Synthesis and Reaction Chemistry of (η^5-Indenyl)(cyclooctadiene)iridium: Migration of Indenyl from Iridium to Cyclooctadiene

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(η^5-Indenyl)(cyclooctadiene)iridium was synthesized in high yield from chloro(cyclooctadiene)iridium dimer and lithium indenide. The reaction chemistry of the above compound was investigated with respect to the displacement of the cyclooctadiene with various nucleophiles. Thus, (η^5-indenyl)dicarbonyliridium could be synthesized in high yield by treating the cyclooctadiene complex with carbon monoxide at atmospheric pressure. However, the addition of trimethylphosphine, PMe_3, to the cyclooctadiene complex resulted not in the displacement of cyclooctadiene but in the migration of indene from iridium to cyclooctadiene forming (2-indenylcyclooct-5-en-1-yl)tris(trimethylphosphine)iridium, I, quantitatively. A single-crystal X-ray structural determination of I was carried out and confirmed the migration of indene to the cyclooctadiene. I crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 10.019$ (1) Å, $b = 18.836$ (3) Å, $c = 29.602$ (4) Å, $V = 5586$ (2) Å^3, and $Z = 8$. The syntheses of a related series of (trimethylsilyl-substituted indenyl)iridium complexes are also reported along with some suggestions for the mechanism of the iridium to cyclooctadiene indenyl migration.

Introduction

Indenylmetal complexes are far more reactive than their corresponding cyclopentadienyl ones for ligand-substitution reactions. This observation was first made by Mawby and co-workers,[2] and the magnitude of this effect has since been quantified for several systems by the elegant work of Basolo and co-workers.[3] One group has taken advantage of this greater reactivity by using indenylmetal complexes as reactive building blocks for synthesizing di- and polynuclear metal complexes.[4] Lately, there has been renewed activity in indenylmetal chemistry, and a recent review article gives an indication of some of the latest results in the field.[5] We felt that there was potential to exploit the facile ring-slippage reaction of indenylmetal complexes for some unique chemistry at transition-metal centers.[6] Our efforts began with an investigation into the chemistry of indenyliridium complexes and demonstrated clearly the η^5 to η^3 transformation which has been presumed to lie behind the indenyl ligand's enhanced reactivity.[7] In this paper, we wish to report further on indenyliridium chemistry and describe the synthesis and reaction chemistry of indenyl(cyclooctadiene)iridium including an unusual migration of indenyl from iridium to cyclooctadiene.

Results and Discussion

Synthesis and Reaction Chemistry of (Ind)Ir(COD). In beginning our study of indenyl iridium complexes, we chose indenyl(cyclooctadiene)iridium, (Ind)Ir(COD), as our starting point. This choice was made principally on the basis that the necessary starting material chloro(cyclooctadiene)iridium dimer, $[Ir(COD)Cl]_2$, could be made in very high yield from commercially available $IrCl_3 \cdot H_2O$ and cyclooctadiene (COD).[8] Thus the route shown in eq 1 represents an overall high-yield synthesis

$$IrCl_3 \cdot 3H_2O + COD \rightarrow [Ir(COD)Cl]_2 \qquad (1a)$$

$$[Ir(COD)Cl]_2 + 2Li^+Ind^- \rightarrow 2(\eta^5\text{-}Ind)Ir(COD) \qquad (1b)$$

of (Ind)Ir(COD) and an efficient use of iridium. The spectral properties of (Ind)Ir(COD) are listed in the Experimental Section and are in excellent agreement with the complex having an η^5 coordination of the indenyl ligand to iridium and the COD coordinating in a bidentate fashion. Baker and Tulip[9] have published a correlation between the ^{13}C NMR shifts of the indenyl quaternary carbons and the degree of distortion of indenyl ligands from η^5 to η^3. Following their correlation, with a ^{13}C quaternary carbon shift of 110.2 ppm in (Ind)Ir(COD), we would expect that the indenyl ligand is only slightly distorted toward the η^3 form.[10]

Our belief that (Ind)Ir(COD) would serve as a useful precursor to a variety of $(Ind)IrL_2$ complexes was bolstered by its reaction with carbon monoxide. Bubbling CO at 1 atm through a hydrocarbon solution of (Ind)Ir(COD) for a few minutes at room temperature leads to its complete

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(2) (a) Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403. (b) Hart-Davis, A. J.; White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 441. (c) White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. (d) Jones, D. J.; Mawby, R. J. *Inorg. Chim. Acta* **1972**, *6*, 157.

(3) (a) Rerek, M. E.; Jie, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Ji, L-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740. (c) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.

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(5) (a) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307 and references therein. (b) See also: Turaki, N. N.; Huggins, J. M.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 424.

(6) There are a few references in the literature to the use of the complexes as catalysts in the area of cyclotrimerization of acetylenes and acetylenes with alkenes: (a) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648. (b) Borrini, A.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181. In the area of alkyne/nitrile cotrimerization to pyridines: (c) Bonneman, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. (b) Bonneman, H.; Brijoux, W. In *Aspects of Homogeneous Catalysis*; Ugo, R., ed.; D. Reidel: Dordrecht, 1984; Vol. 5, p 75. In the area of intermolecular hydroacylation: (e) Marder, T. B.; Roe, D. C.; Milstein, D. *Organometallics* **1988**, *7*, 1451.

(7) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329.

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(9) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

(10) A single-crystal X-ray diffraction study of the structure of (Ind)Ir(COD) confirmed the η^5 nature of the indenyl ligand. The full details of this study as well as the synthesis and structure of a family of $IndIrL_2$ complexes will be published in a separate report.

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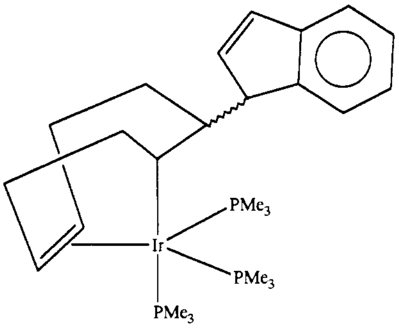

Figure 1. Structure of I, (2-indenylcyclooct-5-en-1-yl)tris(trimethylphosphine)iridium.

conversion to indenyldicarbonyliridium, (Ind)Ir$(CO)_2$ (eq 2). This result may be contrasted with the total absence

$$(\eta^5\text{-Ind})\text{Ir(COD)} + \text{CO} \rightarrow (\eta^5\text{-Ind})\text{Ir(CO)}_2 + \text{COD} \tag{2}$$

of reaction between cyclopentadienyl(cyclooctadiene)iridium, (Cp)Ir(COD), and CO under the identical conditions. (Ind)Ir$(CO)_2$ displays ν_{CO} at 2029 and 1958 cm^{-1} (Nujol mull), positions which are not very different from those in (Cp)Ir$(CO)_2$,[11] showing the indenyl ligand, at least in a crude sense, is not very different electronically from Cp.

