Society, for support of this research. We also wish to thank Professor C. E. Strouse of this department for help and advice on the use of the Syntex diffractometer. Computer time was furnished by the UCLA Campus Computing Network.

Supplementary Material Available: Figure 3, view of the plane through the tricyclic system of molecule **4**; Figure 4, view of molecule **4** showing the axial ligands; Table V, observed and calculated structure factors for **4**; Table X, observed and calculated structure factors for **5**; Table XI, root mean square amplitudes of vibration for **4** and **5** (20 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Taken in part from the Dissertation of B. T. Huie, UCLA, 1975. (b) Part 10: B. T. Huie, C. B. Knobler, G. Firestein, R. J. McKinney, and H. D. Kaesz, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) In order to preserve continuity and facilitate correlation of the results reported in the present work with that of the two preceding relevant publications, ref 3 and 4, the numbering of these derivatives in those papers has been retained in the present work. Since the present paper refers only to the unsubstituted derivatives, the letter index *a* following the compound number has been omitted; this was used in the earlier papers to differentiate these derivatives from the fluoro (letter index *b*) or methyl derivatives (letter index *c*).

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(6) B. T. Huie and C. B. Knobler, Abstracts, American Crystallographic Association Meeting, Berkeley, Calif., March 1974, Paper 1-11.

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(8) The numbers given in parentheses throughout this paper are the estimated standard deviations, and refer to the last digit given.

(9) Part 9: R. J. McKinney, C. B. Knobler, B. T. Huie, and H. D. Kaesz, *J. Am. Chem. Soc.*, **99**, 2988 (1977).

(10) (a) The programs used in this work included locally written data reduction programs; JBPATT, JBFOUR, and PEAKLIST, modified versions of Fourier programs written by J. Blount; local versions of ORFLS (Busing, Martin, and Levy) structure factor calculations and full-matrix least-squares refinement; HPOSN (Hope) to calculate tentative hydrogen positions; ORTEP (Johnson) figure plotting; MGTL (Schomaker and Trueblood) analysis of possible rigid-body motion, least-squares planes; and ORFFE (Busing, Martin, and Levy) distances, angles and error computations. All calculations were performed on the IBM 360-91 computer operated by the UCLA Campus Computing Network. (b) After our refinement was completed we became aware of a revised value d(C-H) = 0.95 Å recommended for use in rigid body analyses; cf. M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(11) The function $\Sigma||F_o| - |F_c||^2$ was minimized in the least-squares refinement and the discrepancy indices were defined as

$$R_F = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \qquad R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

where

$$w = \left[\frac{1}{\sigma(F_o)}\right]^2$$

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Isolation and Structural Characterization of Bis(η^5-cyclopentadienyl)bis(carbonyl)-μ-(*o*-phenylene)-diiridium(*Ir–Ir*), $(C_5H_5)_2(CO)_2Ir_2(C_6H_4)$: A Product Formally Derived from the Double Oxidative Addition of Benzene to Iridium

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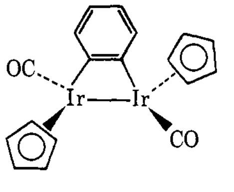
Abstract: During a study of the reaction of (η^5-C_5H_5)Ir$(CO)_2$ and photo-2-pyrone in benzene solution, a yellow, crystalline compound was isolated in low yield. Subsequent studies have shown that this substance can also be obtained in the absence of photo-2-pyrone in comparable yields. The product has been identified as bis(η^5-cyclopentadienyl)bis(carbonyl)-μ-(*o*-phenylene)-diiridium(*Ir–Ir*) (**1**) by means of ^{1}H NMR, IR, and mass spectral analyses as well as by x-ray diffraction techniques. The complex crystallizes in the monoclinic system, space group $P2_1/n$. Crystal parameters are a = 9.734 (4), b = 9.468 (4), c = 17.224 (7) Å, β = 94.20 (4)°, Z = 4. The structure was solved by the heavy atom technique employing Fourier methods and was refined by full-matrix least-squares methods to final discrepancy factors of R = 0.041 and R_w = 0.036. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer and corrections were made for absorption and isotropic extinction. The two iridium atoms are symmetrically σ bonded to the phenylene ring, giving rise to an approximate (noncrystallographic) twofold axis bisecting the iridium–iridium bond and lying in the plane of the phenylene ring. The iridium–iridium bond distance is 2.7166 (2) Å, the two Ir-(C_5H_5) centroid distances are 1.907 (3) and 1.912 (3) Å, the two Ir-(CO) distances average 1.814 (3) Å, and the two iridium to phenylene ring carbon distances are both 2.045 (3) Å. The formation of **1** under these conditions is indicative of the double oxidative addition of one benzene molecule to two iridium atoms. Infrared, ^{1}H NMR, and chemical degradation studies indicate that a phenyliridium hydride intermediate such as (η^5-C_5H_5)Ir(CO)(C_6H_5)(H) (**2**) is produced in the early stages of this reaction sequence. Possible reaction mechanisms are discussed.

The homogeneous catalytic activation of carbon–hydrogen bonds has become the subject of intense research efforts in recent years, since it relates to a new type of homogeneous catalysis, and offers some potentially important new pathways, at least involving arenes, for organic synthesis.[1] This activation is usually postulated to occur as a result of cleavage of the C–H bond by a highly reactive, coordinatively unsaturated transition metal species, and concomitant formation of a C–M–H intermediate. At the present time, however, bona fide examples of this important process which involve *unactivated* C–H bonds and in which the resulting product of oxidative addition has been reasonably well characterized are limited to reactions of tungstenocene, $(C_5H_5)_2W$,[2-5] and of low-valent ruthenium intermediates[6,7] with aromatic hydrocarbons. On the other hand, such aryl-metal hydride intermediates have been widely postulated to account for H-D exchanges involving arenes such as C_6D_6, etc., and various organotransition metal complexes.[1,7-12]

We now report studies relating to the oxidative addition of C-H bonds to organoiridium species, and the structural characterization of bis(η^5-cyclopentadienyl)bis(carbonyl)-μ-(*o*-phenylene)-diiridium(*Ir-Ir*) (**1**), a novel product which is formally derived from the *double oxidative addition* of benzene to iridium. To our knowledge, these results likewise represent the first definitive examples of the oxidative addition of C-H bonds to iridium, an element well known to undergo such interactions with many other types of bonds.[13,14]

Results and Discussion

Discovery and Spectral Properties of 1. Several years ago, we reported that the photochemically induced reaction of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ and photo-2-pyrone in benzene solution produced the novel sandwich complex (η^5-cyclopentadienyl)(η^4-cyclobutadiene)rhodium in low yield.[15] A subsequent attempt was made to extend this reaction for the synthesis of the as yet unknown iridium analogue, $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4H_4)Ir$, from an analogous photolysis reaction between $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ and photo-2-pyrone in benzene solution.[16] A yellow, crystalline product was in fact obtained; however, spectral data indicated the absence of either 2-pyrone or η^4-cyclobutadiene moieties, and the presence of carbonyl substituents and possibly an aromatic residue. At that time, a definite structural assignment could not be made from the data available, and we therefore decided to undertake a single-crystal x-ray crystallographic investigation of the product. These studies revealed the product to have the novel structure **1** (vide infra).



