallographic numbering<sup>6b</sup> of the indenyl group used in this paragraph is shown in Figure 1 and used in Tables I–III and Tables S2 and S3 (supplementary material). Apart from the conformation adopted, discussed above, the main feature of the structure is a strongly slipped<sup>10</sup> indenyl group in which the Ir-C4 and Ir-C9 distances are 2.429 (8) Å (average) are 11% longer than Ir-C1, Ir-C2, and Ir-C3: 2.185 (9) Å (average). It is unclear why the slip observed is so large. On our model,<sup>10</sup> the slip should depend on the trans effect of the ligand trans to the ring junction carbons (C4 and C9),  $PPh_3$  in this case.  $PPh_3$  is much lower in the trans effect series than is H in  $[(Ind)IrHL_2]^+$  which adopts conformer 15 and in which the Ir-C (ring junction) distances are only 8% longer



Figure 1. An ORTEP diagram (ellipsoids at 50% probability level) of 19a showing the crystallographic numbering<sup>6b</sup> and the unsymmetrical staggered conformation of the indenyl ring adopted in the solid state.

Table III. Positional Parameters<sup>a</sup> for the Heavy Atoms of 19a<sup>6b</sup>

		174		
 atom	x	У	z	
 Ir1	0.05836 (3)	0.77355 (2)	-0.34656 (2)	
Cl1	-0.0625 (2)	0.6685(2)	-0.3705 (2)	
P11	0.0955(2)	0.7352(1)	-0.1636(1)	
P12	0.2304(2)	0.6495(1)	-0.3868(1)	
С	0.0839 (9)	0.9157 (6)	-0.3592(7)	
C2	0.0910 (9)	0.8739 (6)	-0.4570 (7)	
C3	-0.0321 (9)	0.8709 (6)	-0.4989 (6)	
C4	-0.1222 (8)	0.9247 (6)	-0.4339 (6)	
C5	-0.2560 (9)	0.9534 (9)	-0.4479 (8)	
C6	-0.3173 (10)	1.0146 (10)	-0.3831 (9)	
C7	-0.2483 (12)	1.0487 (9)	-0.3017 (10)	
C8	-0.1156 (11)	1.0157 (7)	-0.2813 (7)	
C9	-0.0505 (8)	0.9537 (6)	-0.3517 (6)	
C111	0.1648 (7)	0.6086 (5)	-0.0932 (5)	
C121	0.1962 (7)	0.7974 (5)	-0.0960 (5)	
C131	-0.0556 (7)	0.7828(5)	-0.1162 (5)	
C211	0.1952 (7)	0.6500 (6)	-0.5296 (6)	
C221	0.2762 (7)	0.5206 (5)	-0.3301 (6)	
C231	0.3868(7)	0.6627 (6)	-0.3618 (6)	

<sup>a</sup>Estimated standard deviations in parentheses ( $\sigma$ ) in units of the last significant digit of the number itself.

than Ir-C1, Ir-C2, and Ir-C3.

Hapticity Determination from NMR Data. The data now available suggest that <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy may be effective methods for determining the hapticity of a coordinated indenyl group.  $\eta^5$ -Indenyls differ most strikingly from the  $\eta^1$  and  $\eta^3$  forms in that the carbons at the ring junction, C(8) and C(9), are shifted to high field by ca. 40 ppm and so appear at 100–120 ppm instead of 140–160 ppm.

 $\eta^1$ -Indenyls can most readily be detected by the absence of symmetry, so that C(1) and C(3), C(4) and C(7), C(5) and C(6), and C(8) and C(9), as well as H(1) and H(3), all show distinct resonances. The H(3) proton comes at ca.  $\delta$  4, to higher field than is the case for the other forms.

 $\eta^3$ -Indenyls show H(2) at ca.  $\delta$  8–9, to much lower field than in any other form.