When we attempted to extend the range of this reaction with a variety of phosphines intending to prepare a series of bis-ligand compounds, we discovered that transformation of (Ind)Ir(COD) to other (Ind)IrL_2 complexes is not a general reaction. First, there appears to be no reaction between (Ind)Ir(COD) and triphenylphosphine, PPh_3, at room temperature[12] (eq 3).

$$(\eta^5\text{-Ind})\text{Ir(COD)} + \text{PPh}_3 \rightarrow \text{NR} \tag{3}$$

Feeling that this lack of reactivity with PPh_3 was perhaps due in part to a steric problem and also to the need to overcome the COD chelate effect, we continued our investigations with the very small, nucleophilic ligand trimethylphosphine, PMe_3. A rapid reaction did take place between (Ind)Ir(COD) and PMe_3 in toluene solution at room temperature, but it did not lead to the displacement of the COD and the formation of (η^5-Ind)Ir$(PMe_3)_2$ or even (η^3-Ind)Ir$(PMe_3)_3$.[13] Instead we isolated a material, I, with an extremely complex set of NMR spectra and analyzing for the empirical formula $C_{26}H_{46}IrP_3$ (eq 4).

$$(\eta^5\text{-Ind})\text{Ir(COD)} + \text{PMe}_3 \rightarrow \text{I } (\text{C}_{26}\text{H}_{46}\text{IrP}_3) \tag{4}$$

The 200-MHz ^{1}H NMR spectrum of I shows the presence of three unique PMe_3 groups at δ 0.84, 1.11, and 1.24 ppm, a complicated series of resonances from δ 1.75 to 3.30 ppm due to both the COD aliphatic protons as well as coordinated olefinic protons, a resonance at 3.61 ppm due to an allylic/benzylic proton, and resonances from δ 6.75 to 7.60 ppm for aromatic and olefinic protons. The NMR results led us to conclude that I is best formulated as (2-indenylcyclooct-5-en-1-yl)tris(trimethylphosphine)iridium as shown in Figure 1, the product of indenyl migration from iridium to COD. The ^{13}C NMR spectrum is quite complex, and while not all resonances were fully assigned, it is consistent with the above structure. The ^{31}P NMR spectrum displays an ABC pattern, again consistent with the displayed structure with its three similar, but inequivalent PMe_3 ligands.

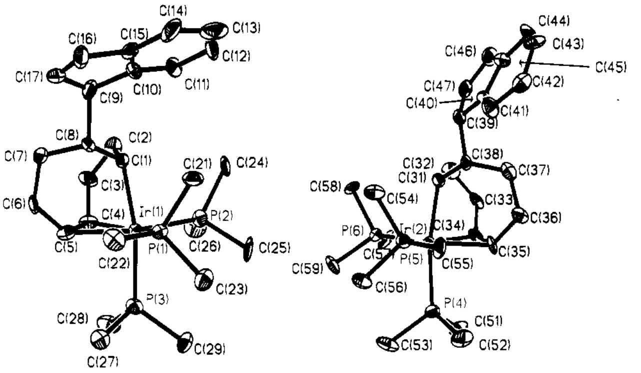

Figure 2. ORTEP plots of the two independent molecules of I.

X-ray Diffraction Study of I. Although we were fairly certain of the connectivity in I from the spectroscopic data, we were unsure of the exact stereochemistry of the molecule, especially the stereochemistry of the indene-to-COD bond. Therefore, we carried out a single-crystal X-ray structural analysis of I, and an ORTEP plot of the two independent molecules of I in the unit cell from the resulting structure is shown in Figure 2. The X-ray structure confirmed that the indenyl group had migrated from iridium to the COD ligand, resulting in the formation of the unusual cyclooctenyl complex. The structure consists of a distorted trigonal-bipyramidal geometry about the iridium atom with two trimethylphosphine ligands and the double bond of the COD ligand occupying the three equatorial sites and the third trimethylphosphine and the σ-bonded carbon from the COD occupying the axial sites. The indenyl group is now σ-bonded to what was formerly one of the olefinic carbons of the COD ring, with the other carbon of that double bond being σ-bonded to the iridium. The overall structural features of I are similar to those of two other structurally characterized cyclooctenyl complexes of iridium: [Ir(COD)(μ-pyrazolyl)(μ-PPh_2)Ir(C_8H_{13})][14] and Ir(C_8H_{13})$(CO)_2$($AsPh_3$).[15] In all cases, the geometry about the central iridium is distorted trigonal-bipyramidal with the σ-bonded carbon of the cyclooctenyl ligand occupying an axial position and the olefinic portion occupying an equatorial position. The Ir to C1 distance in I of 2.18 Å is in line with the similar distances in the above compounds (2.16 and 2.15 Å, respectively). The stereochemistry of the indenyl-to-COD bond has the indenyl group exo to the iridium. This particular geometry has implications for the mechanism of the formation of I and will be discussed later in this paper. A selected list of important bond lengths and angles can be found in Table I, and Table II lists the positional parameters for all non-hydrogen atoms.

As we stated above, I actually crystallizes with two independent molecules in the asymmetric unit and inspection reveals that the two molecules are enantiomers. The molecule crystallizes in the acentric space group $P2_12_12_1$, and the absolute configuration was determined. C1, C8, and C9 in molecule Ia and C31, C38, and C39 in molecule Ib are asymmetric carbons. In molecule Ia, C1, C8, and C9 are in the *S*, *R*, *S* configuration and in molecule Ib, C31, C38, and C39 are in the *R*, *S*, *R* configuration.

Trimethylsilyl-Substituted Indenyl Complexes. In an effort to prevent the migration of the indenyl group to the COD ligand, we also synthesized some novel tri-

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[11] Fischer, E. O.; Brenner, K. S. *Z. Naturforsch., B* **1962**, *17*, 774.

[12] There is a facile reaction between PPh_3 and (Ind)Ir(cyclooctene)$_2$ or (Ind)Ir(ethylene)$_2$ at room temperature yielding (Ind)Ir$(PPh_3)_2$. We will report on this and other (Ind)IrL_2 complexes in a separate paper.

[13] Both of these complexes have been synthesized independently by using (Ind)Ir(cyclooctene)$_2$ or (Ind)Ir(ethylene)$_2$ as the starting complex. Merola, J. S., unpublished results, and ref 7.

[14] Bushnell, G. W.; Stobart, S. R.; Vefghi, R.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 282.

[15] Fernandez, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M.-C.; Foces-Foces, C.; Cano, F. H. *Organometallics* **1987**, *6*, 1751.

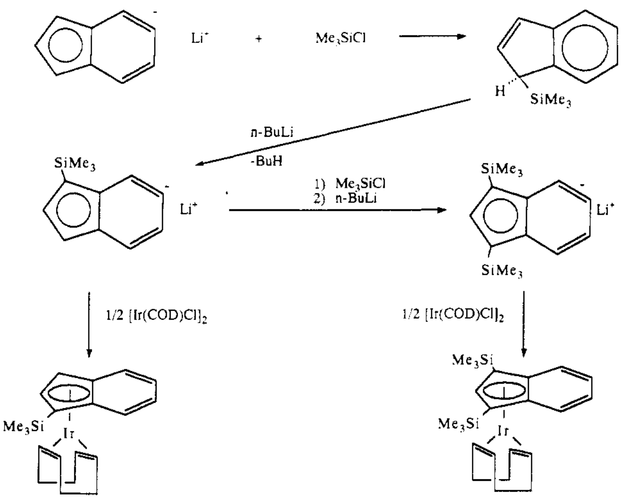
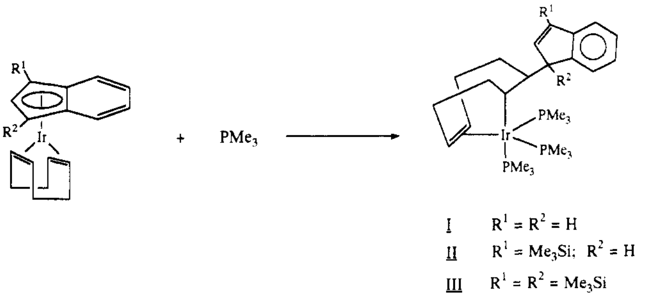


Figure 3. Synthetic routes for (1-(Trimethylsilyl)indenyl)(cyclooctadiene)iridium and (1,3-Bis(trimethylsilyl)indenyl)(cyclooctadiene)iridium.



