# The 'Indenyl Effect' of Iridium(I) Olefin Complexes

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Hart-Davis and Mawby were the first to observe the intrinsic difference in the chemical reactivity of analogous transition metal complexes of the indenyl ligand (η^5-C_9H_7) compared to the cyclopentadienyl ligand (η^5-C_5H_5) [1]. They proposed an η^3- indenyl intermediate to explain the faster rate of associative substitution of CO by PPh_3 in (η^5-C_9H_7)$Mo(CO)_3CH_3$, compared to the analogous cyclopentadienyl complex. Later, Basolo and co-workers determined the rate of substitution of phosphines for one carbonyl ligand in $CpRh(CO)_2$ and the indenyl analogue (η^5-C_9H_7)$Rh(CO)_2$ [2]. Again, second order kinetics were observed and the rate of substitution of one carbonyl ligand by PPh_3 was determined to be a factor of 3.8×10^8 faster with the indenyl complex compared to the cyclopentadienyl complex [2a]. Basolo termed this tremendous rate enhancement the "indenyl ligand effect," and clearly attributed it to a facile ring slippage in the transition state of the indenyl ligand (I) from η^5 toward η^3 (II), with the uncoordinated double bond being stabilized by conjugation within the six-membered ring. The final product (III) results from ligand expulsion and reformation of the η^5-form.

$$ML_n \quad (I) \qquad \xrightarrow{+L'} \qquad ML_nL' \quad (II) \qquad \xrightarrow{-L} \qquad ML_{n-1}L' \quad (III)$$
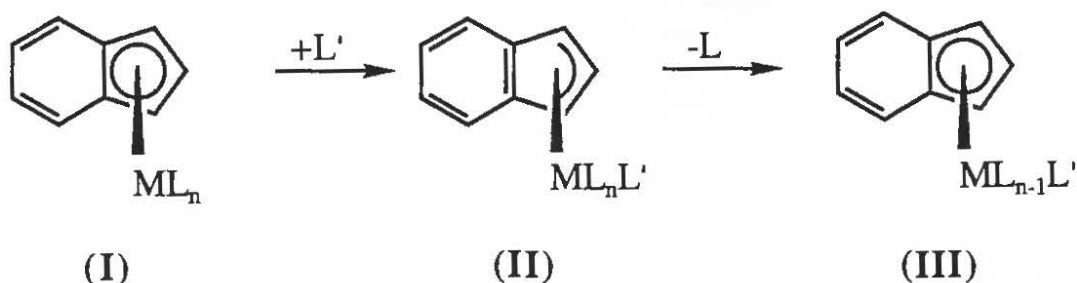
C_9H_7 = indenyl

· Due to this observed enhanced reactivity of indenyl metal complexes in ligand substitution reactions the chemistry of these indenyl complexes have received increased attention, during the past ten years [3-6]. The indenyl complexes (η^5-C_9H_7)$Mo(ol)_2$, where M = Co, Rh and ol = alkene, have been reported to be very active catalysts for intermolecular hydroacylation [7], the cyclo-trimerisation of alkynes to substituted benzenes [8], the cyclo-co-trimerisation of alkynes and nitriles to pyridines [9], and the hydrosilylation of phenyacetylene to give phenylsilyl alkenes [10]. The "indenyl ligand effect," or "indenyl effect," as we shall call it, has also been invoked to explain the lower barrier to ethylene rotation in indenyl ethylene complexes compared to cyclopentadienyl ethylene complexes of rhodium, in particular by Eshtiagh-Hosseini and Nixon [11] for (η^5-C_9H_7)$Rh(\eta^2$-$C_2H_4)_2$, by McGlinchey and co-workers [12] in studies with (η^5-1-MeC_9H_6)$Rh(\eta^2$-$C_2H_4)_2$, and by Marder and co-workers [13] with (η^5-$Me_nC_9H_{7-n}$)$Rh(\eta^2$-$C_2H_4)_2$ (n = 3,4,7).

We have prepared the complexes $CpIr(\eta^2$-$C_8H_{14})CO$ and (η^5-C_9H_7)$Ir(\eta^2$-$C_8H_{14})CO$ in high yield from $[(\eta^2$-$C_8H_{14})_2Ir(CO)Cl]_2$ and thallium cyclopentadiene or potassium indenide, respectively. The 'syn' and 'anti' stereoisomers due to rotation of the cylooctene ring, are shown for (η^5-C_9H_7)$Ir(\eta^2$-$C_8H_{14})CO$ in Scheme I, and were characterized by NOE and two-dimensional NMR techniques.

