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

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The complex ion $[(\eta^5\text{-Ind})IrHL_2]^+$ (Ind = indenyl, L = PPh_3) undergoes substitution with *t*-BuNC, CO, and PMe_3, while the Cp analogue (Cp = cyclopentadienyl) is inert. The phenylcyclopentadienyl complex $[(\eta^5\text{-}PhC_5H_4)IrHL_2]^+$ undergoes rapid substitution with PMe_3 but not with *t*-BuNC or CO. Slipped η^3 and η^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 $[(\eta^5\text{-Ind})IrHL_2]^+$ and $[(\eta^5\text{-}PhC_5H_4)IrHL_2]^+$, but not the Cp analogue. The reactions of the deprotonated complex $[(\eta^5\text{-Ind})IrL_2]$ with a number of electrophiles are also investigated and the resulting cations $[(\eta^5\text{-Ind})IrXL_2]^+$ (X = Me, Et, CH_2Ph, Cl, I) characterized. The ethyl complex loses ethylene at 60 °C by β-elimination, but only in donor solvents, which may attack associatively in the first step of the reaction. In nondonor solvents, the β-elimination is induced by UV photolysis, which may induce ring slip. Allyl bromide reacts with $[(\eta^5\text{-Ind})IrL_2]$ to give $[(\eta^5\text{-Ind})Ir(\eta^3\text{-allyl})L]^+$, via $[(\eta^5\text{-Ind})Ir(\eta^1\text{-allyl})L_2]^+$ as an observed but unisolated intermediate. The structure of the chloro complex $[(\eta^5\text{-Ind})IrClL_2]$ was determined by X-ray methods (space group $P\bar{1}$; a = 11.314 (4) Å, b = 14.469 (5) Å, c = 13.021 (2) Å, α = 87.05 (2)°, β = 100.25 (2)°, γ = 68.43 (2)°; V = 1934.8 (10) Å^3; mol wt = 954.2, Z = 2; $F(000)$ = 944; ρ_{calcd} = 1.638 g cm^{-3}; R = 0.04 for 6379 reflections). Hydrogenation of $[(\eta^5\text{-Ind})IrHL_2]^+$ with Rh/C gives the tetrahydroindenyl complex.

An indenyl complex such as **1** generally substitutes at a higher rate than the corresponding cyclopentadienyl.[1] This "indenyl effect" has been ascribed to the stabilization of a slipped η^3 intermediate (**2**) by recovery of the full aromatic stabilization in the benzo ring of the slipped indenyl group (eq 1).

(1)

1 **2** **3**

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

Results and Discussion

We have reported[5] a simple route to $[(\eta^5\text{-Ind})IrHL_2]^+$ (**3**, Ind = indenyl; L = PPh_3) by a C–H activation sequence from indene and $[IrH_2(solv)_2L_2]^+$ (solv = Me_2CO), and in this paper we compare the reactions of **3** with those of the corresponding cyclopentadienyl $[CpIrHL_2]^+$ (**4**).

We will report several reaction sequences in which incoming ligands cause η^5 to η^3 to η^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 $[(\eta^5\text{-Ind})IrHL_2]A$ (3) with CO. $[(\eta^5\text{-Ind})IrHL_2]A$ (L = PPh_3, A = SbF_6, **3**) slowly reacts with CO (1 atm) at 25 °C over 2–4 days in CH_2Cl_2 to give free indene and the known[6a] $[Ir(CO)_3L_2]BF_4$. 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_3 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

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(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, ...

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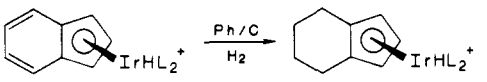


3 5 (2)

prepared from $[IrH_2(acetone)_2L_2]^+$ and PhC_5H_5 at 90 °C for 1 day; cyclopentene and indene give similar reactions.[5,7] 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).