I $R^1 = R^2 = H$
II $R^1 = Me_3Si$; $R^2 = H$
III $R^1 = R^2 = Me_3Si$

Figure 4. Migration from iridium to cyclooctadiene for trimethylsilyl-substituted indenyl Complexes.

methylsilyl-substituted indenyl iridium complexes for this study. Figure 3 shows the routes used to synthesize both [1-(trimethylsilyl)indenyl](cyclooctadiene)iridium and [1,3-bis(trimethylsilyl)indenyl](cyclooctadiene)iridium. We had hoped that perhaps the added bulk of one or two trimethylsilyl groups would inhibit the iridium to COD migration and allow us to study earlier steps along the pathway. In both cases, the migration of indenyl from iridium to cyclooctadiene was still quite facile, being complete within the time of addition of PMe_3 at room temperature (Figure 4). In the case of the mono(trimethylsilyl)indenyl complex, only one isomer is observed, although C–C bond formation at either the 1- or the 3-position on the indenyl ring is possible. Apparently, the migration of indenyl from iridium to COD is a favorable process and cannot be blocked by the placement of bulky groups.

Mechanism of Indenyl Miigration. Initially, the X-ray structural determination that the indenyl group in I is exo to the iridium led us to postulate the mechanism shown in Figure 5 for the indenyl migration. We speculate that the addition of PMe_3 to (η^5-indenyl)(cyclooctadiene)iridium induces ring slippage from η^5 to η^3 to η^1 and eventually to η^0, that is, to free indenide. While we have not been able to detect these intermediates in this particular system, we, and others, have demonstrated the viability of each of these forms for the indenyl ligand.[16-18]

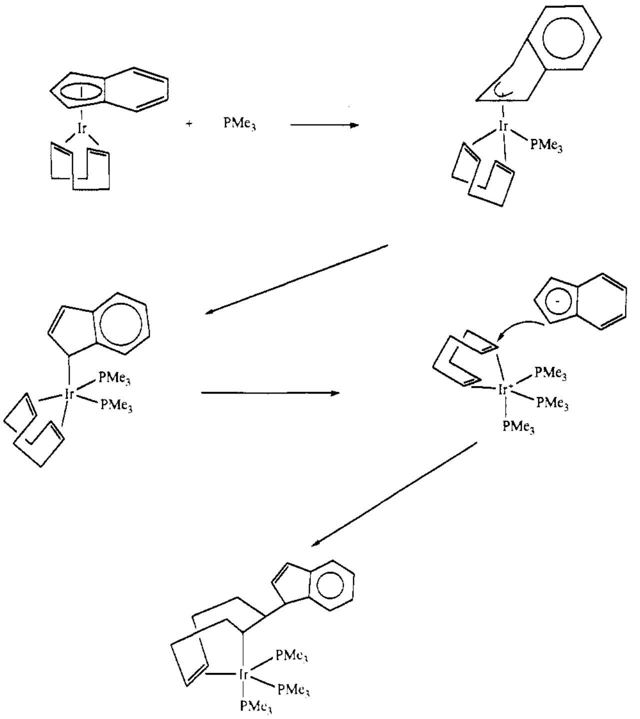


Figure 5. Proposed mechanism for the formation of I.

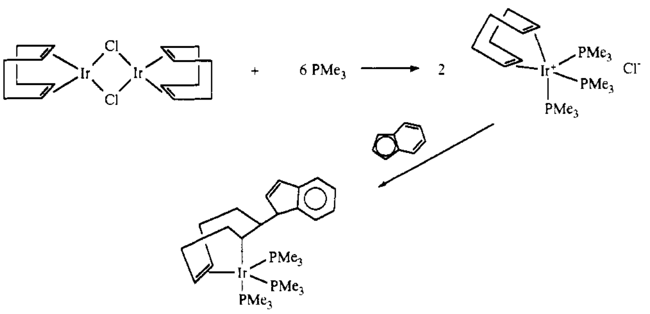


Figure 6. Nucleophilic attack of lithium indenide on (cyclooctadiene)tris(trimethylphosphine)iridium Chloride.

Then, the free indenyl anion attacks one of the double bonds of the coordinated COD to form the final product. Formation of cyclooctenyl complexes via the attack of nucleophiles on coordinated COD is well-known for Pt and Pd,[19] but this would appear to be the first instance of such a reaction for Ir. This last step, the nucleophilic attack of indenide on the COD ligand, is consistent with the exo geometry observed in the final product. That there seems to be a need to invoke slipped-ring intermediates for this chemistry is consistent with the lack of reactivity of (Cp)Ir(COD) under the same reaction conditions. Attempts to force Cp to migrate in a fashion similar to indenyl by either heating or photolyzing a reaction mixture containing (Cp)Ir(COD) and PMe_3 leads to a complex mixture of products and not to clean Cp migration.

We have found corroboration for this final step, the attack of indenyl anion on coordinated COD, by synthesizing (cyclooctadiene)tris(trimethylphosphine)iridium chloride, $[Ir(COD)(PMe_3)_3]Cl$, and demonstrating that addition of indenyllithium to this cationic complex results in the formation of a product identical in all respects to

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(16) η^3 complexes: (a) Reference 7. (b) Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460. (c) Nesmeyanov, A. N.; 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. (d) Forschner, T. C.; Cutler, A. R.; Kullnig, R. K. *Organometallics* **1987**, *6*, 889.

(17) η^1 complexes: (a) Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384. (b) Merola, J. S., unpublished results.

(18) η^0 complexes: (a) Marder, T. B.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1478. (b) Merola, J. S., unpublished results.

Table I. Important Bond Distances (Å) and Angles (deg) for $C_{26}H_{46}IrP_3$ (I)

A. Distances

atom 1	atom 2	dist	atom 1	atom 2	dist
Ir1	P1	2.306 (13)	Ir2	P4	2.320 (14)
Ir1	P1	2.305 (14)	Ir2	P5	2.27 (2)
Ir1	P3	2.293 (14)	Ir2	P6	2.312 (14)
Ir1	C1	2.25 (5)	Ir2	C31	2.27 (4)
Ir1	C4	2.31 (6)	Ir2	C34	2.19 (5)
Ir1	C5	2.21 (5)	Ir2	C35	2.23 (5)
C1	C2	1.63 (7)	C31	C32	1.60 (7)
C1	C8	1.57 (7)	C31	C38	1.51 (8)
C4	C5	1.45 (7)	C34	C35	1.56 (7)
C8	C9	1.59 (8)	C38	C39	1.52 (8)