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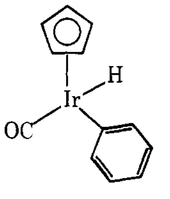

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The presence of an *o*-phenylene unit in **1** formally implies the double oxidative addition of one benzene molecule to two iridium atoms. Considering the unusual structure of **1** and the serendipitous means by which it was derived, it was of subsequent interest to investigate the photolysis of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in benzene in the absence of photo-2-pyrone, in hopes of determining if **1** could be produced. Such studies could also possibly provide insight concerning the mechanistic pathways leading to **1**.

The photolysis of a solution (0.011 M) of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in benzene was conducted over a variety of time periods and temperature ranges. Complex **1** was indeed isolated in every case. The maximum yield of **1** after separation and purification was 6.3% in a run involving an 8-h photolysis at 15 °C. The ^1H NMR spectrum of **1** exhibited singlet and multiplet (A_2B_2) resonances at τ 4.40 and 2.6-2.9, respectively, in an intensity ratio of 10:4. The infrared spectrum of **1** exhibited a strong terminal metal carbonyl absorption at 1945 cm^{-1}, as well as a single medium intensity band at 730 cm^{-1} which may be assignable to an ortho-disubstituted benzene ring. The mass spectrum of **1** clearly indicates the presence of two iridium atoms (derived from ^{191}Ir and ^{193}Ir isotopes) in the strong molecular ion at *m/e* 644-648, as well as ions derived from the losses of one and two carbonyl groups from M^+. A moderately intense band at *m/e* 78 corresponding to C_6H_6 was also always observed in the mass spectrum of **1** (even well-dried samples), and no doubt arises from hydrogenation of the phenylene moiety in the mass spectrometer. The above spectral data of **1** are thus well in accord with the proposed structural formulation.

Table I. Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-}C_5H_5)_2(CO)_2Ir_2(C_6H_4)$

Distances

Ir(1)-Ir(2)	2.7166 (2)	C(1)-C(2)	1.390 (5)
Ir(1)-C(12)	2.045 (2)	C(2)-C(3)	1.406 (5)
Ir(1)-C(17)	1.817 (3)	C(3)-C(4)	1.444 (5)
Ir(2)-C(11)	2.045 (3)	C(4)-C(5)	1.395 (7)
Ir(2)-C(18)	1.811 (3)	C(5)-C(1)	1.391 (5)
Ir(1)-C(1)	2.247 (3)	C(6)-C(7)	1.356 (7)
Ir(1)-C(2)	2.244 (3)	C(7)-C(8)	1.378 (6)
Ir(1)-C(3)	2.244 (3)	C(8)-C(9)	1.412 (7)
Ir(1)-C(4)	2.281 (3)	C(9)-C(10)	1.395 (7)
Ir(1)-C(5)	2.276 (3)	C(10)-C(6)	1.450 (6)
Ir(2)-C(6)	2.239 (4)	C(11)-C(12)	1.386 (3)
Ir(2)-C(7)	2.277 (4)	C(12)-C(13)	1.368 (3)
Ir(2)-C(8)	2.283 (4)	C(13)-C(14)	1.380 (4)
Ir(2)-C(9)	2.234 (4)	C(14)-C(15)	1.363 (5)
Ir(2)-C(10)	2.231 (4)	C(15)-C(16)	1.397 (4)
C(17)-O(1)	1.147 (3)	C(16)-C(11)	1.379 (4)
C(18)-O(2)	1.150 (3)		

Angles

Ir(1)-Ir(2)-C(11)	70.48 (6)	Ir(2)-Ir(1)-C(12)	71.46 (5)
Ir(1)-Ir(2)-C(18)	86.6 (2)	Ir(2)-Ir(1)-C(17)	85.2 (2)
C(12)-Ir(1)-C(17)	88.2 (1)	C(11)-Ir(2)-C(18)	90.2 (1)
Ir(1)-C(12)-C(11)	107.9 (1)	Ir(2)-C(11)-C(12)	109.8 (1)
Ir(1)-C(12)-C(13)	131.3 (3)	Ir(2)-C(11)-C(16)	130.9 (4)
Ir(1)-C(17)-O(1)	178.5 (2)	Ir(2)-C(18)-O(2)	176.7 (3)
C(1)-C(2)-C(3)	110.4 (3)	C(6)-C(7)-C(8)	110.3 (3)
C(2)-C(3)-C(4)	105.7 (3)	C(7)-C(8)-C(9)	106.8 (3)
C(3)-C(4)-C(5)	107.0 (3)	C(8)-C(9)-C(10)	109.3 (3)
C(4)-C(5)-C(1)	110.1 (3)	C(9)-C(10)-C(6)	105.2 (3)
C(5)-C(1)-C(2)	106.8 (3)	C(10)-C(6)-C(7)	108.4 (3)
C(11)-C(12)-C(13)	120.6 (2)	C(12)-C(11)-C(16)	119.2 (3)
C(12)-C(13)-C(14)	119.7 (2)	C(11)-C(16)-C(15)	120.1 (3)
C(13)-C(14)-C(15)	120.8 (3)	C(16)-C(15)-C(14)	119.4 (3)

The Crystallographic Structure of 1. The final structural parameters for **1** are collected in Tables I-IV and a view of the single molecule is given in Figure 1. From the figure it can be seen that the molecule possesses an approximate C_2 axis in the direction Z_M, bisecting the iridium-iridium bond and the phenylene ring. Inspection of the bond angle data given in Table I for the three pairs of bond angles subtended at the iridium atoms gives an indication of the departure from strict C_2 symmetry as does comparison of the orientation angles for the two $\eta^5\text{-}C_5H_5$ rings with the X_M, Y_M, Z_M coordinate system, listed in Table III.