Scheme I

Top View

Top View

Front View

Front View

"Syn Isomer"

"Anti Isomer"
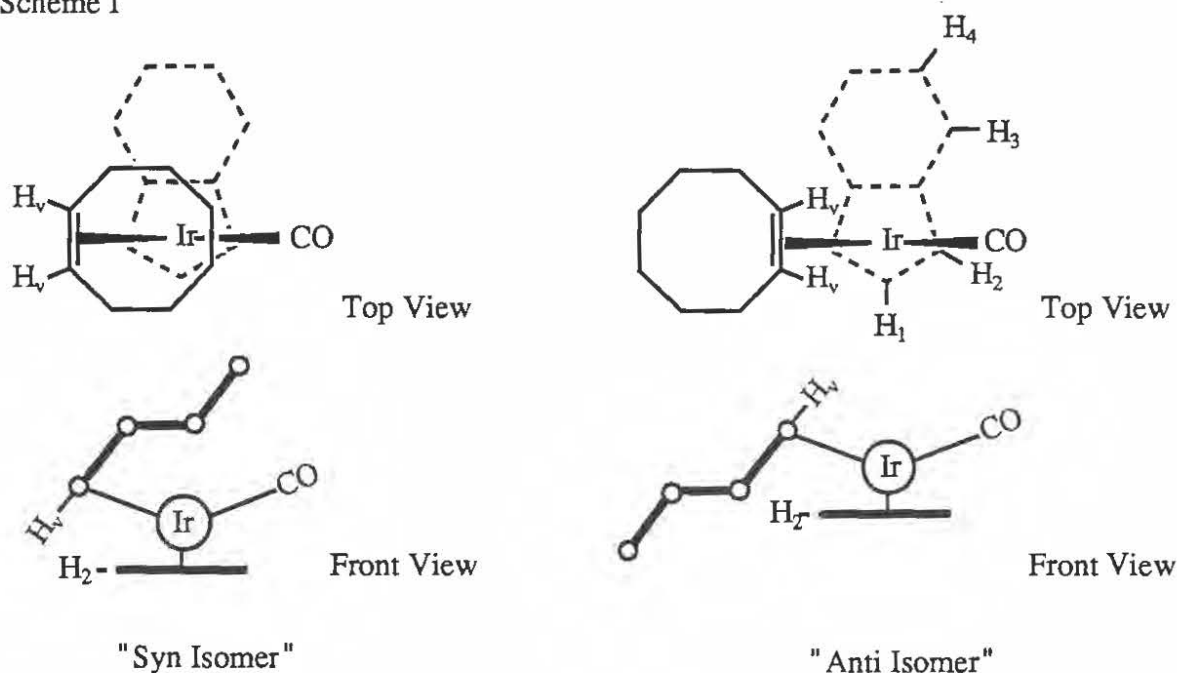
$(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})CO$ was found to be more reactive than $CpIr(\eta^2\text{-}C_8H_{14})CO$ in several circumstances, as shown in Scheme II. The labile cyclooctene ring of $(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-}C_8H_{14})CO$ was readily replaced under mild conditions by other two-electron donors such as

Scheme II

(55%)

(86%)

(98%)

C_2H_4, 1 atm

C_3H_5Br, Δ

CO

HSiPh₃, Δ

(78%)

PPh₃

(96%)

PhCCH, Δ

cyclohexane solvent
(isolated yield)

