74977-98-3; **13**, 74978-00-0; **14**, 74978-02-2; **15**, 74978-04-4; **16**, 74987-45-4; **17**, 74977-75-6; **18**, 74977-77-8; **19**, 74977-79-0; $[Rh_2(CO)_2Cl(DAM)_2]B(C_6H_5)_4$, 70561-97-6; $[Rh_2(CO)_2Cl(DPM)_2]B(C_6H_5)_4$, 67202-35-1; $[Rh_2L_4(DPM)_2](B(C_6H_5)_4)_2$, 74977-80-3; $[IrCl(c\text{-}C_8H_{14})_2]_2$, 12112-67-3; $[Ir_2(CO)_4Cl(DAM)_2]BF_4$, 75023-45-9; $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, 67235-83-0; $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DAM)_2]B(C_6H_5)_4$, 70561-95-4; $[Rh_2(CO)_2(\mu\text{-}SO_2)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, 68080-76-2; $[Ir_2(CO)_3Cl(DPM)_2]B(C_6H_5)_4$, 74977-82-5; $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]PF_6$, 74977-83-6; $[Rh_2(CO)(L)(\mu\text{-}Cl)(DPM)_2]B(C_6H_5)_4$, 74977-85-8.

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Metallacyclic Complexes of Iridium

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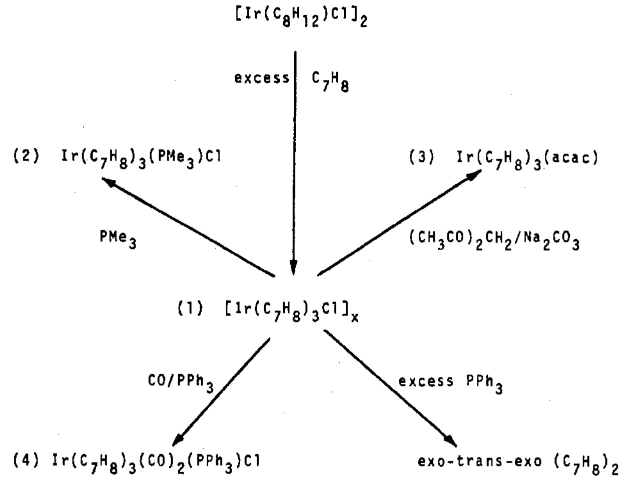
The reaction of norbornadiene with $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ or $[Ir(cyclooctene)_2Cl]_2$ yields a product containing three norbornadiene units, $[Ir(C_7H_8)_3Cl]_x$. Treatment of this product with PMe_3 or acetylacetone yields species containing two of these norbornadiene units half-linked together with exo-trans-exo stereochemistry in a five-membered metallacycle, as confirmed by a single-crystal X-ray diffraction study on the latter, $Ir(C_7H_8)_3(acac)$, space group $P\bar{1}$ (C_i^1, No. 2), $a = 9.239$ (2) Å, $b = 14.267$ (3) Å, $c = 9.638$ (2) Å, $\alpha = 111.95$ (1)°, $\beta = 65.77$ (1)°, $\gamma = 106.70$ (1)°, and $Z = 2$. Treatment of $[Ir(C_7H_8)_3Cl]_x$ with CO and then PPh_3 yields the compound $Ir(C_7H_8)_3(CO)_2(PPh_3)Cl$, believed to contain a six-membered metallacycle comprising two norbornadiene units, linked as in the five-membered case, and an inserted CO group. Degradation of $[Ir(C_7H_8)_3Cl]_x$ with excess PPh_3 leads to the reductive elimination of exo-trans-exo norbornadiene dimer. A compound $Ir(C_7H_8)_3(PPhMe_2)Cl$ is obtained on treatment of $[Ir(C_3H_8)_3]_x$ with $PPhMe_2$. This compound is converted, with excess CO in solution, to $Ir(C_7H_8)_3(CO)_2(PPhMe_2)Cl$, a white compound, which on standing in solution yields a yellow compound with the same empirical formula. This latter compound has been shown crystallographically to contain an eight-membered ring containing iridium linked to an acyl carbonyl group and three norbornadiene residues, the first two joined as in $Ir(C_7H_8)_3(acac)$ and the second joined to the third with exo-cis-endo stereochemistry. For $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl\cdot CH_2Cl_2$, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 9.610$ (7) Å, $b = 30.81$ (2) Å, $c = 10.248$ (7) Å, $\beta = 103.52$ (3)°, and $Z = 4$. The coordination at iridium is square pyramidal with the acyl CO group in the apical position and the CO group trans to Cl.