The phenylene ring possesses near sixfold symmetry, the average C-C bond distance being 1.379 (3) Å with individual values barely significantly different from this value. The $\eta^5\text{-}C_5H_5$ rings on the other hand do deviate significantly from idealized D_{5h} symmetry but there are no readily apparent structural reasons for this discrepancy. The thermal ellipsoids of the carbon atoms in ring 2 are indicative of a large amplitude librational motion about the pseudo-C_5 axis for this ring—a feature now commonly found in structural results for metal-cyclopentadienyl complexes. The atoms of ring 1, however, do

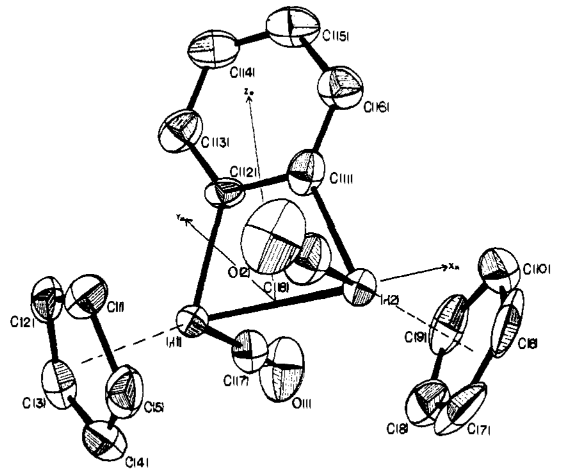


Figure 1. Perspective view of the $(C_5H_5)_2(CO)_2Ir_2(C_6H_4)$ molecule. Thermal ellipsoids are at the 50% probability level.

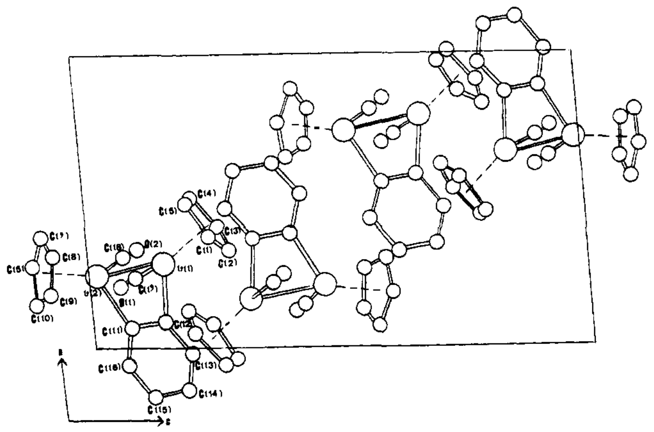


Figure 2. An [010] projection of the molecular packing. The numbered atoms in the molecule define the asymmetric unit.

Table II. Atom Distances from Least-Squares Planes (Å)

Plane (1)[a] $0.5957X - 0.2398Y + 0.7665Z + 3.1700 = 0$

Atom	C(1)	C(2)	C(3)	C(4)	C(5)	Ir(1)[b]
Dist from plane	0.002	0.004	−0.003	0.001	−0.003	1.907

Plane (2) $-0.1098X - 0.3672Y + 0.9236Z + 8.4944 = 0$

Atom	C(6)	C(7)	C(8)	C(9)	C(10)	Ir(2)[b]
Dist from plane	0.002	−0.003	−0.001	−0.001	0.003	−1.912

Plane (3) $0.2780X - 0.8475Y + 0.4523Z + 2.1129 = 0$

Atom	C(11)	C(12)	C(13)	C(14)
Dist from plane	−0.013	0.009	0.001	−0.025
Atom	C(15)	C(16)	Ir(1)[b]	Ir(2)[b]
Dist from plane	0.026	0.001	−0.095	0.046

Plane (4) $0.2547X - 0.8732Y + 0.4155Z + 1.7590 = 0$

Atom	Ir(1)	Ir(2)	C(11)	C(12)
Dist from plane	0.000	0.000	−0.047	0.047

[a] The form of the least-squares plane is $lX + mY + nZ + d = 0$ where X, Y, Z are orthogonal coordinates with Y and Z coincident with the crystal axes. The weights used were, for the ith atom, $w_i = 1/(a\sigma_x b\sigma_y c\sigma_z)^{2/3}$. [b] These atoms were not included in the calculation of the least-squares plane.

Table III. Some Dihedral Angles between Least-Squares Planes and Lines

Plane 1[a] and X_M 47.9°	Plane 2 and X_M 50.7°
Plane 1 and Y_M 45.2°	Plane 2 and Y_M 44.7°
Plane 1 and Z_M 76.7°	Plane 2 and Z_M 72.5°
Plane 1 and plane 2 44.1°	
Plane 3 and plane 4 3.0°	

[a] Planes as defined in Table II.

not show such extensive anisotropy, presumably because of the differing environment for this ring compared to that for ring 2. The two iridium atoms show very small but significant departures from the plane of the phenylene ring, the dihedral angle between the two appropriate planes being 3°. The iridium-iridium bond distance of 2.7166 (2) Å is very comparable to that found in $(NO)_4[P(C_6H_5)_3]_2Ir_2$ (2.717 Å),[17] while the Ir-CO bond distances [average 1.814 (3) Å] are in accord with previously reported values.[18] The Ir-C bond distances to the phenylene ring [2.045 (3) Å] are somewhat shorter than previously reported Ir-C(phenyl) distances.[19]