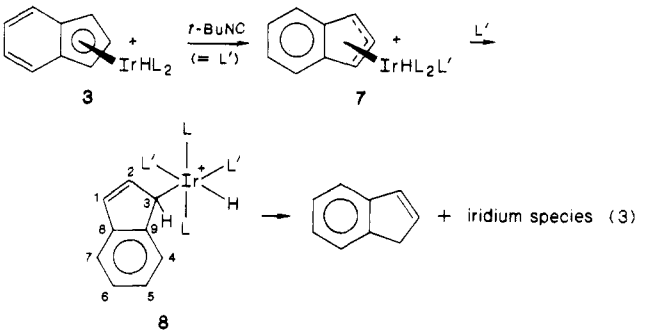
Reaction of $[(\eta^5\text{-Ind})IrHL_2]$A (3) with Isonitrile. The reaction with **3** with 1.5 equiv of *t*-BuNC is very rapid at room temperature to give free indene and an unstable iridium species which shows both terminal and bridging *t*-BuNC groups by IR (ν(NC) 2152.3 (s), 2059.5 (sh), 1584.6 (m), and 1568.3 (w) cm^{-1}). 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 $[Ir_2L_4(t\text{-BuNC})_3]^{2+}$, and it may be $[L_2Ir(\mu\text{-RNC})_2IrL_2(CNR)]^{2+}$. 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 δ −14.2 (J(P,H) = 9 Hz). A peak due to a single coordinated *t*-BuNC at δ 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 $[(\eta^3\text{-Ind})IrL_2(t\text{-BuNC})H]^+$ (**7**). This assignment of an η^3 structure is based on an assumed 18e configuration for **7** and on the resonance positions[6b] observed for the η^3-indenyl group itself (H(2), δ 8.5; H(1) and H(3), δ 4.41), which, as we shall see, differ from those characteristic for the η^1- and η^5-binding modes. In slipping to η^3, the indenyl H(2) protons tend to move ca. 2 ppm to lower field from the δ 5–7 typical for the η^1- and η^5-binding modes.[4b] For the η^5 complex **3**, H(2) resonates at δ 6.59 and, for the η^3 complex **7**, resonates at δ 8.5, so the η^5 to η^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 δ −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 $[(\eta^1\text{-Ind})IrL_2(t\text{-BuNC})_2H]^+$ (**8**) on the basis of the fact that the analogous $(\eta^5\text{-Ind})IrMeL_2^+$ gives a well-characterized η^1-Ind derivative with *t*-BuNC (see below), which has a similar NMR spectrum. In particular, H(3) appears at δ 3.98 for **8**, close to the value of δ 4.0 in the fully characterized methyl analogue but different from the values of δ 5.2–5.8 found for η^5-Ind groups. The cis disposition of H and η^1-Ind groups is probable on the basis of the value of δ(Ir–H) which is appropriate[7b] for H trans to *t*-BuNC but not H trans to (η^1-Ind) and by analogy with the structures of a large number of derivatives[7,8] 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 η^5-Ind group via the intermediate η^3 and η^1 stages.



Reaction of $[(\eta^5\text{-Ind})IrMeL_2]$A (9a) with Isonitrile. We studied the analogous methyl $[(\eta^5\text{-Ind})IrMeL_2]^+$ (**9a**) because reductive elimination reactions that form sp^3–sp^3 C–C bonds tend to be slow, and so the intermediate η^1-Ind form should now be stable.

The corresponding η^1-Ind complex $[(\eta^1\text{-Ind})IrMe(t\text{-BuNC})_2L_2]^+$ (**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 (^{1}H NMR δ 1.31 and 0.89) and by analogy with other *cis,cis,trans*-$[IrX_2L_2(PPh_3)_2]^+$ complexes.[7,8]

The ^{1}H and ^{13}C NMR chemical shifts (see Experimental Section) indicate that an η^1 structure is adopted. In particular H(1) and H(3) and C(1) and C(3) show distinct resonances, as expected for an η^1 structure but in contrast to the single resonance observed for the η^3 and η^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 (^{1}H NMR), resonances were seen strongly resembling those of the η^3-Ind species observed in the case of the hydride. In particular, this η^3-Ind species shows a resonance at δ 8.58 in a region (δ 7–9) characteristic for the H(2) proton of an η^3-Ind structure and a triplet methyl resonance at δ 0.18, showing that the two PPh_3 ligands are still attached to the metal. The η^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 η^1 complex **10**, described above, showed no trace of **11a** in the ^{1}H NMR, suggesting that dissociation of *t*-BuNC did not occur to any substantial extent, but a small amount of a different η^3-complex **11b** was observed. The appearance of H(2) at δ 8.38 and the appearance of a doublet Ir–Me resonance at δ 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 η^3-indenyl complex via an η^1-intermediate.