Introduction

Metallacycles have gained acceptance recently as probable intermediates in a variety of metal-catalyzed processes. In particular, they have been postulated in olefin reactions such as dimerization, cyclic ketone formation, and metathesis.[2-11] Separately, the isolation of metallacyclic compounds from reactions involving unsaturated precursors has been achieved in several cases, i.e., with Ni,[12] Pt,[13] Fe,[14] Co,[15] Ir,[16,17] and Rh.[18] Invariably the unsaturated organic precursor is strained, as in the case of cyclopropenes or norbornadienes,[8,12] or particularly reactive, as in the case of acetylenes,[13,14] allenes,[17,18] or butadienes.[12] Very recently, however, the formation of a metallacyclopentane derivative from simple olefins has been reported.[7,8] The synthesis of saturated metallacycles by other routes, with a view to investigating their reactivity as model intermediates, has also been the subject of several recent studies.[19,20]

Scheme I



We report here the coupling of norbornadiene on iridium(I) to form metallacyclic products containing two linked norbornadiene molecules. A further sequence of reactions leading to complexes containing three linked norbornadiene moieties is also described. The structure of these products including

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(1) (a) Harvard University. (b) Concordia University. (c) Université Louis Pasteur.

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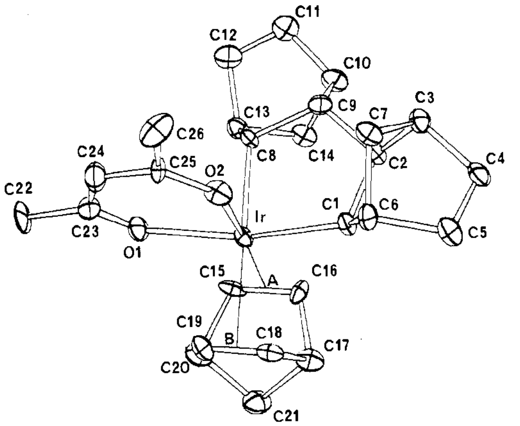


Figure 1. Molecular structure of $Ir(C_7H_8)_3(acac)$.

two X-ray determinations is discussed.

Results and Discussion

When $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ (or $[Ir(cyclooctene)_2Cl]_2$) is reacted with excess norbornadiene in acetone at room temperature, 1,5-cyclooctadiene (or cyclooctene) is displaced, and a microcrystalline compound **1** is produced with an empirical formula $Ir(C_7H_8)_3Cl$. **1** is not readily soluble, and its structure could not be determined by solution methods but it is probably not monomeric. However it undergoes a series of reactions shown in Scheme I. The more soluble PMe_3 adduct **2** was prepared by refluxing **1** with excess PMe_3 in CH_2Cl_2. Similarly **3**, $Ir(C_7H_8)_3(acac)$, was prepared by reaction of 2,4-pentanedione and Na_2CO_3 in acetone. Since conventional modes of chelation for norbornadiene and acac ligands in **1** and **2** would result in unusual coordination numbers for Ir, a determination of the molecular structure of **3** was carried out by an X-ray diffraction study, the result of which is shown in Figure 1. Details of the structure are presented later, but we note the important structural features here.

The iridium atom is essentially in an octahedral environment, with a norbornadiene and the acetylacetonate ligand chelating conventionally. The remaining two norbornadienes and the iridium atom form a saturated five-membered metallacycle, in which the two remaining norbornadiene molecules are half-coupled in an exo-trans-exo stereochemistry. Compounds **1** and **2** appear to be of analogous structure, the infrared spectra showing similarities in the 1300–1400-cm^{-1} region (aside from PMe_3 or acac modes) and the ^1H NMR spectrum of **2** resembling that of **3**. For example, the uncoordinated olefin resonances at τ 3.62 (1 H), 3.98 (1 H), and 4.09 (2 H) of **2** are found at τ 3.68 (1 H), 3.98 (1 H), and 4.11 (2 H) for **3**. Further NMR assignments are presented in the Experimental Section.