B. Angles

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P1	Ir1	P2	99.9 (5)	P4	Ir2	P5	94.2 (6)
P1	Ir1	P3	93.9 (5)	P4	Ir2	P6	97.4 (5)
P1	Ir1	C1	90 (1)	P4	Ir2	C31	90 (1)
P1	Ir1	C4	150 (1)	P4	Ir2	C34	90 (1)
P1	Ir1	C5	116 (1)	P4	Ir2	C35	88 (1)
P2	Ir1	P3	98.9 (6)	P5	Ir2	P6	102.0 (6)
P2	Ir1	C1	89 (1)	P5	Ir2	C31	91.0 (6)
P2	Ir1	C4	107 (1)	P5	Ir2	C34	154 (1)
P2	Ir1	C5	144 (1)	P5	Ir2	C35	113 (1)
P3	Ir1	C1	170 (1)	P6	Ir2	C31	88 (1)
P3	Ir1	C4	95 (1)	P6	Ir2	C34	103 (1)
P3	Ir1	C5	83 (1)	P6	Ir2	C35	144 (1)
C1	Ir1	C4	78 (1)	C31	Ir2	C34	82 (2)
C1	Ir1	C5	88 (2)	C31	Ir2	C35	84 (2)
C4	Ir1	C5	37 (2)	C34	Ir2	C35	41 (2)

that formed by the addition of PMe_3 to (Ind)Ir(COD) (Figure 6).

Several observations suggest that the degree of separation of the indenyl anion from the iridium cation is dependent on the nature of the solvent. First, the reaction between (η^5-Ind)Ir(COD) and PMe_3 takes place equally well in pentane, toluene, or THF solution, and it is difficult to imagine any great amount of charge separation in the former two solvents. Second, trapping experiments using chlorotrimethylsilane, Me_3SiCl, gave different results depending on the solvent used. Thus, addition of PMe_3 to (Ind)Ir(COD) in THF solution in the presence of an excess of Me_3SiCl led to the formation of 1-(trimethylsilyl)indene and $[Ir(COD)(PMe_3)_3]Cl$. This result is consistent with the formation of free indenyl anion along the reaction path. However, the same reaction in toluene yielded only I. That is to say, the indenyl anion was never "free" enough to be intercepted by the Me_3SiCl. Apparently, the [indenyl anion]/[iridium cation] forms as a tight ion pair and remains as a tight ion pair in the nonpolar solvents used in this study. However, THF is sufficiently polar to induce ion-pair separation and the indenyl anion then becomes accessible for reaction with the Me_3SiCl. These results are shown schematically in Figure 7.

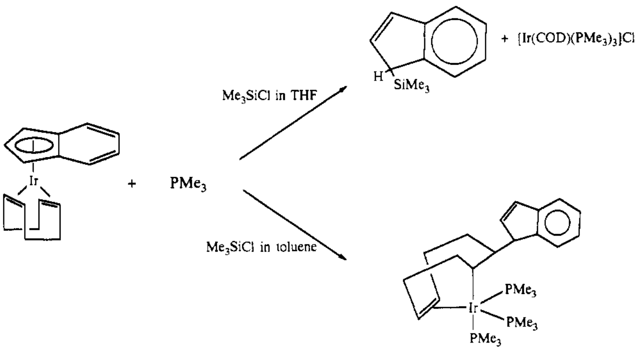

Figure 7. Trapping of indenide with chlorotrimethylsilane.

The coupling of Cp-like ligands with diolefins in platinum chemistry had been reported in 1976 for a platinum norbornadiene (NBD) compound.[21] In that case, starting with (η^1-Cp)$_2$Pt(NBD), a rearrangement occurred on standing to yield products in which one of the Cp ligands converted to η^5 and the second coupled with the norbornadiene, (η^5-Cp)Pt(Cp–norbornenyl). Both endo and exo isomers of this compound were found, and the authors speculate that the endo product arises from an intramolecular coupling process, while the exo product suggested the intermediacy of free cyclopentadienide which attacks a double bond in norbornadiene in a fashion similar to that which we propose is occurring in our system. More recently, two different authors have published on the coupling of Cp-like ligands with cyclooctadiene on platinum.[22,23] In one case, a crystal structure determination of a complex with pentamethylcyclopentadiene (Cp*) was carried out, again showing an exo geometry.[23] This latter author also suggested that an $\eta^1 \leftrightarrow \eta^5$ interconversion is important for the process of coupling Cp ligands with cyclooctadiene and found that the coupling proceeds in the order Cp* ≫ Cp > Ind. Since this system appears to begin with a Bis-η^1-Cp configuration and the Cp–COD coupling occurs upon $\eta^1 \rightarrow \eta^5$ conversion, this order is consistent with our current understanding of the various Cp-like ligands.

At this point, it appears that a mechanism in which the indenyl group migrates as an indenide ion is an operative one, but the degree of separation of the anion from the cation depends on the solvent. We are currently investigating the mechanism in more detail as part of an in-depth study of nucleophilic attack on $[Ir(COD)(PMe_3)_3]Cl$ and will report on our results in the near future.[24]

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[19] See, for example: White, D. A. *J. Chem. Soc. A* **1971**, 145 and references therein.

[21] Hill, M. N. S.; Johnson, B. F. G.; Keating, T.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 1197.

[22] Anderson, G. K. *Organometallics* **1986**, *5*, 1903.

[23] O'Hare, D. *Organometallics* **1987**, *6*, 1766.

Table II. Positional Parameters and Their Estimated Standard Deviations for $C_{26}H_{46}IrP_3$ (I)