Reaction of $[(\eta^5\text{-Ind})IrHL_2]$A (3) with PMe_3. **3** reacts with PMe_3 in CH_2Cl_2 at ambient temperature over 24 h to give as thermodynamic product *trans*-$[(\eta^1\text{-Ind})IrH(PMe_3)_4]$A (**12**), which can be isolated and fully characterized. The new complex **12** shows a quintet Ir–H reso-

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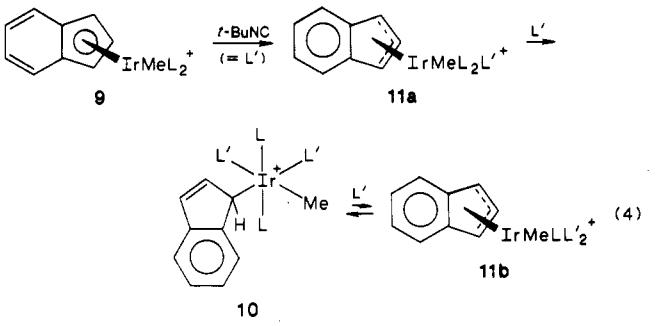
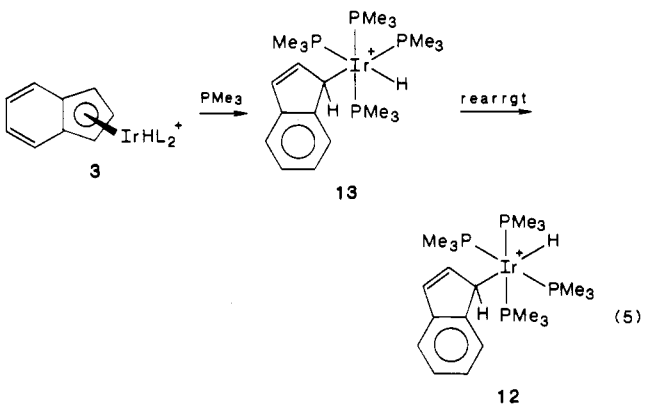
(8) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816.

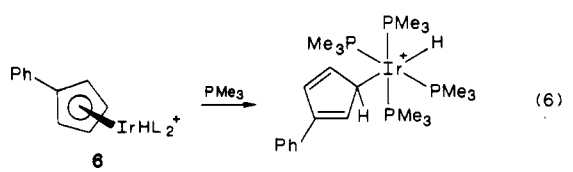


nance at δ −21.6 ($^1J(P,H_{cis})$ = 14.5 Hz) appropriate[7,8] for H trans to a carbon ligand and cis to four equivalent PMe_3 groups. During the early stages of the reaction (2–12 h), the cis isomer **13** was detected by ^1H NMR. The Ir–*H* resonance for **13** at δ −11.82, a chemical shift appropriate for H trans to a phosphine, appears as a doublet ($^2J(P,H_{trans})$ = 149 Hz) of quartets ($^2J(P,H_{cis})$ = 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 η^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*-$[Ir(PMe_3)_4(X)H]^+$ (X = alkyl) and ascribed to the failure of PMe_3 to dissociate to give a reactive 16e intermediate.[9]

A Phenylcyclopentadienyl Effect? The cyclopentadienyl and tetrahydroindenyl complexes **4** and **5** were inert to PMe_3 under conditions in which the indenyl complex **3** reacts. The phenylcyclopentadienyl complex **6** also reacts to give the η^1-PhCp complex shown in eq 6. Steric effects may be responsible for the phenyl group appearing at the 3-position of the C_5 ring in the product. The Ir–*H* resonance appears at δ −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_3 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 η^3-Ind intermediate just as efficiently as would PMe_3. It will be interesting to see how general this phenylcyclopentadienyl effect will be.