The yellow crystalline compound **4** was isolated from the treatment of **1** in CH_2Cl_2 with CO, followed by addition of 1 mol of PPh_3. The ^1H NMR spectrum shows the presence of the uncoordinated vinyl groups, and the infrared spectrum shows the presence of both acyl (ν_{CO} 1695 cm^{-1}) and terminal carbonyl (ν_{CO} 2020 cm^{-1}) groups. Elemental analysis and molecular weight data (osmometrically in $CHCl_3$ solution) indicate the five-coordinate structure shown in Figure 2, which results from the insertion of CO into the iridiacyle.

The mass spectral data of these complexes are of interest. Complex **1** was thermally degraded in the spectrometer and showed no parent peak but peaks corresponding to $[Ir(C_7H_8)Cl]_2^+$, $C_{14}H_{16}^+$, $C_7H_8^+$, $C_5H_6^+$ (relative abundances 4.6, 42.2, 100, 92.2). Similar observations were found with **2**. Complex **3**, however, showed a parent peak, but significantly, no norbornadiene dimer ion was detected. Peaks that correspond to products resulting from two stepwise retro-Diels–Alder reactions (i.e., $Ir(C_7H_8)(acac)(C_9H_{10})^+$ and $Ir(C_7H_8)(acac)(C_4H_4)^+$) were observed. Further details are found in the Experimental Section.

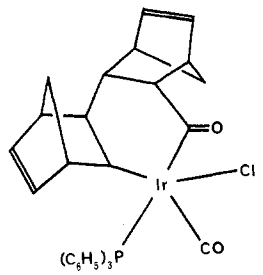
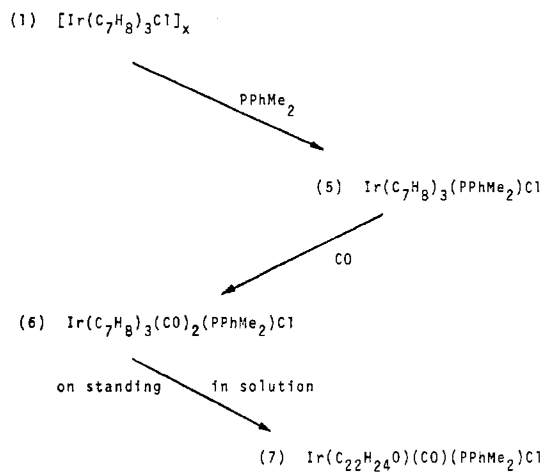


Figure 2. Presumed structure of $Ir(C_7H_8)_3(CO)_2(PPh_3)Cl$.

Scheme II



The appearance of dimeric norbornadiene products from **1** and **2** seemed to indicate that the dimerization of olefins via a metallacyclic intermediate was indeed a feasible catalytic pathway. Hence we found that on refluxing **1** with excess PPh_3 in $CHCl_3$ for 1 h, reductive elimination of norbornadiene dimer could be induced. After separation, the ^1H spectrum of the volatile organic products (25–50% yield) was identical with that of the exo-trans-exo dimer.[21] The reaction, however, could not be made genuinely catalytic (more than one turnover) despite varying conditions, no doubt because of the stability of the iridium–triphenylphosphine product formed. It might be noted however that analogous rhodium complexes are active catalysts for norbornadiene dimerization.[22] In view of these observations we have sought catalysts for the dimerization of simple olefins via a metallacyclic route. Catalysts which very effectively dimerize olefins in this manner have been discovered recently by Schrock and co-workers.[7]