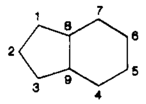
atom	x	y	z	B, Å^2
Ir1	0.07913 (7)	0.04731 (4)	−0.02970 (2)	3.30 (1)
Ir2	0.00853 (7)	0.22767 (3)	0.25207 (2)	3.18 (1)
P1	−0.0180 (5)	−0.0043 (2)	0.0334 (2)	3.57 (9)
P2	−0.0296 (5)	−0.0148 (3)	−0.0858 (2)	4.6 (1)
P3	−0.0590 (6)	0.1458 (2)	−0.0275 (2)	4.7 (1)
P4	0.1236 (5)	0.2741 (3)	0.3136 (2)	4.6 (1)
P5	0.0706 (6)	0.1129 (3)	0.2671 (2)	4.1 (1)
P6	0.1588 (5)	0.2596 (3)	0.1967 (2)	4.4 (1)
C1	0.241 (2)	−0.0304 (8)	−0.0282 (5)	3.4 (3)
C2	0.324 (2)	−0.021 (1)	−0.0706 (6)	5.7 (5)
C3	0.341 (2)	0.055 (1)	−0.0844 (7)	6.4 (6)
C4	0.240 (2)	0.104 (1)	−0.0629 (6)	4.7 (5)
C5	0.242 (2)	0.119 (1)	−0.0159 (6)	5.0 (5)
C6	0.351 (2)	0.1018 (9)	0.0162 (7)	5.4 (5)
C7	0.423 (2)	0.032 (1)	0.0142 (6)	5.4 (5)
C8	0.321 (2)	−0.0314 (8)	0.0142 (6)	4.7 (5)
C9	0.408 (2)	−0.103 (1)	0.0202 (6)	5.2 (5)
C10	0.331 (2)	−0.1686 (9)	0.0198 (6)	4.6 (5)
C11	0.268 (2)	−0.2026 (9)	−0.0150 (7)	5.5 (5)
C12	0.200 (2)	−0.263 (9)	−0.0055 (8)	6.6 (6)
C13	0.191 (2)	−0.291 (1)	0.038 (1)	9.1 (7)
C14	0.262 (2)	−0.260 (1)	0.0721 (8)	7.9 (6)
C15	0.332 (2)	−0.199 (1)	0.0635 (7)	4.8 (5)
C16	0.409 (2)	−0.155 (1)	0.0924 (7)	7.0 (6)
C17	0.463 (2)	−0.103 (1)	0.0693 (7)	5.6 (5)
C21	−0.005 (2)	−0.1013 (9)	0.0369 (7)	5.6 (5)
C22	0.039 (2)	0.024 (1)	0.0892 (6)	5.9 (6)
C23	−0.203 (2)	0.006 (1)	0.0409 (8)	6.3 (6)
C24	0.013 (2)	−0.1080 (9)	−0.0976 (7)	6.1 (5)
C25	−0.209 (2)	−0.026 (1)	−0.0866 (8)	7.7 (6)
C26	−0.007 (3)	0.024 (1)	−0.1428 (6)	8.3 (7)
C27	−0.062 (2)	0.1933 (9)	0.0274 (7)	5.7 (5)
C28	−0.009 (3)	0.220 (1)	−0.0638 (7)	7.4 (6)
C29	−0.243 (2)	0.145 (1)	−0.0420 (7)	5.7 (5)
C31	−0.129 (2)	0.1938 (9)	0.2004 (6)	3.9 (4)
C32	−0.186 (2)	0.262 (1)	0.1764 (7)	6.1 (5)
C33	−0.209 (2)	0.322 (1)	0.2107 (8)	6.2 (6)
C34	−0.139 (2)	0.3104 (9)	0.2529 (7)	4.4 (4)
C35	−0.168 (2)	0.2579 (9)	0.2878 (6)	4.2 (4)
C36	−0.298 (2)	0.215 (1)	0.2862 (7)	6.0 (5)
C37	−0.344 (2)	0.182 (1)	0.2417 (8)	5.9 (6)
C38	−0.237 (2)	0.143 (1)	0.2161 (5)	4.2 (4)
C39	−0.296 (2)	0.093 (1)	0.1795 (6)	4.6 (5)
C40	−0.388 (2)	0.0396 (9)	0.1945 (5)	3.8 (4)
C41	−0.379 (2)	−0.008 (1)	0.2256 (7)	5.9 (5)
C42	−0.489 (3)	−0.056 (1)	0.2379 (6)	7.5 (6)
C43	−0.588 (2)	−0.062 (1)	0.2089 (7)	6.6 (5)
C44	−0.606 (2)	−0.012 (1)	0.1778 (7)	7.2 (6)
C45	−0.504 (2)	0.037 (1)	0.1687 (6)	5.4 (5)
C46	−0.491 (2)	0.092 (1)	0.1356 (7)	6.4 (6)
C47	−0.369 (2)	0.124 (1)	0.1418 (6)	5.1 (5)
C51	0.086 (3)	0.366 (1)	0.3273 (6)	6.5 (6)
C52	0.080 (3)	0.234 (1)	0.3695 (6)	7.8 (6)
C53	0.313 (2)	0.278 (2)	0.3180 (8)	9.1 (7)
C54	0.065 (2)	0.047 (1)	0.2197 (6)	5.4 (5)
C55	−0.019 (2)	0.062 (1)	0.3108 (6)	5.9 (5)
C56	0.245 (2)	0.092 (1)	0.2872 (7)	5.7 (5)
C57	0.147 (3)	0.355 (1)	0.1803 (7)	8.5 (7)
C58	0.144 (2)	0.218 (1)	0.1401 (6)	6.9 (6)
C59	0.341 (2)	0.248 (1)	0.2040 (8)	8.1 (7)

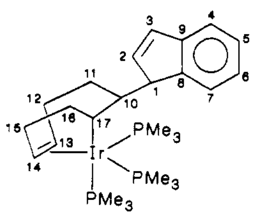
Conclusion

The facility with which the indenyl ligand undergoes hapticity changes, and even displacement from a metal, has led to an unusual reaction pathway for indenyl metal chemistry. The reaction chemistry of (η^5-Ind)Ir(COD) with PMe_3 and the X-ray crystal structure of the resulting product point to a mechanism in which the product is formed via the indenyl ligand separating from the metal as free indenide followed by attack by the indenide on one of the coordinated double bonds of COD. We have already begun to investigate the addition of nucleophiles in general to $Ir(COD)(PMe_3)_3^+$ and will report on those results in the near future.[24] We also plan to continue our investigations into aspects of (indenyl)iridium chemistry with an eye toward exploiting the indenyl transformations for accelerating or altering organic transformations at the iridium center.

Experimental Section

All of the following reactions were carried out under a nitrogen atmosphere either in a Vacuum-Atmospheres Dri-Lab or in standard Schlenck ware. Iridium chloride hydrate was purchased from Engelhard minerals, indene and cyclooctadiene were purchased from Aldrich Chemicals, and trimethylphosphine was purchased from Strem Chemicals. $[Ir(COD)Cl]_2$ was synthesized following the literature procedure.[6] All solvents were of reagent-grade quality and were dried by using the appropriate technique and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer Model 783 infrared spectrophotometer. Proton (200 MHz) and carbon-13 (50 MHz) NMR spectra were recorded on a Magnachem A-200 NMR spectrometer. Phosphorus-31 (145 MHz) NMR spectra were recorded on Bruker AM360 NMR spectrometer. For the purposes of the NMR assignments in the experimentals, please refer to the following indenyl numbering schemes:





Preparation of (η^5-Indenyl)(cyclooctadiene)iridium. $[Ir(COD)Cl]_2$, 2.0 g (2.98 mmol), was dissolved in 50 mL of THF. To this solution was added indenyllithium, 0.73 g (5.98 mmol), as a solid, and the resulting solution was stirred at room temperature for 1 h. At the end of 1 h, the THF was removed at reduced pressure and the residue was extracted with 6 × 50-mL portions of pentane. The pentane was slowly evaporated and cooled to deposit pale yellow crystals. The crystals were collected and dried to yield 2.15 g (5.17 mmol, 86% yield) of (η^5-indenyl)(cyclooctadiene)iridium identified on the basis of the following information: Anal. Found (Calcd for $C_{17}H_{19}Ir$): C, 48.82 (49.14); H, 4.80 (4.60); Ir, 46.13 (46.25). NMR spectra: ^1H (200 MHz) δ 1.65–1.86 (m, 8 H, COD CH_2), 3.99 (m, 4 H, COD CH), 5.00 (d, 2 H, indenyl H1/H3), 5.76 (t, 1 H, indenyl H2), 6.98–7.16 (m, 4 H, indenyl H4–H7); $^{13}C\{^1H\}$ (50 MHz): δ 34.36 (COD CH_2), 51.35 (COD CH), 72.80 (indenyl C1/C3), 85.15 (indenyl C2), 110.23 (indenyl C8/C9), 121.75 and 124.89 (indenyl C4–C7).