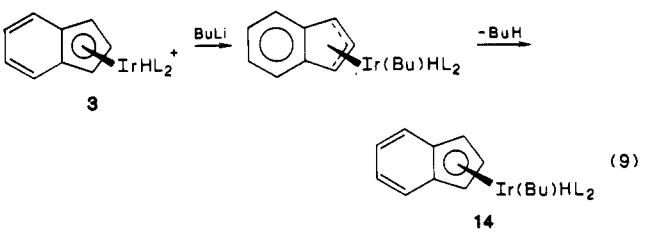
The phenyl group probably favors ring slippage because the C=C group liberated from the metal in an η^5 to η^3 slip process is stabilized by conjugation with the aromatic ring.

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_3, **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.

$$CpIrHL_2^+ \xrightarrow{\text{BuLi/TMEDA}} \text{no reaction} \quad (7)$$

$$IndIrHL_2^+ \xrightarrow{NEt_3} IndIrL_2 \quad (8)$$

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_3 or *n*-BuLi, but the tetrahydroindenyl complex **5** resists *n*-BuLi.



Merola[4b] 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**.

$$[Ir(coe)_2Cl]_2 \xrightarrow{\text{Li[Ind]}} [(Ind)Ir(coe)_2] \xrightarrow{L} \underset{\mathbf{14}}{[(Ind)IrL_2]} \quad (10)$$

Merola identifies **14** as an η^5-Ind complex. We agree on the basis of the ^{13}C NMR resonance position for C(8,9) at δ 115.8. In free indan, this resonance appears at δ 144 close to the positions we observe for our η^1-Ind complexes (δ 147.4 and 154) and that Merola observes for $[(\eta^3\text{-Ind})Ir(PMe_3)_3]$ (δ 156.7).

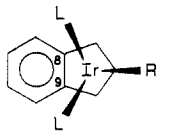
Reactions of $[(\eta^5\text{-Ind})IrL_2]$ (14) with H_2. We were interested to find that **14** could be hydrogenated, with loss of indene. The reaction takes place with H_2 in THF over 2 h to precipitate $IrH_5(PPh_3)_2$, identified by its characteristic IR band at 1948 cm^{-1}. The indenyl group is completely removed from the metal and appears as indene among the final products. In contrast $[(\eta^5\text{-Ind})IrHL_2]^+$ (**3**) does not undergo hydrogenation in THF, even though $[IrH_2(THF)_2L_2]^+$, the analogous cationic product, is known and stable. Probably **14** has a much higher tendency to slip to the 16e $(\eta^3\text{-Ind})IrL_2$ 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

(9) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580–6.

Merola[4b] observed a PMe_3-induced slip to give $(\eta^3$-Ind)$Ir(PMe_3)_3$.

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 δ −8.21 (t, ^2J(P,H) = 13 Hz) appeared and grew in intensity with time in step with resonances at δ 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 $[(\eta^5$-Ind)$IrL_2]$ (14) with Halocarbons To Give Alkyls. The nucleophilic species **14** reacts with MeI, EtI, or $PhCH_2Br$ to give the corresponding methyl, ethyl, or benzyl complexes $[(\eta^5$-Ind)$IrRL_2]^+$ (**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_3 groups ("ortho shift"). In the similar case of $[(\eta^5$-Ind)$IrHL_2]^+$, we ascribed[10] the shift to the ring current of the indenyl benzo ring in a conformer of type **15**, which



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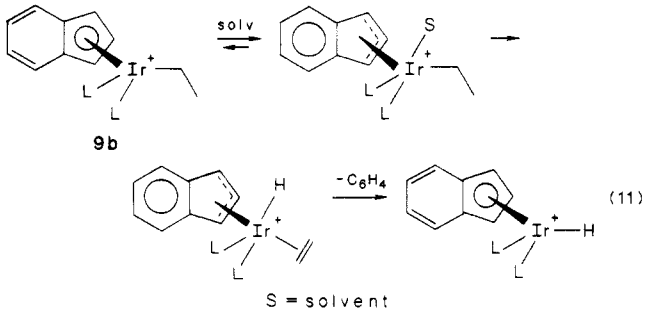
is adopted by **3** (R = H) and by **9a** (R = Me), **9b** (R = Et), and **9c** (R = $PhCH_2$). The reason we believe this conformer is adopted[5,10] is that the high trans effect of R leads to an increase in the Ir–C(8,9) distances (verified crystallographically[10] in the case of R = H), which in turn 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 β-Elimination in $(\eta^5$-Ind)$IrEtL_2$ (9b). The ethyl complex **9b** is particularly interesting in that it undergoes solvent dependent β-elimination to give C_2H_4 and $[(\eta^5$-Ind)$IrHL_2]^+$ (**3**). The reverse reaction,