Table IV. Root Mean Square Amplitudes of Vibration

	Axes		
Atom	Major	Intermed	Minor
Ir(1)	0.184 (1)	0.157 (1)	0.155 (1)
Ir(2)	0.202 (1)	0.177 (1)	0.157 (1)
C(1)	0.276 (5)	0.177 (3)	0.137 (2)
C(2)	0.253 (6)	0.225 (5)	0.159 (2)
C(3)	0.238 (5)	0.210 (4)	0.140 (2)
C(4)	0.295 (6)	0.201 (4)	0.158 (2)
C(5)	0.311 (7)	0.217 (5)	0.165 (2)
C(6)	0.292 (6)	0.247 (7)	0.183 (3)
C(7)	0.321 (8)	0.242 (6)	0.139 (3)
C(8)	0.365 (9)	0.236 (7)	0.130 (4)
C(9)	0.409 (10)	0.230 (8)	0.112 (2)
C(10)	0.350 (9)	0.224 (7)	0.181 (2)
C(11)	0.210 (6)	0.173 (6)	0.128 (2)
C(12)	0.238 (6)	0.178 (5)	0.174 (4)
C(13)	0.252 (7)	0.204 (7)	0.177 (4)
C(14)	0.258 (6)	0.216 (6)	0.166 (2)
C(15)	0.276 (7)	0.228 (6)	0.141 (2)
C(16)	0.240 (7)	0.215 (6)	0.175 (2)
C(17)	0.231 (7)	0.221 (6)	0.187 (2)
C(18)	0.242 (8)	0.215 (6)	0.197 (2)
O(1)	0.355 (6)	0.256 (4)	0.192 (4)
O(2)	0.333 (6)	0.260 (4)	0.189 (4)

A projection of the unit cell contents onto the (010) plane illustrating the molecular packing is given in Figure 2.

There are several other reported x-ray structures which contain similar *o*-phenylene groups bonded to metal atoms. Dahl et al.[20] have described the structure of the $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ anion, obtained by the reaction of $(PtCl_4)_4$ and $(C_6H_5)_3CCl$ in benzene. Each C_6H_4 unit was shown to be bound to two different platinum atoms, and there were two bridging chlorine atoms. The reaction of $Os_3(CO)_{12}$ with $(C_6H_5)_3P$ gave $Os_3(CO)_7[P(C_6H_5)_2](C_6H_4)$, whose x-ray structure indicated a C_6H_4 fragment bridging three osmium atoms.[21] Other osmium and ruthenium cluster compounds which contain multiply bridging C_6H_4 units have since been reported.[22-25] An x-ray structure of the novel complex $(C_6F_4)Fe_2(CO)_8$, derived from $Fe_3(CO)_{12}$ and tetrafluorobenzyne, has also indicated the presence of a C_6F_4 group bridging the two iron atoms.[26]

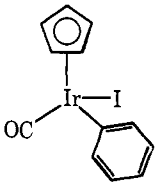
Reaction Pathways Leading to 1. It seems reasonable to assume that the photochemically induced reaction of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ with benzene proceeds in the initial stages by means of the oxidative addition of a C-H bond of benzene to an activated form or derivative of this organoiridium compound. An intermediate product such as $(\eta^5\text{-}C_5H_5)Ir(CO)(C_6H_5)(H)$ (**2**) might therefore be expected to be formed, and possibly be detectable by spectroscopic means, or even be isolated.

Preliminary studies in fact indicated that when the solvent was removed following the photolysis reaction and a ^{1}H NMR spectrum was immediately taken of the residue, resonances in the aromatic, cyclopentadienyl, and metal hydride regions were clearly evident. Column chromatography of the reaction mixture on alumina under nitrogen subsequently produced a band containing unreacted $(\eta^5\text{-}C_5H_5)Ir(CO)_2$, a very air- and thermally sensitive pale-yellow band, and a yellow-brown band which contained the *o*-phenylene complex **1.**

Elucidation of the components comprising the intermediate air- and thermally sensitive band has proved to be difficult, but some evidence relating to its composition is available both by spectroscopic and chemical degradative methods. When the band is removed from the column, it is pale yellow. Even if the solvent is removed immediately, the color of the product nevertheless changes to a dark brown. An infrared spectrum of the dark residue exhibited strong metal-carbonyl stretching fequencies at 2010 and 1955 cm^{-1}, a medium intensity band at 2175 cm^{-1} assignable to an Ir–H stretching frequency, as well as frequencies in the usual aromatic C–H stretching and bending regions. A ^{1}H NMR spectrum of the residue showed two multiplets in the aromatic region centered at τ 2.35 and 2.95, two closely spaced singlets in the $(\eta^5\text{-}C_5H_5)Ir$ region at τ 4.76 and 4.79, and a very distinct high-field singlet at τ 25.5 assignable to an Ir–H resonance. These spectroscopic data are therefore at least indicative of the presence of a phenyliridium hydride complex such as **2.** The data also suggest the presence of one or more closely related products, but it is not known at present if they are formed during the photolysis process or result from degradation of **2** on solvent removal.

When the dark residue from this band was allowed to stand at room temperature under nitrogen for several hours, the spectral characteristics of the material changed. An infrared spectrum indicated that the Ir–H absorption at 2175 cm^{-1} had disappeared, although the carbonyl region remained essentially the same. The NMR spectrum still contained peaks in the aromatic and cyclopentadienyl regions, although the Ir–H resonance had disappeared. Similar changes in spectral characteristics were also observed when the collected band was allowed to stand under nitrogen at −78 °C for a period of several days, indicating the thermal lability of the product.

Chemical evidence for the formation of **2** was likewise obtained by reactions of the air-sensitive band before solvent removal. Thus, portions of the freshly chromatographed solution were immediately treated at ambient temperatures with iodomethane and with bromine, respectively. Workup of the reaction mixtures produced air-stable solids which on the basis of ^{1}H NMR, infrared, and mass spectral measurements as well as by elemental analyses could be characterized as $(\eta^5\text{-}C_5H_5)Ir(CO)(C_6H_5)I$ (**3**) and $(\eta^5\text{-}C_5H_5)Ir(CO)Br_2$ (**4**), respectively. The reaction of this air-sensitive band with iodomethane is analogous to a similar reaction between $(\eta^5\text{-}C_5H_5)_2W(C_6H_5)(H)$ [derived from oxidative addition of C_6H_6 to $(C_5H_5)_2W$] and iodomethane to produce $(\eta^5\text{-}C_5H_5)_2W(C_6H_5)I$,[2] a process which probably proceeds by loss of CH_4.[27]



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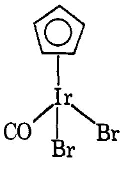

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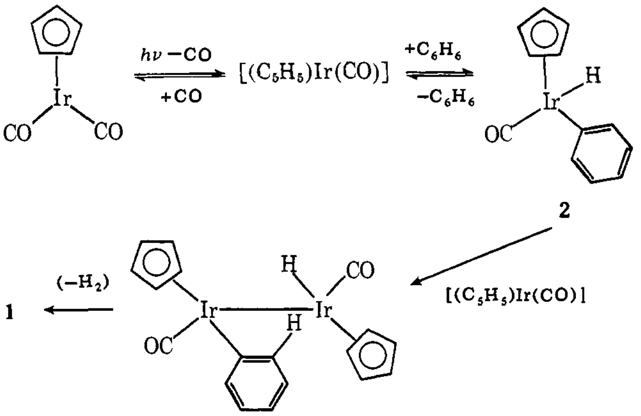
When a portion of the freshly chromatographed air-sensitive band was allowed to stand for several days at room temperature under nitrogen, the solution darkened considerably. Subsequent chromatography of the solution produced a moderate yield of a yellow solid which was shown to be **1** by comparisons with an authentic sample. Since **1** could not be detected in the freshly chromatographed air-sensitive band, it must be derived from this band by a thermal decomposition process.