Alkane Dehydrogenation by 9a.  $[(\eta^5\text{-Ind})\text{IrL}_2\text{Me}]$ (9a), unlike its hydride analogue 3, was active for cyclooctane dehydrogenation in the presence of t-BuCH—CH<sub>2</sub> (20 equiv). Only 0.4 turnover of cyclooctene was produced after 24 h at 110 °C. Since many tens of turnovers are obtained from other, closely related catalysts,<sup>11</sup> 9a was not studied further.

<sup>(11)</sup> Crabtree, R. H. Chem. Rev. 1985, 85, 245-69. Baudry, D.; Ephritikine, M.; Felkin, H.; Holmes-Smith, J. J. Chem. Soc., Chem. Commun. 1983, 788.

Table IV. Selected <sup>13</sup>C NMR Data<sup>a</sup>

complex	no.	C(1,3)	C(2)	C(4-7)	C(8,9)	other peaks
$(\eta^{5}\text{-Ind})\text{IrHL}_{2}^{+}$	3	75.82	92.67	122.23 129.87	114.87	
$(\eta^5$ -Ind)IrL <sub>2</sub>	14	71.61	92.62	121.85 131.87	115.81	
$(\eta^{5}\text{-Ind})\text{Ir}(\text{Bz})\text{L}_{2}^{+}$	9c	78.86	97.57	123.41 129.87	118	
$(\eta^2$ -Ind)IrClL <sub>2</sub> <sup>+</sup>	19a	74.09	96.23	124.44 130.31	117.59	
$(\eta^5$ -Ind)IrL(allyl) <sup>+</sup>	18	79.8	89.8	123 129.87	106.5	39.8, 72.3 (allyl)
$(\eta^1$ -Ind)IrMeL' <sub>2</sub> L <sub>2</sub> +	10	116.78 <sup>b</sup> 98.77 <sup>c</sup>	112.5 <sup>d</sup>	122.7–125.26 <sup>e</sup>	$147.4 \\ 154.05$	171, $168.5^{f}$ 66, 59.56 <sup>g</sup> 29.4, 29.9 <sup>h</sup> 30.2 <sup>i</sup>
indan		32.9	25.3	124.3 126	144	
indene		124.43 <sup>b</sup> 37.53°	121.6 <sup>d</sup>	125.31 126.93 132.72	$144.5 \\ 145.66$	

<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 25 °C. Positions in ppm ( $\delta$ ). BZ =  $\eta^1$ -benzyl; allyl =  $\eta^3$ -allyl; L = PPh<sub>3</sub>; L' = t-BuNC. If PPh<sub>3</sub> present, bands at  $\delta$  128–136 were seen and assigned to the Ph groups. <sup>b</sup>C(1). <sup>c</sup>C(3). <sup>d</sup>C(2). <sup>e</sup>C(4–7), four bands seen. <sup>f</sup>Me<sub>3</sub>CNC. <sup>e</sup>Me<sub>3</sub>C. <sup>h</sup>Me<sub>3</sub>C. <sup>i</sup>Ir-Me.

## Conclusion

We have shown that a series of  $\eta^1$  and  $\eta^3$  intermediates can be observed or isolated in the reactions of a variety of ligands with  $\eta^5$ -indenyl complexes. The corresponding cyclopentadienyl and tetrahydroindenyl complexes do not react because the "indenyl effect" does not operate. Unexpectedly, the phenylcyclopentadienyl complexes did show enhanced reactivity, which we attribute to facile slip as a result of conjugation of the free Cp C=C bond of the slipped form with the phenyl substituent. The hydrides that can slip appear to be much better kinetic proton acids. Solvent-induced  $\beta$ -elimination, photo- $\beta$ -elimination, and photoreductive elimination reactions have been observed and ascribed to ring slip.

## **Experimental Section**

Reactions were carried out under purified  $N_2$  or Ar using standard Schlenk tube techniques. NMR spectra were recorded on a Bruker WM250 or WM500, a Varian CFT-20 (<sup>31</sup>P), or a JEOL FX 90Q instrument. Proton NMR integrals were within 5% of the calculated values unless noted. Materials were purchased from Aldrich, Strem, or Alfa Chemical Co. GC was performed on a Varian 3700 instrument using a 25-m Carbowax 20M capillary column.