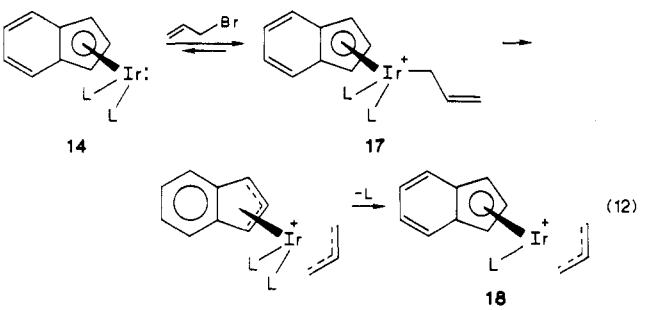


formation of **9b** from **3** and C_2H_4 (1 atm, 25 °C), was not observed in any solvent, however, and is probably contrathermodynamic. Even at room temperature **9b** β-eliminates in THF over several minutes. On the other hand, the same complex is stable in C_6H_6 or CH_2Cl_2 at room temperature and even in refluxing 1,3-$C_2H_4Cl_2$ (80 °C) for several hours. In refluxing acetone (60 °C), β-elimination is observed. The most reasonable explanation is that associative substitution of THF or acetone can occur to give a solvated species $[(\eta^3$-Ind)$IrRL_2$(solv)]. If this loses the solvent, the 16e intermediate could β-eliminate or slip back to the η^5 form.

β-Photoelimination in $[(\eta^5$-Ind)$IrEtL_2]^+$ (9b) and Reductive Photoelimination of Indene from $[(\eta^5$-Ind)$IrHL_2]^+$ (3). In noncoordinating solvents, such as CH_2Cl_2, **9b** is thermally stable presumably because no solvento species is formed. Interestingly photolysis (254 nm, 4 × 8 W lamps, 30 h) smoothly induces β-elimination in noncoordinating solvents. We propose that illumination causes slip by promoting a metal d_π electron to an M–L(σ^*) level. The resulting 16e species can β-eliminate whatever the solvent.

$[(\eta^5$-Ind)$IrHL_2]^+$ (**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 η^1 form. As we saw above, reductive elimination of an η^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 η^1-allyl complex, **17**, is formed first and then rearranges to an η^3-allyl, **18**, as the final product. The structures of **17** and **18** follow



from their spectral data. In particular, the off-resonance ^{1}H-decoupled ^{13}C NMR spectrum of the final product **18** shows the characteristics resonances for η^3-allyl at δ 39.8 (triplet, C(1,3)) and 72.3 (doublet, C(2)). Peaks at δ 79.0 (d, C(1,3)), 89.8 (d, C(2)), and 123 (s, C(8,9)) characterize the η^5-Ind group. The presence of one PPh_3 group is shown by microanalysis and also by integration of the aromatic versus the allyl resonances in the ^{1}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_3 group and resonance positions for the η^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 ^{1}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 $[(\eta^5$-Ind)$IrL_2]$ (14) with Halogens. Only Cl_2 and I_2 were studied in detail. Both attack **14** electrophilically to give the halo cations that can be isolated as BF_4^- salts.

The chloro species **19a** is particularly interesting in relation to our suggestion[5,10] 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

(10) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 529–35.

Table I. Crystallographic Data for [(Ind)IrCl(PPh$_3$)$_2$]BF$_4$ (19a)

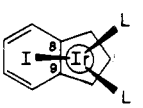
formula	$IrClP_2C_{45}H_{37}BF_4$
MW	954.2
a, Å	11.314 (4)
b, Å	14.469 (5)
c, Å	13.021 (2)
α, deg	87.05 (2)
β, deg	100.25 (2)
γ, deg	68.43 (2)
V, Å^3	1934.8 (10)
F(000)	944
μ(Mo Kα), cm^{-1}	36.39
λ(Mo Kα), Å	0.71069
ρ_{calcd}, g cm^{-3}	1.638
Z	2
obsd reflctns	6379
R	0.04
space group	$P\bar{1}$

Table II. Selected Bond Angles (deg) and Distances (Å) for 19a

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	90.05 (8)	P11–Ir–P12	101.93 (6)
Cl–Ir–P12	89.02 (8)		

trans effects of Cl and PPh$_3$ 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 ^{1}H NMR spectrum of **19a** at 300 K shows a very weak ortho-shifted peak at δ 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 ^{1}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.