In order to determine if the reaction between $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ and benzene could be thermally initiated, a sample of $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ in benzene (same concentration as in the photochemically induced reactions) was refluxed for 23 h in the absence of light. $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ was recovered unchanged (80%), and no other organometallic products such as **1** or **2** could be detected.

A plausible reaction pathway leading to **1** and consistent with the above data can be outlined (Scheme I). Clearly, this photochemically induced reaction between $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ and benzene is a very complicated process, and other organometallic intermediates as well as other reaction pathways can be envisioned.[28] Our investigations relating to this and other examples of photochemically induced activation of C–H bonds by transition metals are therefore continuing.

Scheme I



Experimental Section

All reactions were conducted under a nitrogen atmosphere. The nitrogen was dried with P_2O_5 and H_2SO_4, and trace oxygen was removed using BTS catalyst (BASF). Benzene and hexane were dried over calcium hydride and freshly distilled under argon. Column chromatography unless otherwise specified was carried out under nitrogen using Ventron-Alfa neutral grade alumina which had been deactivated with 5% water and degassed. ^{1}H NMR spectra were taken on either a Varian A-60 or a Perkin-Elmer R-12A spectrometer, while IR spectra were recorded on a Beckman IR-10 unit and were calibrated vs. polystyrene. Mass spectra were recorded on a Perkin-Elmer Hitachi RMU 6L instrument. Melting points were obtained in sealed tubes under nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. $(\eta^5\text{-}C_5H_5)Ir(CO)_2$ was prepared according to a literature procedure.[29]

Photolysis of η5-Cyclopentadienyldicarbonyliridium in Benzene. A solution of η^5-cyclopentadienyldicarbonyliridium (1.00 g, 3.2 mmol) and 300 mL of benzene was added to a quartz Schlenk tube under nitrogen. The Schlenk tube was placed in a large water bath and, while nitrogen was slowly bubbled through the solution with magnetic stirring, the reaction solution was irradiated with a Hanovia lamp (450 W, Vycor filter) for 3.7 h.

The solution was then reduced in volume under reduced pressure to ca. 50 mL, 5 g of alumina added, and the solvent removed in vacuo. This coated alumina was added to an alumina column (2 × 50 cm) which had been packed dry under nitrogen. Elution of the column with hexane brought down a yellow band which upon solvent removal gave 0.140 g (14% recovery) of η^5-cyclopentadienyldicarbonyliridium.

Subsequent elution with 3:1 hexane–benzene produced a pale-yellow, thermally air sensitive band which was collected under nitrogen. See following experiments and the Results and Discussion section for characterization of this band.

Table V. Experimental Details of the X-Ray Diffraction Study of $(\eta^5\text{-}C_5H_5)_2(CO)_2Ir_2(C_6H_4)$

A. Crystal Parameters at Ambient Temperature

Derived standard unit cell	Cell used in refinement
$a = 9.734$ Å	$a = 9.734\ (4)$ Å
$b = 9.468$ Å	$b = 9.468\ (4)$ Å
$c = 20.354$ Å	$c = 17.224\ (7)$ Å
$\beta = 122.62°$	$\beta = 94.20\ (4)°$
Space group $P2_1/c$ [C_{2h};^{5} no. 14]	Space group $P2_1/n$[a]

Data for both cells
$V = 1583.2\ (8)\ A^3$
$Z = 4$
Mol wt 646.71
ρ(calcd) = 2.714 g cm^{-3}
ρ(obsd)[b] = 2.7 (1) g cm^{-3}

B. Measurement of Intensity Data

Radiation: Mo Kα (Zr filter) $\lambda_{K\alpha 1} = 0.70926$ Å $\lambda_{K\alpha 2} = 0.7135$ Å
Attenuator: nickel foil. Used for reflections exceeding 50 000 counts—filter factor (FF) = 4.63 (5).
Take-off angle: 6.00 (5)°
Detector aperture: 2 mm diameter
Crystal-detector aperture distance: 17.3 cm
Incident beam collimator: 0.8 mm
Source-crystal distance: 21.7 cm
Crystal orientation: Aligned approximately along [100]
Reflections measured: 2083 in the region $+h, +k, \pm l$ with $2° \leq 2\theta \leq 52°$
Scan type: θ–2θ
Scan speed: variable from 4°/min to 0.61°/min. Actual value determined from a preset intensity maximum and a prescan for each reflection.
Scan range: $\Delta(2\theta) = (0.8 + 0.5 \tan \theta)°$ centered about the average peak position.
Background measurement: stationary crystal, stationary counter; one quarter scan time at beginning and end of 2θ scan
Standard reflections: intensity control ($10\bar{9}$); orientation control ($51\bar{9}$, $40\bar{8}$, $22\bar{8}$) measured every 50 reflections. No significant deviation from average was observed.

C. Treatment of Intensity Data

Conversion to I and $\sigma(I)$:
$I = [P - 2(B_1 + B_2)](FF/n_s)$
P = total count, B = background
$n_s = 20.1166/\text{scan speed}$
$\sigma(I) = [(P + 4(B_1 + B_2)(FF^2/n_s) + (CI)^2]^{1/2}$
Absorption correction:
$\mu = 170.0\ \text{cm}^{-1}$
Grid $8 \times 8 \times 12$
Max and min transmission factors 0.154 and 0.0246

D. Agreement Indices of Least-Squares Refinement

k (scale factor)	0.2459 (5)
g (isotropic extinction coefficient	$2.13\ (9) \times 10^3$
n (number of variables)	200
m (number of observations)	2083
m/n (overdetermination ratio)	10.4
$S = [\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$	0.651
$R = (\Sigma\lvert F_o - F_c\rvert/\Sigma\lvert F_o\rvert)$	0.041
$R_w = (\Sigma w\lvert F_o - F_c\rvert^2/\Sigma w F_o^2)^{1/2}$	0.036

[a] $P2_1/n$ is a nonstandard setting for space group $P2_1/c$ and has the equipoints $\pm(x, y, z)$ and $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. [b] Density as determined by the flotation method.