**Hydrido**( $\eta^5$ -phenylcyclopentadienyl)bis(triphenylphosphine)iridium(III) Hexafluoroantimoniate (6). A mixture of phenylcyclopentadiene (5 mL), [IrH<sub>2</sub>(acetone)<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub>]SbF<sub>6</sub> (1.07 g, 1.0 mmol), and t-BuCH=CH<sub>2</sub> (0.5 mL) was degassed by freeze/thaw cycling, the frozen mixture sealed (with a Teflon tap) in a glass tube in vacuo, and the mixture heated to 90 °C for 1 day. The resulting solid was separated from the supernatant and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the title complex as a pale yellow solid, yield 900 mg, 82%. Anal. Calcd for C<sub>47</sub>H<sub>40</sub>P<sub>2</sub>SbF<sub>6</sub>Ir·CH<sub>2</sub>Cl<sub>2</sub>: C, 48.29; H, 3.55. Found: C, 47.93; H, 3.56. <sup>1</sup>H NMR (acetone-d<sub>6</sub>) (reported as position ( $\delta$ ), multiplicity [coupling constant (Hz)], assignment): -14.9, t (28.2); 5.54, c, Cp; 7.40, c, Ar.

 $\dot{Hy}$ drido ( $\eta^5$ -4,5,6,7-tetrahydroindenyl) bis (triphenylphosphine) iridium (III) Hexafluoroantimoniate (5). [(Ind)IrHL<sub>2</sub>]SbF<sub>6</sub> (535 mg, 0.5 mmol) in EtOH (20 mL) was stirred under 1 atm of H<sub>2</sub> for 4 days in the presence of 5% Rh/Al<sub>2</sub>O<sub>3</sub> (0.5 g). The suspension was filtered through Celite and the solvent evaporated to give the crude product, which was recrystallized as a pale yellow solid from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (yield 494 mg, 92%). Anal. Calcd for IrC<sub>45</sub>H<sub>42</sub>P<sub>2</sub>SbF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 47.15; H, 3.78. Found: C, 47.22; H, 4.11. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): -14.53, t (28.2); 1.49-2.8, c, Ind H(4-7); 4.86, c, Ind H(1,3); 5.83, c, Ind H(2), 7.38. Reactions of 3. (i) With CO. 1 (214 mg, 0.2 mmol) in acetone (5 mL) was stirred under CO (1 atm) for 2 days. The solution volume

was reduced to ca. 2 mL by evaporation and  $Et_2O$  added. The product (yield 80%) was identified as  $[IrH_2(CO)_2L_2]SbF_6$  by comparison (<sup>1</sup>H NMR, IR) with an authentic sample. The same reaction carried out in  $CH_2Cl_2$  (2 mL) gave  $[Ir(CO)_3L_2]SbF_6$  identified as above. (ii) With t-BuNC. 1 (214 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was treated with t-BuNC (0.1 mL, 1 mmol) at room temperature for 2 h, the solution volume was reduced to 2 mL by evaporation, and  $Et_2O$ /heptanes (2:1 v/v, 60 mL) were added to precipitate a yellow product. Anal. Found: C, 47.60; H, 4.69; P, 4.63; F, 9.72. <sup>1</sup>H NMR studies of the reaction revealed the intermediates 7 and 8 noted in the text. (iii) With PMe<sub>3</sub>. To  $[(Ind)IrHL_2]SbF_6$  (214 mg, 0.2 mmol) in  $CD_2Cl_2$  (5 mL) was added an excess (0.5 mL) of PMe<sub>3</sub>, and the mixture was stirred for 1 day. The product, isolated by addition of heptane, was recrystallized from  $CH_2Cl_2/Et_2O/heptane$  to give the pale cream product trans-[ $(\eta^1$ -Ind)IrH(PMe<sub>3</sub>)<sub>4</sub>]SbF<sub>6</sub> (12) (yield 146 mg, 86%). Anal. Calcd for C<sub>21</sub>H<sub>44</sub>P<sub>4</sub>F<sub>6</sub>IrSb: C, 29.72; H, 5.22. Found: C, 30.10; H, 5.01.