19b

Crystal Structure of [(Ind)IrClL$_2$]$^+$ (19a). Figure 1 shows the structure of the [(Ind)IrClL$_2$]$^+$ cation of **19a**. The crystallographic numbering[6b] 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[10] 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,[10] 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 than Ir–C1, Ir–C2, and Ir–C3.

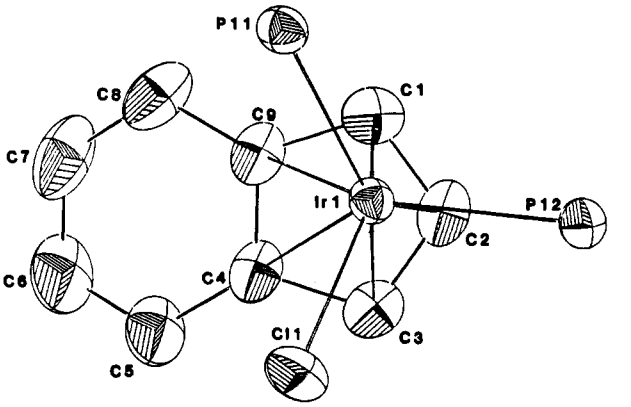


Figure 1. An ORTEP diagram (ellipsoids at 50% probability level) of **19a** showing the crystallographic numbering[6b] and the unsymmetrical staggered conformation of the indenyl ring adopted in the solid state.

Table III. Positional Parameters[a] for the Heavy Atoms of 19a[6b]

atom	x	y	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)
C	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)

[a] Estimated standard deviations in parentheses (σ) in units of the last significant digit of the number itself.

Hapticity Determination from NMR Data. The data now available suggest that ^{1}H and ^{13}C NMR spectroscopy may be effective methods for determining the hapticity of a coordinated indenyl group. η^5-Indenyls differ most strikingly from the η^1 and η^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.

η^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. δ 4, to higher field than is the case for the other forms.

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

Alkane Dehydrogenation by 9a. [(η^5-Ind)IrL$_2$Me] (**9a**), unlike its hydride analogue **3**, was active for cyclooctane dehydrogenation in the presence of t-BuCH=CH$_2$ (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,[11] **9a** was not studied further.

(11) 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 ^{13}C NMR Data[a]

complex	no.	C(1,3)	C(2)	C(4–7)	C(8,9)	other peaks
(η^5-Ind)IrHL$_2^+$	3	75.82	92.67	122.23 129.87	114.87	
(η^5-Ind)IrL$_2$	14	71.61	92.62	121.85 131.87	115.81	
(η^5-Ind)Ir(Bz)L$_2^+$	9c	78.86	97.57	123.41 129.87	118	
(η^2-Ind)IrClL$_2^+$	19a	74.09	96.23	124.44 130.31	117.59	
(η^5-Ind)IrL(allyl)$^+$	18	79.8	89.8	123 129.87	106.5	39.8, 72.3 (allyl)
(η^1-Ind)IrMeL'$_2$L$_2^+$	10	116.78[b] 98.77[c]	112.5[d]	122.7–125.26[e]	147.4 154.05	171, 168.5[f] 66, 59.56[g] 29.4, 29.9[h] 30.2[i]
indan		32.9	25.3	124.3 126	144	
indene		124.43[b] 37.53[c]	121.6[d]	125.31 126.93 132.72 134.84	144.5 145.66	

[a] In CD_2Cl_2 at 25 °C. Positions in ppm (δ). BZ = η^1-benzyl; allyl = η^3-allyl; L = PPh_3; L' = *t*-BuNC. If PPh_3 present, bands at δ 128–136 were seen and assigned to the Ph groups. [b] C(1). [c] C(3). [d] C(2). [e] C(4–7), four bands seen. [f] Me_3CNC. [g] Me_3C. [h] Me_3C. [i] Ir-*Me*.