Further elution of the column with 1:3 hexane-benzene removed a yellow-brown band. After reducing the volume of solvent, the band was rechromatographed on a smaller alumina column (0.5 × 5 cm). Elution of this column with 1:4 hexane-benzene gave a yellow band which upon solvent removal and subsequent recrystallization from methylene chloride-heptane gave 0.015 g (2%) of bis(η^5-cyclopentadienyl)bis(carbonyl)-μ-(o-phenylene)-diiridium(*Ir-Ir*) (**1**), mp 225-227 °C.

Table VI. Atomic Coordinates for $(\eta^5\text{-}C_5H_5)_2(CO)_2Ir_2(C_6H_4)$[a]

Atom	x	y	z
Ir(1)	0.19130 (1)	0.12812 (1)	0.34300 (1)
Ir(2)	0.24081 (1)	0.25693 (1)	0.48321 (1)
C(1)	0.0693 (4)	0.0583 (4)	0.2339 (2)
C(2)	0.1482 (4)	0.1758 (4)	0.2180 (2)
C(3)	0.1059 (3)	0.2938 (3)	0.2597 (2)
C(4)	−0.0063 (3)	0.2449 (5)	0.3031 (2)
C(5)	−0.0254 (4)	0.1021 (5)	0.2856 (2)
C(6)	0.3047 (5)	0.0896 (4)	0.5704 (2)
C(7)	0.1656 (5)	0.0807 (4)	0.5595 (2)
C(8)	0.1057 (4)	0.2045 (5)	0.5822 (2)
C(9)	0.2143 (6)	0.2955 (4)	0.6092 (2)
C(10)	0.3400 (5)	0.2272 (5)	0.6030 (2)
C(11)	0.4136 (3)	0.2665 (3)	0.4227 (1)
C(12)	0.3923 (2)	0.1925 (2)	0.3534 (1)
C(13)	0.4947 (3)	0.1819 (3)	0.3034 (2)
C(14)	0.6206 (3)	0.2449 (4)	0.3222 (2)
C(15)	0.6467 (3)	0.3117 (3)	0.3918 (2)
C(16)	0.5411 (3)	0.3257 (3)	0.4420 (2)
C(17)	0.2449 (3)	−0.0325 (3)	0.3944 (2)
C(18)	0.1762 (3)	0.4167 (3)	0.4357 (2)
O(1)	0.2763 (3)	−0.1355 (3)	0.4260 (1)
O(2)	0.1386 (3)	0.5219 (2)	0.4083 (1)

[a] Standard deviations in parentheses.

Anal. Calcd for $C_{18}H_{14}Ir_2O_2$: C, 33.72; H, 2.23. Found: C, 33.42; H, 2.18.

NMR ($CDCl_3$) τ 4.40 (s, 10 H, η^5-C_5H_5), 2.6-2.9 (m, A_2B_2, 4 H, C_6H_4); IR (KBr) 1945 (s), 1415 (m), 1080-1055 (m), 1000 (m), 810 (s), 730 cm^{-1} (s); mass spectrum m/e (%) 644-648 (50, M^+), 616-620 (28, $M - CO^+$), 588-592 (100, $M - 2CO^+$), 321-323 (50, $(C_5H_5)_2Ir^+$), 78 (31, $C_6H_6^+$).

Continued elution of the original column with benzene yielded a small amount of a brown band whose ^1H NMR spectrum exhibited multiplet absorptions in both the aromatic region (τ 2.3-3.2) and cyclopentadienyl region (τ 4.6-5.3). The product has not been characterized further at the present time.

Reactions of the Air-Sensitive Band Obtained from the Photolysis of η^5-Cyclopentadienyldicarbonyliridium in Benzene. The pale yellow air-sensitive band which was eluted from the column (vide supra) and collected under nitrogen was divided into several portions.

To the first portion was added 1 mL of iodomethane and the mixture stirred under nitrogen for 24 h. The solvent was removed under reduced pressure to give a brown product which was washed with hexane and dried in vacuo.

Anal. Calcd for $C_{12}H_{10}IIrO$: C, 29.45; H, 2.06. Found: C, 29.17; H, 2.18.

NMR (acetone-d_6) τ 4.00 (s, 5 H, η^5-C_5H_5), 2.3-3.2 (m, 5 H, C_6H_5); IR (KBr) 3110 (w), 2025 (vs), 1260 (w), 1095 (m), 1055 (m), 1020 (m), 835 (w), 800 (w), 735 (m), 695 cm^{-1} (m); mass spectrum m/e (%) 488-490 (100, M^+), 460-462 (46, $M - CO^+$), 435 (m*), 411-413 (7, $M - C_6H_5^+$), 383-385 (88, $C_5H_5IrI^+$), 361-363 (57, $M - I^+$), 333-335 (94, $C_5H_5IrC_6H_5^+$), 284-286 (10, $C_5H_5IrCO^+$), 256-258 (31, $C_5H_5Ir^+$), 191-193 (5, Ir^+).

To a second portion was added bromine dropwise, and a precipitate immediately formed. The addition was continued until formation of the precipitate ceased. The yellow precipitate was filtered, washed with hexane, and dried in vacuo.

Anal. Calcd for $C_6H_5Br_2IrO$: C, 16.19; H, 1.13. Found: C, 16.55; H, 1.39.

NMR ($CDCl_3$) τ 3.99 (s, η^5-C_5H_5); IR (KBr) 3150 (w), 2065 (s), 855 cm^{-1} (w); mass spectrum m/e (%) 414-420 (19, $M - CO^+$), 382-386 (5, Ir_2^+), 349-355 (3, $IrBr_2^+$), 335-339 (100, $C_5H_5IrBr^+$), 270-274 (18, $IrBr^+$), 255-257 (62, $C_5H_4Ir^+$), 191-193 (9, Ir^+), 80-82 (100, HBr^+).