**Reaction of 6 with Trimethylphosphine.** To  $[(PhC_5H_4)$ -IrHL<sub>2</sub>]SbF<sub>6</sub> (210 mg, 0.19 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added an excess (0.5 mL) of PMe<sub>3</sub>, and the mixture was stirred for 1 day. The product was isolated with heptane and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O/heptane to give a pale cream product (yield 114 mg, 66%). <sup>1</sup>H NMR: -21.56, quintet ( $J(P,H_{cis}) = 14.7$  Hz), Ir-H; 1.4-2.4, complex, PMe; 7.2-7.8, Ar. Anal. Calcd for IrC<sub>23</sub>H<sub>46</sub>P<sub>4</sub>SbF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 29.61; H, 4.97; P, 12.74. Found: C, 29.78; H, 4.70; P, 12.51.

 $(\eta^5$ -Indenyl)bis(triphenylphosphine)iridium(I) (14). To [(Ind)IrHL<sub>2</sub>]SbF<sub>6</sub> (534 mg, 0.5 mmol) in THF (30 mL) at -78 °C was added *n*-BuLi (313  $\mu$ L of 1.6 M solution in hexane, 0.5 mmol) dropwise with stirring. The mixture was warmed to room temperature, the solvents were evaporated, and the residue was extracted with C<sub>6</sub>H<sub>6</sub> (3 × 10 mL). The combined extracts were concentrated to 5 mL by evaporation, heptanes (5 mL) were added, and the mixture kept at -20 °C for 2 days. Orange crystals (yield 374 mg, 90%) were filtered, washed with cold pentane, and identified by comparison with an authentic sample.

Methyl ( $\eta^5$ -indenyl)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (9a). (Ind)IrL<sub>2</sub> (250 mg, 0.3 mmol) in THF (20 mL) was treated with MeI (1.5 mL, 100 mol equiv) at -78 °C and the reaction mixture warmed to 20 °C and allowed to stir in the dark for an hour. Excess NaBF<sub>4</sub> or NaSbF<sub>6</sub> (3 mmol) was added. The pale yellow product was precipitated with Et<sub>2</sub>O (20 mL) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, yield 308 mg, 93%. Anal. Calcd for IrC<sub>46</sub>H<sub>40</sub>P<sub>2</sub>BF<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 55.37; H, 4.34; P, 6.09. Found: C, 53.06; H, 4.70; P, 5.51. The following compounds were prepared similarly. [(Ind)IrEtL<sub>2</sub>]SbF<sub>6</sub> (9b): as above except that EtI was used and stirring was continued for 4 h; yield 72%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.15, t (7.2), Me; 2.58, c, CH<sub>2</sub>; 5.8, t (2.8), Ind H(1), H(3), 6.33, c, Ind H(2); 5.37 and 7.16, dd (3.1, 6.3), Ind H(4-7); 6.698, 7.37, 7.54, c, PPh<sub>3</sub>. The compound decomposed too quickly to allow analytical data to be obtained. [(Ind)Ir- $(CH_2Ph)L_2$  SbF<sub>6</sub> (9c): as above except that PhCH<sub>2</sub>Br was used and stirring was continued for 2 h; yield 83%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 5.8, t (3), Ind H(1), H(3); 6.3, c, Ind H(2); 5.4 and 7.1, dd (3, 6), Ind H(4-7); 6.7-7.6, c, PPh3 and PhCH2. Anal. Calcd for  $IrC_{52}H_{47}P_2BF_4:2CH_2Cl_2: C, 53.55; H, 4.24; P, 5.11.$  Found: C, 53.60; H, 4.70; P, 5.51.  $[(\eta^5-Ind)Ir(\eta^3-allyl)L]SbF_6$  (18): as above except that CH2=CHCH2Br was used, stirring was continued for 1 h, and the crude product was stirred in acetone for 2 days to isomerize the initially formed  $[(\eta^5-Ind)Ir(\eta^1-allyl)L_2]SbF_6$ , yield 62%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.27, dd (10.5, 13), allyl H<sub>anti</sub>; 3.67, d (6.7), allyl H<sub>syn</sub>; 5.068 c, allyl, H<sub>cent.</sub>; 6.09, c, Ind H(1), H(3); 6.18, c, Ind H(2); 7.21, dd (3.1, 6.6), Ind H(4-7); 7.4-7.8, c, PPh<sub>3</sub>. Anal. Calcd for IrC<sub>30</sub>H<sub>27</sub>PBF<sub>4</sub>·0.33CH<sub>2</sub>Cl<sub>2</sub>: C, 47.85; H, 3.66. Found: C, 48.69; H, 3.83. The intermediate [(Ind) $Ir(\eta^1-allyl)L_2$ ]SbF<sub>6</sub> (17) had the following <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 4.81, dd (10, 2.1), allyl IrCH<sub>2</sub>; 4.57, d (16.4), allyl ==CH<sub>2</sub>; 6.03, c, allyl, CH; 6.13, c, Ind H(1), H(3); 6.71, d (2.4), Ind H(2); 5.39 and 7.3, dd (3.1, 6.3), Ind H(4-7);