Conclusion

We have shown that a series of η^1 and η^3 intermediates can be observed or isolated in the reactions of a variety of ligands with η^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 β-elimination, photo-β-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 (^{31}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(η^5-phenylcyclopentadienyl)bis(triphenylphosphine)iridium(III) Hexafluoroantimoniate (6). A mixture of phenylcyclopentadiene (5 mL), [IrH$_2$(acetone)$_2$(PPh$_3$)$_2$]SbF$_6$ (1.07 g, 1.0 mmol), and *t*-BuCH=CH$_2$ (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_2Cl_2/Et_2O to give the title complex as a pale yellow solid, yield 900 mg, 82%. Anal. Calcd for $C_{47}H_{40}P_2SbF_6Ir\cdot CH_2Cl_2$: C, 48.29; H, 3.55. Found: C, 47.93; H, 3.56. ^1H NMR (acetone-d_6) (reported as position (δ), multiplicity {coupling constant (Hz)}, assignment): −14.9, t (28.2); 5.54, c, Cp; 7.40, c, Ar.

Hydrido(η^5-4,5,6,7-tetrahydroindenyl)bis(triphenylphosphine)iridium(III) Hexafluoroantimoniate (5). [(Ind)IrHL$_2$]SbF$_6$ (535 mg, 0.5 mmol) in EtOH (20 mL) was stirred under 1 atm of H_2 for 4 days in the presence of 5% Rh/Al_2O_3 (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_2Cl_2/Et_2O (yield 494 mg, 92%). Anal. Calcd for $IrC_{45}H_{42}P_2SbF_6\cdot CH_2Cl_2$: C, 47.15; H, 3.78. Found: C, 47.22; H, 4.11. ^1H NMR (acetone-d_6): −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)$_2$L$_2$]SbF$_6$ by comparison (^1H NMR, IR) with an authentic sample. The same reaction carried out in CH_2Cl_2 (2 mL) gave [Ir(CO)$_3$L$_2$]SbF$_6$ identified as above. **(ii) With *t*-BuNC.** 1 (214 mg, 0.2 mmol) in CH_2Cl_2 (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. ^1H NMR studies of the reaction revealed the intermediates 7 and 8 noted in the text. **(iii) With PMe_3.** 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_3, 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*-[(η^1-Ind)IrH(PMe$_3$)$_4$]SbF$_6$ (**12**) (yield 146 mg, 86%). Anal. Calcd for $C_{21}H_{44}P_4F_6IrSb$: C, 29.72; H, 5.22. Found: C, 30.10; H, 5.01.

Reaction of 6 with Trimethylphosphine. To [(PhC$_5$H$_4$)IrHL$_2$]SbF$_6$ (210 mg, 0.19 mmol) in CH_2Cl_2 (5 mL) was added an excess (0.5 mL) of PMe_3, and the mixture was stirred for 1 day. The product was isolated with heptane and recrystallized from CH_2Cl_2/Et_2O/heptane to give a pale cream product (yield 114 mg, 66%). ^1H 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 $IrC_{23}H_{46}P_4SbF_6\cdot CH_2Cl_2$: C, 29.61; H, 4.97; P, 12.74. Found: C, 29.78; H, 4.70; P, 12.51.

(η^5-Indenyl)bis(triphenylphosphine)iridium(I) (14). To [(Ind)IrHL$_2$]SbF$_6$ (534 mg, 0.5 mmol) in THF (30 mL) at −78 °C was added *n*-BuLi (313 μL 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_6H_6 (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(η^5-indenyl)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (9a). (Ind)IrL$_2$ (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 $NaBF_4$ or $NaSbF_6$ (3 mmol) was added. The pale yellow product was precipitated with Et_2O (20 mL) and recrystallized from CH_2Cl_2/Et_2O, yield 308 mg, 93%. Anal. Calcd for $IrC_{46}H_{40}P_2BF_4\cdot CH_2Cl_2$: 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$_2$]SbF$_6$ (**9b**): as above except that EtI was used and stirring was continued for 4 h; yield 72%. ^1H NMR (CD_2Cl_2): 1.15, t (7.2), Me; 2.58, c, CH_2; 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_3. The compound decomposed