(71%)
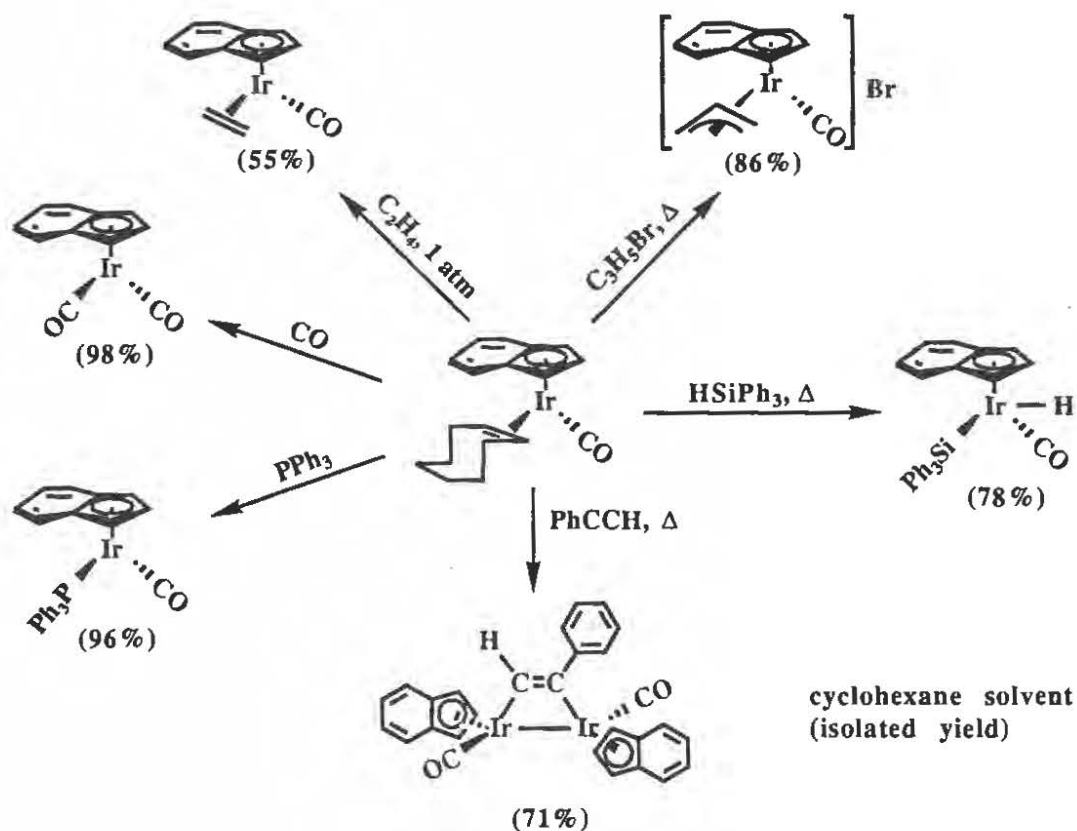
triphenylphosphine, carbon monoxide, ethylene, or phenylacetylene; $CpIr(\eta^2-C_8H_{14})CO$ was not reactive under identical or more severe conditions. The complex $(\eta^5-C_9H_7)Ir(\eta^2-C_8H_{14})$-CO readily oxidatively added C-Br and Si-H bonds, again under mild conditions, and was found to be a robust and long-lived catalyst for the hydrosilylation and hydrogenation of alkenes and alkynes. The rate of reaction of triphenylsilane with $(\eta^5-C_9H_7)Ir(\eta^2-C_8H_{14})CO$ was determined to be associative in nature. This rate was found to be accelerated by the addition of excess cyclooctene, and we have proposed the formation of the slipped indenyl complex $(\eta^1-C_9H_7)Ir(\eta^2-C_8H_{14})_2\,CO$ to account for this rate acceleration. This η^1-intermediate was not observed, but the complex $(\eta^1-C_9H_7)Ir(CO)_3$, shown below, has been observed when $(\eta^1-C_9H_7)Ir(CO)_2$ is under a CO atmosphere, and has been spectroscopically characterized. The reports of only a few characterized η^1 and η^3-intermediates [3a,14,15] points to the difficulty in the isolation of such intermediates.
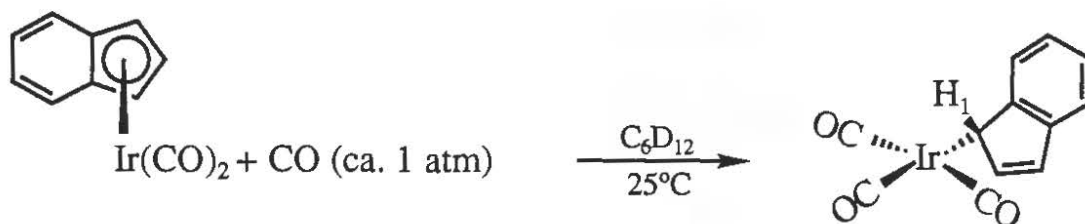
For $CpIr(\eta^2-C_2H_4)L$ and $(\eta^5-C_9H_7)Ir(\eta^2-C_2H_4)L$, where L = ethylene or CO, the barrier to ethylene rotation about the iridium-ethylene bond axis, interchanging inner (H_i) and outer (H_o) ethylene protons, as shown for $(\eta^5-C_9H_7)Ir(\eta^2-C_2H_4)_2$ below, was determined by lineshape fitting of variable-temperature ^{1}H NMR spectra. The free energies of activation were found to be 5-6 kcal/mole less for the indenyl complexes than for the corresponding cyclopentadienyl complexes (14 and 20 kcal/mole, respectively). This lowering of the barrier to ethylene rotation is attributed to a transition state effect, i.e., an η^3-slipped indenyl intermediate during rotation, rather than a ground state effect, i.e., differential metal ethylene π-bonding.