The third portion of the air-sensitive band was allowed to stand at room temperature for several days under nitrogen, during which time the solution darkened considerably in color. Subsequent chromatography on silica and elution with benzene-hexane mixtures yielded a yellow solid which was shown by ^1H NMR, IR, and TLC to be identical with bis(η^5-cyclopentadienyl)bis(carbonyl)-μ-(o-phenylene)-diiridium(*Ir-Ir*) (**1**).

Table VII. Thermal Parameters for $(\eta^5\text{-}C_5H_5)_2(CO)_2Ir_2(C_6H_4)$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir(1)	0.00510 (1)	0.00740 (2)	0.00171 (1)	−0.00031 (2)	0.00022 (1)	0.00011 (1)
Ir(2)	0.00672 (1)	0.00871 (2)	0.00170 (1)	−0.00061 (2)	0.00051 (1)	−0.00022 (1)
C(1)	0.0102 (5)	0.0126 (5)	0.0021 (1)	0.0009 (5)	−0.0012 (2)	−0.0006 (2)
C(2)	0.0085 (5)	0.0115 (5)	0.0018 (1)	0.0009 (5)	−0.0006 (2)	0.0014 (2)
C(3)	0.0054 (4)	0.0131 (5)	0.0027 (5)	0.0027 (1)	0.0003 (2)	0.0028 (2)
C(4)	0.0082 (4)	0.0179 (6)	0.0021 (1)	0.0029 (6)	−0.0002 (2)	0.0014 (3)
C(5)	0.0085 (5)	0.0173 (8)	0.0033 (2)	−0.0046 (5)	−0.015 (2)	0.0015 (3)
C(6)	0.0180 (7)	0.0145 (7)	0.0020 (1)	0.0048 (5)	0.0012 (2)	0.0027 (2)
C(7)	0.0154 (6)	0.0139 (6)	0.0030 (1)	−0.0034 (5)	0.0012 (2)	0.0014 (2)
C(8)	0.0118 (5)	0.0239 (8)	0.0030 (8)	0.0030 (6)	0.0031 (2)	0.0049 (3)
C(9)	0.0328 (10)	0.0132 (7)	0.0013 (1)	−0.0057 (8)	0.0039 (3)	−0.0012 (2)
C(10)	0.0146 (7)	0.0208 (9)	0.0026 (1)	−0.0075 (7)	−0.0013 (3)	0.0008 (3)
C(11)	0.0078 (4)	0.0109 (4)	0.0021 (1)	0.0024 (4)	0.0005 (2)	0.0003 (2)
C(12)	0.0035 (3)	0.0076 (4)	0.0027 (1)	0.0003 (3)	0.0004 (4)	0.0008 (2)
C(13)	0.0085 (5)	0.0113 (5)	0.0031 (1)	0.0020 (4)	0.0016 (2)	0.0009 (2)
C(14)	0.0066 (4)	0.0103 (4)	0.0042 (2)	0.0003 (5)	0.0016 (2)	0.0001 (3)
C(15)	0.0043 (4)	0.0116 (5)	0.0050 (2)	0.0012 (4)	0.0003 (2)	0.0008 (2)
C(16)	0.0070 (4)	0.0107 (5)	0.0035 (1)	0.0006 (4)	−0.0004 (2)	0.0008 (2)
C(17)	0.0104 (4)	0.0113 (5)	0.0024 (1)	−0.0005 (4)	−0.0001 (2)	0.0000 (2)
C(18)	0.0099 (5)	0.0115 (6)	0.0030 (1)	0.0017 (4)	0.0010 (2)	0.0001 (2)
O(1)	0.0251 (5)	0.0108 (3)	0.0039 (1)	0.0041 (4)	−0.0003 (2)	0.0014 (2)
O(2)	0.0204 (4)	0.0103 (3)	0.0047 (1)	0.0057 (4)	0.0017 (2)	0.0008 (2)

[a] Standard deviations in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-\Sigma_i\Sigma_j h_i h_j \beta_{ij}]$ with $i, j = 1, 2, 3$.

Continued elution with hexane-benzene removed a very small amount of a red material which was not further characterized.

Attempted Thermolysis of η^5-Cyclopentadienyldicarbonyliridium in Benzene. A solution of η^5-cyclopentadienyldicarbonyliridium (0.140 g, 0.45 mmol) in 42 mL of benzene was refluxed under nitrogen for 23 h in the absence of light. The solution was cooled and stirred at room temperature for an additional 39 h, and then was added to an alumina column (2 × 15 cm) packed dry under nitrogen. Elution of the column with hexane produced a yellow band which upon solvent removal yielded 0.110 g (80% recovery) of η^5-cyclopentadienyldicarbonyliridium. No other products could be detected.

Collection of X-Ray Diffraction Data. The complex crystallizes in the monoclinic system as well-formed diamond-shaped platelets with the forms $(10\bar{1}, \bar{1}01)$ being predominant. Photographic studies using Weissenberg and precession methods showed $2/m$ Laue symmetry and indicated the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. These absences are consistent with space group $P2_1/n$, an alternative setting for $P2_1/c$. Final lattice parameters determined from a least-squares refinement of the angular settings for 15 accurately centered reflections on an Enraf-Nonius CAD-4 diffractometer are given in Table V, along with details of experimental conditions, data collection, and treatment of intensity data.

A well-formed crystal, aligned approximately along the [100] direction, was used for data collection. The crystal dimensions were measured and the faces indexed and absorption corrections were applied to the intensity data. The 18 boundary planes and their distances from an origin point within the crystal are as follows: $\{001\}$, 0.171 mm; $\{011\}$, 0.126 mm; $(111, 1\bar{1}1, \bar{1}1\bar{1}, \bar{1}\bar{1}\bar{1})$, 0.141 mm; $(\bar{1}11, 11\bar{1}, 1\bar{1}\bar{1}, \bar{1}\bar{1}1)$, 0.136 mm; $(10\bar{1}, \bar{1}01)$, 0.058 mm; $(\bar{1}0\bar{1}, 101)$, 0.135 mm. Corrections were also applied for Lorentz and polarization effects.