too quickly to allow analytical data to be obtained. [(Ind)Ir(CH_2Ph)L_2]SbF_6 (**9c**): as above except that $PhCH_2Br$ was used and stirring was continued for 2 h; yield 83%. ^1H NMR (CD_2Cl_2): 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, PPh_3 and $PhCH_2$. Anal. Calcd for $IrC_{52}H_{47}P_2BF_4 \cdot 2CH_2Cl_2$: C, 53.55; H, 4.24; P, 5.11. Found: C, 53.60; H, 4.70; P, 5.51. [(η^5-Ind)Ir(η^3-allyl)L]SbF_6 (**18**): as above except that CH_2=$CHCH_2Br$ was used, stirring was continued for 1 h, and the crude product was stirred in acetone for 2 days to isomerize the initially formed [(η^5-Ind)Ir(η^1-allyl)L_2]SbF_6, yield 62%. ^1H NMR (CD_2Cl_2): 1.27, dd (10.5, 13), allyl H_{anti}; 3.67, d (6.7), allyl H_{syn}; 5.068 c, allyl, H_{cent}; 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_3. Anal. Calcd for $IrC_{30}H_{27}PBF_4 \cdot 0.33CH_2Cl_2$: C, 47.85; H, 3.66. Found: C, 48.69; H, 3.83. The intermediate [(Ind)Ir(η^1-allyl)L_2]SbF_6 (**17**) had the following ^1H NMR (CD_2Cl_2): 4.81, dd (10, 2.1), allyl $IrCH_2$; 4.57, d (16.4), allyl =CH_2; 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_3.

Chloro(η^5-indenyl)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (19a). (Ind)IrL_2 (250 mg, 0.3 mmol) in THF (20 mL) was kept under a Cl_2 atmosphere (1 atm) for 2 h at 25 °C. Excess $NaBF_4$ (330 mg, 3 mmol) was added. The pale yellow product was precipitated with Et_2O (20 mL) and recrystallized from CH_2Cl_2/Et_2O (yield 93%). ^1H NMR (CD_2Cl_2): 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_3. The following compound was prepared similarly. [(Ind)$IrIL_2$]BF_4 (**19b**): as above except that I_2 (38 mg, 0.3 mmol in 10 mL of THF) was used and stirring was continued in the dark for 1 h; yield 90%. ^1H NMR (CD_2Cl_2): 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_3; 7.3, c, meta PPh_3; 7.14, c, ortho PPh_3. Anal. Calcd for $IrIC_{45}H_{37}P_2BF_4 \cdot CH_2Cl_2$: C, 52.33; H, 3.73. Found: C, 52.15; H, 3.43.

Methyl(η^1-indenyl)bis(triphenylphosphine)bis(*tert*-butyl isocyanide)iridium(III) Hexafluoroantimoniate (10). To [(Ind)$IrMeL_2$]SbF_6 (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_2Cl_2/Et_2O/hexane. Anal. Calcd for $C_{56}H_{58}P_2N_2IrSbF_6 \cdot 1.25CH_2Cl_2$: 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. ^1H NMR (CD_2Cl_2): −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). ^{13}C NMR (CD_2Cl_2): 30.2, Ir–Me; 29.4 and 29.9, Me_3CNC; 66.0 and 59.6, Me_3CNC; 168.5 and 171.0, Me_3CNC; 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_3.

Crystallography. A crystal of **19a** (0.2 × 0.2 × 0.2 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 ($2\theta > 15°$) during normal alignment procedures using Mo radiation (λ = 0.710 698 Å). Data (8981 points) were collected at room temperature by using 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 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.[12a] 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.[12b] A final cycle of refinement [function minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor of R = 4.0% [$R = \sum(||F_o| - |F_c||/|F_o|) \times 100$]. Anomalous dispersion corrections were made for Cl and Ir; scattering factors were taken from Cromer and Mann;[12c] in the final stages of refinement, a weight of $1/\sigma(F^2)$ was applied.

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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_2, 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; $PhCH_2Br$, 100-39-0; CH_2=$CHCH_2Br$, 106-95-6; Rh, 7440-16-6; phenylcyclopentadiene, 88243-06-5; *trans*-hydrido(η^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.

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