7.4-7.8, c, PPh<sub>3</sub>. Chloro( $\eta^{5}$ -indenyl)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (19a). (Ind)IrL<sub>2</sub> (250 mg, 0.3 mmol) in THF (20 mL) was kept under a Cl<sub>2</sub> atmosphere (1 atm) for 2 h at 25 °C. Excess NaBF<sub>4</sub> (330 mg, 3 mmol) was added. The pale yellow product was precipitated with Et<sub>2</sub>O (20 mL) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O (yield 93%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 5.4, c, Ind H(1), H(3); 5.58, t (2), Ind H(2); 7, c, Ind H(4-7); 7.2-7.5, c, PPh<sub>3</sub>. The following compound was prepared similarly. [(Ind)IrIL<sub>2</sub>]BF<sub>4</sub> (19b): as above except that I<sub>2</sub> (38 mg, 0.3 mmol in 10 mL of THF) was used and stirring was continued in the dark for 1 h; yield 90%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 5.73, c, Ind H(2); 5.53, t (2.4), Ind H(1), H(3); 6.33, c, Ind H(2); 7.45, c, para PPh<sub>3</sub>; 7.3, c, meta PPh<sub>3</sub>; 7.14, c, ortho PPh<sub>3</sub>. Anal. Calcd for IrIC<sub>4</sub>5H<sub>37</sub>P<sub>2</sub>BF<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 52.33; H, 3.73. Found: C, 52.15; H, 3.43.

Methyl( $\eta^1$ -indenyl)bis(triphenylphosphine)bis(tert-butyl isocyanide)iridium(III) Hexafluoroantimoniate (10). To [(Ind)IrMeL<sub>2</sub>]SbF<sub>6</sub> (433 mg, 0.4 mmol) in acetone (5 mL) was added t-BuNC (0.1 mL, 1 mmol), and the mixture was stirred for 6 h at room temperature. The solvents were evaporated, and the residue was recrystallized from acetone/CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O/hexane. Anal. Calcd for C<sub>56</sub>H<sub>58</sub>P<sub>2</sub>N<sub>2</sub>IrSbF<sub>6</sub><sup>+1.2</sup>SCH<sub>2</sub>Cl<sub>2</sub>: C, 50.09; H, 4.50; N, 2.10; P, 4.65. Found: C, 50.15; H, 4.35; N, 2.51; P, 4.94. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): -0.05, t (6.3), Ir-Me; 0.89 and 1.31, s, t-Bu; 4.01, c, Ind H(3); 6.33, d (7.5), Ind H(1); 6.84, c, Ind H(2); 6.13 and 7.06, c, H(4-7). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): 30.2, Ir-Me; 29.4 and 29.9, Me<sub>3</sub>CNC; 66.0 and 59.6, Me<sub>3</sub>CNC; 168.5 and 171.0, Me<sub>3</sub>CNC; 98.8, Ind C(3); 112.5, Ind C(2); 116.8, Ind C(1); 125.2-122.7, C(4-7) four peaks; 154.0, 147.4; C(8-9); 128.6-135, PPh<sub>3</sub>.