Preparation of (η^5-Indenyl)dicarbonyliridium. IndIr(COD), 1.0 g (2.4 mmol), was dissolved in 100 mL of pentane. Carbon monoxide was then bubbled through the solution at 1-atm pressure for 1 h. The pentane was then removed at reduced pressure to yield 0.8 g (2.2 mmol, 92% yield) of (η^5-indenyl)dicarbonyliridium, identified on the basis of the following information: Anal. Found (Calcd for $C_{11}H_7IrO_2$): C, 36.93 (36.36); H, 2.28 (1.94); Ir, 56.72 (52.89). IR (Nujol): ν_{CO} = 2029, 1958 cm^{-1}; pentane, ν_{CO} = 2042, 1979 cm^{-1}. NMR spectra: ^1H (200 MHz) δ 5.08 (d, J = 2.7 Hz, 2 H, indenyl H1/H3), 5.50 (t, J = 2.7 Hz, 1 H, indenyl H2), 6.18 (br s, 4 H, indenyl H4–H7); $^{13}C\{^1H\}$ δ 70.58 (indenyl C1/C3), 93.24 (indenyl C2), 115.13 (indenyl C8/C9), 119.42, 125.81 (indenyl C4–C7), 171.72 (carbonyl carbon). The preparation and characterization of this compound have recently been reported by another author.[4b]

Preparation of 1-(Trimethylsilyl)indene. Trimethylchlorosilane, 25 g (230 mmol), was dissolved in 100 mL of THF and cooled to 0 °C. An addition funnel was charged with 20 g (164 mmol) of indenyllithium in 200 mL of THF. The indenyllithium solution was added dropwise to the trimethylchlorosilane solution over a period of 1 h. The mixture was then allowed to warm to room temperature and stirred for an additional hour.

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(24) A preliminary account of this work has been presented: Merola, J. S.; Kacmarcik, R. T. Presented at the 191st National Meeting of American Chemical Society, New York, April 1986, INOR 228.

The THF was removed at reduced pressure leaving an oily residue with white solids. The residue was extracted with pentane, and 6.8 g of a white, pentane insoluble solid (LiCl) was removed by filtration. The pentane and excess trimethylchlorosilane were removed from the filtrate at reduced pressure to yield 30 g (159 mmol, 97% yield) of 1-(trimethylsilyl)indene identified on the basis of its ^{1}H and ^{13}C NMR spectra and used in following steps without further purification. NMR spectra: ^{1}H (200 MHz) δ -0.02 (s, 9 H, Si(CH_3)$_3$), 3.46 (t, J = 1 Hz, 1 H, indenyl CHSi(CH$_3$)$_3$), 6.61–7.03 (AB multiplet, 2 H, indenyl olefin), 7.28–7.62 (m, 4 H, aromatic); ^{13}C{^{1}H} (50 MHz) δ -2.56 (SiCH$_3$), 46.55 (CHSi(CH$_3$)$_3$), 121.45, 122.94, 124.11, 125.27, 129.35, 135.6 (aromatic and olefinic CH), 144.52, 145.64 (aromatic quaternary C).

Preparation of [1-(Trimethylsilyl)indenyl]lithium. 1-(Trimethylsilyl)indene, 10 g (53 mmol), was dissolved in 200 mL of pentane. *n*-Butyllithium, 24 mL (2.2M, 53 mmol), was added over a few minutes. During the addition, solids formed in the reaction mixture. The mixture was stirred overnight to ensure complete reaction. The mixture was filtered, and the collected solids were washed with pentane and dried to yield 10.3 g (53 mmol, 100% yield) of [1-(trimethylsilyl)indenyl]lithium. This material was not characterized except for its successful use in following experiments.

Preparation of [1-(Trimethylsilyl)indenyl](cyclooctadiene)iridium. [Ir(COD)Cl]$_2$, 1.0 g (1.48 mmol), was dissolved in 100 mL of THF. [1-(Trimethylsilyl)indenyl]lithium, 0.6 g (3.1 mmol), was added as a solid, and the reaction mixture was stirred for 1 h at room temperature. The THF was then removed at reduced pressure, and the residue was extracted with several portions of pentane. The pentane was evaporated to yield 1.35 g (2.7 mmol, 91% yield) of yellow [1-(trimethylsilyl)-indenyl](cyclooctadiene)iridium identified on the basis of the following information: Anal. Found (Calcd for $C_{20}H_{27}IrSi$): C, 49.40 (49.25); H, 6.01 (5.58). NMR spectra: ^{1}H (200 MHz, C_6D_6) δ 0.24 (s, 9 H, Si(CH_3)$_3$), 1.54–1.80 (m, 8 H, COD CH_2), 3.86–3.97 (m, 4 H, COD CH), 5.05 (d, J = 2.5 Hz, 1 H, H2), 5.70 (d, J = 2.5 Hz, 1 H, H3), 6.98–7.33 (m, 4 H, aromatic H); ^{13}C{^{1}H}(50 MHz, C_6D_6) δ -0.25 (Si(CH$_3$)$_3$), 32.85, 32.68 (COD CH$_2$), 50.35, 50.59 (COD CH), 74.7, 76.72, 89.54 (indenyl C1–C3), 112.99, 114.6 (indenyl C8, C9), 121.52, 121.61, 124.00, 124.10 (indenyl C4–C7).

Preparation of [1,3-Bis(trimethylsilyl)indenyl]lithium. Trimethylchlorosilane, 8 g (74 mmol), was dissolved in 100 mL of THF, and the resulting solution was cooled to 0 °C. An addition funnel was charged with [1-(trimethylsilyl)indenyl]lithium, 10 g (54 mmol), in 100 mL of THF. The [(trimethylsilyl)indenyl]-lithium solution was added dropwise to the Me$_3$SiCl solution over a period of 1 h. At the end of the addition, the cooling bath was removed and the mixture was allowed to warm to room temperature and stirred for an additional hour. Then the THF was removed at reduced pressure to yield an oily residue with white solids. The residue was extracted with pentane (200 mL) and filtered. No attempts were made to isolate the bis(trimethylsilyl)indene, but 24 mL (2.2 M, 53 mmol) of *n*-butyllithium solution was added directly to the pentane extract, and the solution was stirred overnight at room temperature. The resulting white precipitate was filtered, washed with pentane, and dried to yield 10 g (38 mmol, 70% yield) of [1,3-bis(trimethylsilyl)indenyl]-lithium. No attempts were made to characterize this material except for its successful use in making the desired iridium complex.

Preparation of [1,3-Bis(trimethylsilyl)indenyl](cyclooctadiene)iridium. [Ir(COD)Cl]$_2$, 0.5 g (0.74 mmol), was dissolved in 50 mL of THF. [1,3-Bis(trimethylsilyl)indenyl]lithium, 0.4 g (1.5 mmol), was added as a solid, and the reaction mixture was stirred at room temperature for 1 h. The THF was removed at reduced pressure, and the residue was extracted with pentane. The pentane was evaporated to yield 0.8 g (1.4 mmol, 93% yield) of yellow [1,3-bis(trimethylsilyl)indenyl](cyclooctadiene)iridium identified on the basis of the following information: Anal. Found (calcd for $C_{23}H_{35}IrSi_2$): C, 49.49 (49.34); H, 6.18 (6.30); Ir, 35.70 (34.33); Si, 9.23 (10.03). NMR spectra: ^{1}H NMR (200 MHz, C_6D_6) δ 0.29 (s, 18 H, Si(CH_3)$_3$), 1.58–1.85 (m, 8 H, COD CH_2), 3.78 (m, 4 H, COD CH), 5.61 (s, 1 H, indenyl H$_2$), 6.93–6.98 and 7.33–7.38 (AA′BB′ pattern, 4 H, indenyl H4–H7); ^{13}C{^{1}H} (50 MHz, C_6D_6) δ 0.03 (Si(CH$_3$), 33.4 (cyclooctadiene CH$_2$), 50.9 (cyclooctadiene CH), 79.9 (indenyl C1/C3), 94.2 (indenyl C2), 115.9 (indenyl C8/C9), 123.0, 124.2 (indenyl C4–C7).