Structure Solution and Refinement. Computations were carried out on a CDC 6600 computer using local modifications of Zalkin's FORDAP Fourier program, Prewitts SFLS-5 full-matrix least-squares routine, and various locally written programs. Scattering factors for all nonhydrogen atoms were taken from the tabulation by Cromer and Waber.[30] The hydrogen atom scattering factor used was that tabulated by Stewart.[31] The agreement factors are defined in Table I with the weights being evaluated as $w^{1/2} = 2LpF_o/\sigma(I)$. Coordinates for the two iridium atoms were obtained from examination of a three-dimensional Patterson function. Two cycles of isotropic unit weight refinement gave $R = 0.131$ and $R_w = 0.144$. At this stage of refinement a difference electron density map was obtained and found to reveal the positions for the 18 carbon and 2 oxygen atoms. Coordination of a six-membered ring to the two iridium atoms was readily apparent at this stage and so resolved the question of the stoichiometry of the molecule. Subsequent anisotropic variable weight refinement of all the nonhydrogen atoms led to $R = 0.055$ and $R_w = 0.050$. Hydrogen atoms were included as a fixed contribution using a C–H bond distance of 1.0 Å and assigned temperature factors equal to that of the carbon atom to which they were attached. A correction for isotropic secondary extinction in the framework of the Zachariasen[32] theory was also applied, the worst extinction prior to refinement being $(F_o)^2/(F_c)^2 = 0.67$. The final value for g indicated a particle radius of 0.15 μ or alternatively a mosaic spread half-width of 27 s. The final least-squares agreement indices based on all 2083 independent observations are displayed in Table V, while the final positional and thermal parameters are listed in Tables VI and VII, respectively. In the final cycle of least-squares refinement, all parameter shifts were less than 0.40 times their estimated standard deviation while the shifts in coordinates were less than 0.15 times their esd. A final difference Fourier map revealed no peaks larger than one-eighth the average value for a carbon peak; of these the largest were located near the iridium atoms. A compilation of observed and calculated structure factors is available (see paragraph at end of paper regarding supplementary material).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for financial support. M.D.R. is also grateful to the Alexander von Humboldt-Stiftung, Bonn/Bad Godesberg, Germany, for a fellowship.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Chiral Metal Complexes. 4.[1] Resolution of Racemic Tertiary Phosphines with Chiral Palladium(II) Complexes. The Chemistry of Diastereomeric Phosphine Pd(II) Species in Solution, and the Absolute Configuration of [(*S*)-Isopropyl-*tert*-butylphenylphosphine]-[(*R*)-*N,N*-dimethyl-α-(2-naphthyl)-ethylamine-3*C,N*]chloropalladium(II) Determined by X-Ray Diffraction

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Abstract: Resolution of racemic tertiary phosphines of the types $PAr^1Ar^2Ar^3$ (**P^1***) and $PArR^1R^2$ (**P^2***) have been achieved with chloro-bridged chiral Pd(II) complexes, (+)-di-μ-chloro-bis[(*S*)-*N,N*-dimethyl-α-phenylethylamine-2*C,N*]dipalladium (**1**) ([(*S*)-**Pd^1**]$_2$), and (−)-di-μ-chloro-bis[(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine-3*C,N*]dipalladium (**2**) ([(*R*)-**Pd^2**]$_2$), or with (+)-*cis*-dichlorobis[(*S*)-*sec*-butyl isocyanide]palladium (**3**) by virtue of the solubility difference between diasteromeric monophosphine compounds, [(*S*)-**Pd^1**-**P^1***], [(*R*)-**Pd^2**-**P^2***], or (RNC)(**P^1***)PdCl$_2$. Racemic phospholene, $PhPCH{=}C(Me)CH_2CH_2$ (**P^3***), was resolved via the bisphospholene complex, [(*R*)-**Pd^2**-(**P^3***)$_2$]. Addition of the achiral diphos, $Ph_2PCH_2CH_2PPh_2$, caused the preferential crystallization of one diastereomeric complex leaving one enantiomeric phospholene ligand in solution. Chiral tertiary phosphines thus obtained are (optical purity and resolving agent) PPh(*t*-Bu)Me (77.8%, **2**); PPh(*t*-Bu)(*i*-Pr) (~100%, **2**), $PhPCH{=}C(Me)CH_2CH_2$ (43.6%, **2**), PPh(α-Naph)-(*p*-PhC_6H_4) (—, **3**), PPh(α-Naph)(*p*-$MeOC_6H_4$) (—, **3**), P(α-Naph)Ph(*o*-MeC_6H_4) (—, **1**), and PPh(α-Naph)(*p*-$EtOC_6H_4$) (—, **1**). The molecular structure and absolute configuration of [(*S*)-isopropyl-*tert*-butylphenylphosphine][(*R*)-*N,N*-dimethyl-α-(2-naphthyl)ethylamine-3*C,N*]chloropalladium(II) has been determined by single-crystal x-ray diffraction methods. The compound crystallizes in the monoclinic space group $C_2{}^2$-$P2_1$ with two molecules in the unit cell of dimensions $a = 10.409$ (4) Å, $b = 10.094$ (4) Å, $c = 13.151$ (5) Å, $\beta = 109.38$ (2)°, and $V = 1303.5$ Å^3; $\rho_{\text{calcd}} = 1.397$ and $\rho_{\text{obsd}} = 1.39$ g cm^{-3}. The full-matrix least-squares refinement of the structure resulted in a final agreement index of 0.037 for the 3756 independent data for which $F_o{}^2 > 3\sigma(F_o{}^2)$. The palladium complex has a distorted square-planar geometry. The tertiary phosphine is coordinated trans to the amine nitrogen atom while the chloro ligand (Pd–Cl = 2.404 (2) Å) is opposite the ortho-metalated naphthyl ring (Pd–C = 2.049 (2) Å). The Pd–P and Pd–N bond distances are 2.286 (2) and 2.167 (4) Å, respectively. The absolute configuration of the coordinated tertiary phosphine is *S*, thus confirming the predicted configuration based upon stereochemical correlations.

In the last decade catalytic asymmetric syntheses of various types have been achieved with transition metal catalysts containing chiral phosphines.[3] The importance of a chiral center at the phosphorus atom was recognized for some instances of catalytic asymmetric hydrogenation[4] and alkylation.[5] Tedious steps are required to obtain phosphines with a chiral phosphorus atom.[6-11] Previously,[12] we have briefly reported the use of a chiral chelate palladium complex **1** for optical resolution of various triarylphosphines. We have found that **1** is not effective for resolution of tertiary phosphines other than triarylphosphines. Fortunately two other palladium complexes (**2, 3**) were found to be effective for resolution of tertiary phosphines. The efficiency of each compound, however, varies depending upon the type of phosphines. Therefore, we are interested in elucidating factors determining the resolution efficiency. In this paper we report some details of the