**Crystallography.** A crystal of 19a  $(0.2 \times 0.2 \times 0.2 \text{ mm})$  was sealed in a capillary and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections  $(2\theta > 15^{\circ})$  during normal alignment

procedures using Mo radiation ( $\lambda = 0.710698$  Å). Data (8981 points) were collected at room temperature by using a variable scan rate, a  $\theta$ -2 $\theta$  scan mode, and a scan width of 1.2° below K $\alpha_1$ and 1.2° above  $K\alpha_2$  to a maximum  $2\theta$  of 116°. Backgrounds were measured at each side of the scan for a time equal to the total scan time. The intensities of three standard reflections were remeasured every 97 reflections and the intensities showed less than 8% variation, and so corrections for decomposition were not made. Data were corrected for Lorentz, polarization, and background effects, but not for absorption (in view of the regular crystal shape). After removal of redundant data, 6379 reflections were considered observed  $[I > 3\sigma(I)]$ . The structure was solved by direct methods using MULTAN 80. Successive least-squares/ difference Fourier cycles allowed location of all the non-hydrogen atoms.<sup>12a</sup> Hydrogen positional parameters were calculated, assigned U = 0.03, and included in the final cycles of refinement. Refinement of scale factors and positional and thermal parameters was carried out to convergence.<sup>12b</sup> A final cycle of refinement [function minimized  $\sum (|F_0| - |F_c|)^2$ ] led to a final agreement factor of R = 4.0% [ $R = \sum (||F_0| - |F_c||/|F_0|) \times 100$ ]. Anomalous dispersion corrections were made for Cl and Ir; scattering factors were taken from Cromer and Mann;<sup>12c</sup> in the final stages of refinement, a weight of  $1/\sigma(F^2)$  was applied.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (A.H. and R.T.), and the National Science Foundation (R.H.C.) for funding.

**Registry No.** 3, 91410-23-0; 5, 119787-61-0; 6, 119787-59-6; 7, 119787-65-4; ,, 119787-66-5; **9a**, 119793-89-4; **9b**, 119787-70-1; **9c**, 119787-72-3; **10**, 119787-84-7; **12**, 119787-68-7; **14**, 119787-62-1; **17**, 119787-78-9; **18**, 119787-74-5; **19a**, 119787-80-3; **19b**, 119787-82-5;  $[IrH_2(acetone)_2(PPh_3)_2]SbF_6$ , 89509-77-3; *t*-BuCH==CH<sub>2</sub>, 558-37-2;  $[IrH_2(CO)_2L_2]SbF_6$ , 119787-63-2;  $[Ir(CO)_3L_2]SbF_6$ , 119787-64-3; *t*-BuNC, 7188-38-7; EtI, 75-03-6; PhCH<sub>2</sub>Br, 100-39-0; CH<sub>2</sub>==CHCH<sub>2</sub>Br, 106-95-6; Rh, 7440-16-6; phenylcyclopentadiene, 88243-06-5; *trans*-hydrido( $\eta^1$ -3-phenylcyclopentadienyl)tetrakis(triphenylphosphine)iridium (III) hexafluoroantimoniate, 119787-76-7.

**Supplementary Material Available:** Tables of hydrogen atom positions (Table S2), anisotropic thermal parameters (Table S3), and further bond distances and angles (Table S4) (6 pages); a listing of structure factors (Table S1) (46 pages). Ordering information is given on any current masthead page.

<sup>(12) (</sup>a) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.;
DeClerq, J. P.; Woolfson, M. M. Report; University of York: York, UK.
(b) Stewart, J. M., ed., Technical Report TR 446; Computer Center, University of Maryland: College Park, MD. (c) Cromer, D. T.; Mann, T. B. Acta Crystallogr., Sect. A 1968, A24, 321-4.