Reaction between (Ind)Ir(COD) and PMe$_3$. (Ind)Ir(COD), 0.5 g (1.2 mmol), was dissolved in 50 mL of toluene. Then, PMe$_3$, 0.4 g (5.3 mmol), was added and the resulting solution stirred at room temperature for 0.5 h. (NMR tube experiments indicate that this reaction is actually complete on mixing.) The toluene was removed at reduced pressure, and the residue was extracted with pentane (all material was pentane soluble). The pentane solution was evaporated slowly and cooled to precipitate white crystals which were filtered and dried to yield 0.65 g (1.0 mmol, 83% yield) of I identified on the basis of the following information: Anal. Found (Calcd for $C_{26}H_{46}IrP_3$): C, 48.31 (48.51); H, 7.26 (7.20); Ir, 29.67 (29.86); P, 13.98 (14.43). NMR Spectra: ^{1}H (200 MHz, C_6D_6) δ 0.84 (d, J_{P-H} = 6.6 Hz, 9 H, P(CH_3)$_3$), 1.11 (d, J_{P-H} = 5.6 Hz, 9 H, P(CH_3)$_3$), 1.24 (d, J_{P-H} = 5.9 Hz, 9 H, P(CH_3)$_3$), 1.76–3.30 (a series of complex multiplets not fully assigned but due to COD aliphatic and olefinic protons), 3.61 (br d, J = 6.8 Hz, 1 H, H1), 6.76 (dd, J_{H3-H2} = 5.6 Hz, J_{H1-H2} = 1.2 Hz, 1 H, H2), 6.90 (dd, J_{H3-H2} = 5.6 Hz, J_{H1-H3} = 2.0 Hz, 1 H, H3), 7.20–7.60 (m, 4 H, H4–H7); ^{13}C{^{1}H} (50 MHz, C_6D_6) δ 18.52 (complex m, P(CH$_3$)$_3$), 22.30 (complex m, P(CH$_3$)$_3$), 26.22–59.76 (a series of complex resonances not assigned but due to carbons C1 and C10–C17), 120.91, 123.76, 125.12, 126.10 (C4–C7), 129.88, 141.72 (C8 and C9), 145.21, 148.25 (C2, C3); ^{31}P{^{1}H} (145.8 MHz, C_6D_6) a complex ABC pattern not fully analyzed but centered at δ -59.55 with respect to external H_3PO_4.

Preparation of [Ir(COD)(PMe$_3$)$_3$]Cl. [Ir(COD)Cl]$_2$, 4.0 g (6.0 mmol), was dissolved in 200 mL of toluene to yield a red-orange solution. PMe$_3$, 2.9 g (36 mmol), was dissolved in 20 mL of toluene and added dropwise to the [Ir(COD)Cl]$_2$ solution over a period of 20 min. During the addition the reaction mixture turned yellow and a white solid began to precipitate. The mixture was stirred overnight, and the product was collected by filtration, washed with toluene and then pentane, and dried to yield 6.0 g (10.6 mmol, 88% yield) of [Ir(COD)(PMe$_3$)$_3$]Cl identified on the basis of the following information: Anal. Found (Calcd for $C_{17}H_{39}ClIrP_3$): C, 34.93 (36.19); H, 7.12 (6.98); Cl, 6.17 (6.28); Ir, 33.60 (34.07); P, 16.72 (16.47). NMR spectra: ^{1}H (200 MHz) δ 1.60 (m, 27 H, P(CH_3), 2.1–2.6 (m, 8 H, COD CH_2), 3.30 (br s, 4 H, COD CH); ^{13}C{^{1}H} (50 MHz) δ 20.1 (m, PCH$_3$), 34.3 (q, J_{P-C} = 2.5 Hz, COD CH$_2$), 68.9 (q, J_{P-C} = 4.9 Hz, COD CH).

Reaction between [Ir(COD)(PMe$_3$)$_3$]Cl and Indenyllithium. [Ir(COD)(PMe$_3$)$_3$]Cl, 0.5 g (0.9 mmol), was slurried in 50 mL of THF. Indenyllithium, 0.12 g (1 mmol), was added, and the mixture was stirred at room temperature for 1 h. The THF was removed under reduced pressure, and the residue was extracted with pentane. The pentane was slowly evaporated with cooling to deposit 0.46 g (79% yield) of I whose spectral properties were identical with those of 1 as prepared above.

Reaction between [1-(Trimethylsilyl)indenyl](cyclooctadiene)iridium and PMe$_3$. [1-(Trimethylsilyl)indenyl](cyclooctadiene)iridium, 0.5 g (1.03 mmol), was dissolved in 50 mL of toluene. Then, PMe$_3$, 0.4 g (5.3 mmol), was added, and the resulting solution stirred at room temperature for 0.5 h. The toluene was removed at reduced pressure, and the residue was extracted with pentane (all material was pentane-soluble). The pentane solution was evaporated slowly and cooled to precipitate white crystals which were filtered and dried to yield 0.63 g (0.88 mmol, 85% yield) of II identified on the basis of the following information: Anal. Found (Calcd for $C_{29}H_{54}IrP_3Si_1$): C, 49.03 (48.65); H, 7.71 (7.60). NMR spectra: ^{1}H NMR (200 MHz, C_6D_6) δ 0.34 (s, 9 H, Si(CH_3)$_3$), 0.85 (d, J_{P-H} = 6.0 Hz, 9 H, P(CH_3)$_3$), 1.11 (d, J_{P-H} = 5.9 Hz, 9 H, P(CH_3)$_3$), 1.25 (d, J_{P-H} = 6.0 Hz, 9 H, P(CH_3)$_3$), 1.76–3.40 (a series of complex multiplets not fully assigned but due to COD aliphatic and olefinic protons), 3.62 (br d, J = 8 Hz, 1 H, H1), 7.1–7.6 (m, H2 and H4–H7); ^{13}C{^{1}H} (50 MHz, C_6D_6) δ -0.77 (Si(CH$_3$)$_3$), 18.7 (complex m, P(CH$_3$)$_3$), 22.30 (complex m, P(CH$_3$)$_3$), 26.07–61.36 (a series of complex resonances not assigned but due to carbons C1 and C10–C17), 121.96, 123.56, 125.27, 126.07 (C4, C5, C6, C7), 141.86 (C3), 148.31, 149.24 (C8, C9), 152.26 (C2); ^{31}P{^{1}H} (145.8 MHz, C_6D_6; an ABC pattern analyzed as follows): δ(1) -59.3, δ(2) -59.5, δ(3) -60.1, J_{1-2} = 10.2 Hz, J_{2-3} = 17.5 Hz, J_{1-3} = 38 Hz.