(a) Ground State   (b) After Rotation
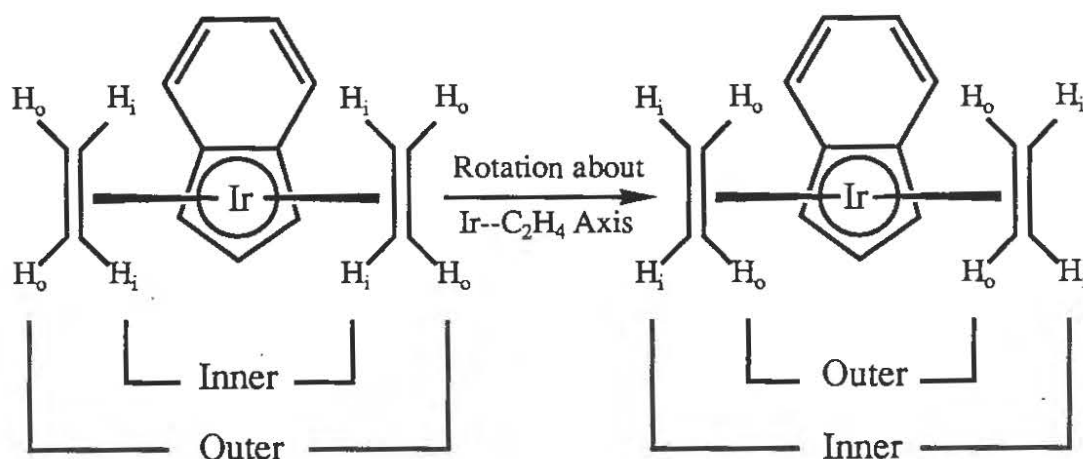
References

1.	Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. (A)* **1969**, 2403.

2. (a) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.
    (b) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208.

3. (a) Habib, A.; Tanke, R. S.; Holtz, E. M.; Crabtree, R. H. *Organometallics*, **1989**, *8*, 1225.
    (b) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.
    (c) Ceccon, A.; Gambaro, A.; Saverio, S.; Valle, G.; Venzo, A. *J. Chem. Soc., Chem. Commun.* **1989**, 51.
    (d) Marder, T. B.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1478.

4. (a) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012.
    (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

5. (a) Turaki, N. N.; Huggins, J. M.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 424.
    (b) Yang, G. K.; Berman, R. G. *Organometallics* **1985**, *4*, 129.
    (c) Rest, A. J.; Whitwell, L.; Graham, W. A.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624.
    (d) Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

6. For a comparative review of Cp and Indenyl chemistry see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

7. Marder, T. B.; Roe, D. C.; Milstein, S. *Organometallics* **1988**, *7*, 1451.

8. (a) Borrini, A.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181.
    (b) Caddy, P.; Green, M.; Smart, L. W.; White, N. *J. Chem. Soc., Chem. Commun.* **1978**, 839.

9. Bonneman, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.

10. Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984.

11. Eshtiagh-Hosseini, H.; Nixon, J. F. *J. Less Common Met.* **1978**, *61*, 107.

12. Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Rodgers, C. A.; Churchill, J. W.; Zeller, J.; Kanz, S.-W.; Albright, T. A. *Organometallics* **1986**, *5*, 1656.

13. Kakkar, A. K.; Taylor, N. J.; Calabrese, J. C.; Nugent, W. A.; Roe, D. C.; Connaway, E. A.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 990.

14. Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384.

15. (a) Merola, J. S.; Kacmarcik, R.-T.; Van Engen, V. *J. Am. Chem. Soc.* **1986**, *108*, 329.
    (b) Forschner, T. C.; Cutler, A. R.; Kulling, R. K. *Organometallics* **1987**, *6*, 889.
    (c) Nesmeyanov, A. W.; Ustynyuk, N. A.; Makarova, L. G.; Andrianov, V. G.; Struchkov, Yu. T.; Andrae, S.; Ustynyuk, Yu. A.; Malyugina, S. G. *J. Organomet. Chem.* **1978**, *159*, 189.