Reaction between [1,3-Bis(trimethylsilyl)indenyl](cyclooctadiene)iridium and PMe$_3$. [1,3-Bis(trimethylsilyl)-indenyl](cyclooctadiene)iridium, 0.5 g (0.89 mmol), was dissolved in 50 mL of toluene. Then, PMe$_3$, 0.25 g (3.3 mmol), was added

Table III. Summary of Experimental Parameters for X-ray Crystal Structure Determination of I

formula	$C_{26}H_{46}IrP_3$
fw	643.78
F(000)	2592
cryst dimens, mm	0.14 × 0.16 × 0.38
radiatn	Mo Kα; λ = 0.71073 Å
temp, °C	22 ± 1
space group	$P2_12_12_1$
a, Å	10.019 (1)
b, Å	18.836 (3)
c, Å	29.602 (4)
V, Å^3	5586 (2)
Z	8
ρ(calcd), g/cm^3	1.53
μ, cm^{-1}	49.4
monochromator	graphite crystal, incident beam
attenuator	Zr foil, factor 21.1
takeoff angle, deg	2.8
detector aperture	2.0–2.5 mm horizontal, 4.0 mm vertical
crystal–detector dist, cm	21
scan type	ω–2θ
scan rate, deg/min	2–5 (in ω)
scan width, deg	1.0 + 0.350 tan θ
max 2θ, deg	54.0°
no. of reflctns measd	6818 total, 5525 unique
correctns	Lorentz-polarization; linear decay (from 0.974 to 1.131 on I); reflection averaging (agreement on *I* = 3.0%); empirical absorption (from 0.80 to 1.00 on I)
solution	Patterson method
hydrogen atoms	included as fixed contribution to the structure factor
minimizatn functn	$\sum w(\lvert F_o\rvert - F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
anomalous dispersn	all non-hydrogen atoms
reflectns included	3660 with $F_o^2 > 3.0\sigma(F_o^2)$
parameters refined	541
unweighted/weighted agreement factor	0.044/0.048
esd of observn of unit weight	1.21
convergence, largest shift	0.07σ
high peak in final diff map, e/Å^3	1.05 (15)

and the resulting solution stirred at room temperature for 1 h. The toluene was removed at reduced pressure, and the residue was extracted with pentane (all material was pentane soluble). The pentane solution was evaporated slowly and cooled to precipitate yellow crystals which were filtered and dried to yield 0.52 g (0.66 mmol, 745% yield) of III identified on the basis of the following information: Anal. Found (Calcd for $C_{32}H_{62}IrP_3Si_2$): C, 49.03 (48.77); H, 7.71 (7.93). NMR spectra: ^1H (200 MHz, C_6D_6) δ 0.02 (s, 9 H, $Si(CH_3)_3$), 0.05 (s, 9 H, $Si(CH_3)_3$), 0.93 (d, J_{P-H} = 6.6 Hz, 9 H, $P(CH_3)_3$), 1.26 (d, J_{P-H} = 5.6 Hz, 9 H, $P(CH_3)_3$), 1.29 (d, J_{P-H} = 6.2 Hz, 9 H, $P(CH_3)_3$), 1.8–3.3 (a series of complex multiplets not fully assigned but due to COD aliphatic and olefinic protons), 6.66 (s, 1 H, H2), 7.2–7.8 (m, H4–H7); $^{13}C\{^1H\}$ (50 MHz, C_6D_6) δ −0.85 ($Si(CH_3)_3$ on C3), −0.63 ($Si(CH_3)_3$ on C1), 18.7 (d, J_{P-C} = 23 Hz, $P(CH_3)_3$), 22.25 (t, J_{P-C} = 22 Hz, $P(CH_3)_3$), 25.5–50.8 (a series of complex resonances not assigned but due to carbons C1 and C10–C17), 119.92, 123.05, 123.42, 124.11 (C4–C7), 130.44 (C2), 145.64, 148.30 (C8, C9), 152 (C3); $^{31}P\{^1H\}$ (145.8 MHz, C_6D_6; an ABC pattern analyzed as follows) δ(1) −58.76, δ(2) −59.7, δ(3) −60.62, J_{1-2} = 12.9 Hz, J_{2-3} = 10.5 Hz, J_{1-3} = 52 Hz.

X-ray Experiment.[25] Pale yellow crystals of I were grown by slow evaporation of a pentane solution. A pale yellow rectangular crystal of I having approximate dimensions of 0.14 × 0.16 × 0.38 mm was mounted in a glass capillary with its long axis roughly parallel to the ϕ axis of the goniometer. Preliminary examination and data collection were performed with Mo K$_\alpha$ (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator. Details of the data collection experiment are listed in Table III.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 20 reflections in the range $6 < \theta < 9°$, measured by the computer-controlled diagonal slit method of centering. The orthorhombic cell parameters generated are listed in Table III. From the systematic absences of *h*00, *h* = 2*n* + 1, 0*k*0, *k* = 2*n* + 1, and 00*l*, *l* = 2*n* + 1, and from subsequent least-squares refinement, the space group was confirmed to be $P2_12_12_1$ (No. 19).

The structure was solved by using the Patterson heavy-atom method which revealed the positions of the two Ir atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the structure factor calculations at their calculated positions (C–H distance = 0.97 Å) but were not refined. Due to a shortage of strong data, the hydrogen atoms of the phosphine methyl groups were not included. Neutral atom scattering factors were taken from ref 26. Anomalous dispersion effects were included in *Fc*;[27] the values for *f′* and *f″* were taken from ref 28. Only the 3660 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The absolute configuration was determined in this case, by convergence of each enantiomeric pair using a unit weighting scheme (solution 1, R/R_w = 0.055/0.063 and esd = 6.869; solution 2, R/R_w = 0.065/0.071 and esd = 7.703) showing solution 1 to be the proper choice. The final cycle of refinement included 541 variable parameters and converged (largest parameter shift was 0.27 times its esd) with unweighted and weighted agreement factors of $R_1 = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$ = 0.044 and $R_2 = (\sum w(\lvert F_o\rvert - \lvert F_c\rvert)/\sum wF_o^2)^{1/2}$ = 0.048. The standard deviation of an observation of unit weight was 1.21. The final difference Fourier map showed no significant residual electron density. The highest peak in the final difference Fourier had a height of 1.05 e/Å^3 with an estimated error based on ΔF of 0.15. Plots of $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ versus $\lvert F_o\rvert$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

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Registry No. I, 118494-43-2; II, 118494-44-3; III, 118494-45-4; $[Ir(COD)Cl]_2$, 12112-67-3; IndIr(COD), 102525-11-1; PMe_3, 594-09-2; $[Ir(COD)(PMe_3)_3]Cl$, 118494-48-7; indenyllithium, 32334-19-3; (η^5-indenyl)dicarbonyliridium, 12153-08-1; 1-(trimethylsilyl)indene, 18053-75-3; [1-(trimethylsilyl)indenyl]lithium, 55563-48-9; [1-(trimethylsilyl)indenyl](cyclooctadiene)iridium, 118494-46-5; [1,3-bis(trimethylsilyl)indenyl]lithium, 56423-66-6; [1,3-bis(trimethylsilyl)indenyl](cyclooctadiene)iridium, 118494-47-6.

Supplementary Material Available: Tables of bond lengths, bond angles, general temperature factor expressions, *U*'s, root-mean-square amplitudes of thermal vibrations, and significant least-squares planes for $C_{26}H_{46}IrP_3$ (I) (9 pages); a listing of observed and calculated structure factor amplitudes for I (20 pages). Ordering information is given on any current masthead page.

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[25] The single-crystal X-ray structural analysis was carried out at Oneida Research Services, One Halsey Road, Whitesboro, NY 13492.

[26] Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

[27] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[28] Cromer, D. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.