In view of the stability of the PMe_3 adduct **2** (vis-à-vis PPh_3), the reaction of **1** with PMe_2Ph was investigated (Scheme II). When **1** was refluxed in $CHCl_3$ with 1 mol of PMe_2Ph, an insoluble salmon-colored product **5** precipitated, which is analyzed as $Ir(C_7H_8)_3(PMe_2Ph)Cl\cdot 0.25CHCl_3$. The mass spectrum of **5** shows the highest *m/e* peak at 642, corresponding to the species $Ir(C_7H_8)_3(PMe_2Ph)Cl^+$, which apparently undergoes the stepwise loss of three C_5H_6 groups, suggesting a possible trimeric formulation. Further the infrared spectrum of **5** bears no resemblance to that of **1** or **2**. The insolubility of **5** precluded further spectroscopic study, but it was readily converted into the more soluble carbonyl complex **6**, $Ir(C_7H_8)_3(CO)_2(PMe_2Ph)Cl$, by treatment of a suspension of **5** with CO. The infrared spectrum of this white microcrystalline complex in CH_2Cl_2 solution shows two sharp

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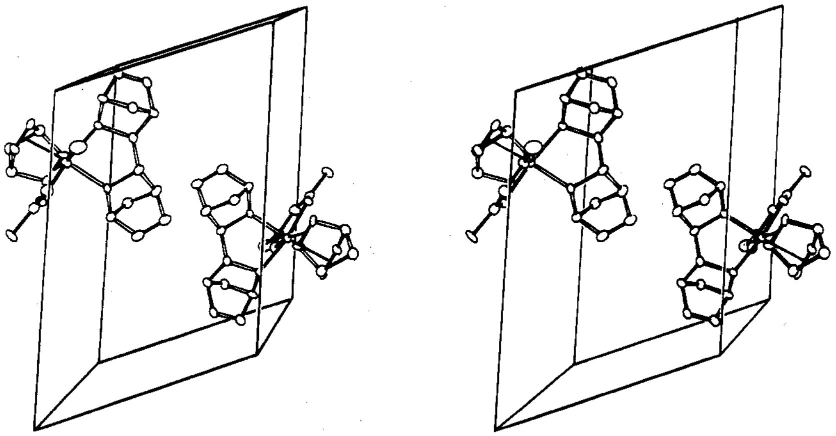

Figure 3. Crystal packing of $Ir(C_7H_8)_3(acac)$.

terminal-carbonyl bands at 2065 and 2010 cm^{-1}. On standing in $CHCl_3$ solution over several hours, **6** isomerizes to the yellow complex **7**, which exhibits one terminal (2010 cm^{-1}) and one acyl CO (1680 cm^{-1}) infrared absorption band. Mass spectra of **6** and **7** are very similar, showing the highest peak for $Ir(C_7H_8)_3(CO)_2(PMe_2Ph)Cl^+$, and the ^1H NMR spectra show the presence of uncoordinated vinyl groups at τ 3.95 (for **6**) and 3.90 (for **7**), which integrate for three double bonds per phosphine ligand in the molecule. (See Experimental Section for further mass spectral and NMR data.)

Compound **7** has been the subject of a single-crystal X-ray diffraction study. The molecule structure is shown in Figure 3. Although details of the structure are given later, the most significant feature of this molecule is the presence of an eight-membered metallacycle comprising an iridium atom, one carbonyl group, and three coupled norbornadiene moieties. The acyl group is linked in the exo position on norbornadiene A, which is further coupled to norbornadiene B in exo-trans-exo fashion. These two dienes appear to be those already coupled in compound **3**. However the third norbornadiene C, which was bound as a chelate in **3**, has now inserted into the original metallacycle and is bound to B in exo-cis-endo fashion. This implies that *insertion of the coordinated double bond of C into the metal-carbon σ bond of the metallacycle has occurred by cis addition.* Such a mechanism has been proposed in many catalytic processes involving olefin dimerization or polymerization. Two further observations can be made. It is clear that catalysts for the trimerization of olefins via seven-membered metallacycles are indeed feasible, for example, the trimerization of ethylene to cyclohexane. Indeed, although we have not liberated the cycloheptanone derivative from **6** or **7**, the mass spectra of both these species show peaks at *m/e* 304 of moderate relative intensity, which correspond to those of the ketone. Secondly, the five-coordinate iridium(III) complex **7** (d^6 formal configuration) shows a relatively undistorted octahedral geometry with one site vacant. Difference syntheses show no significant residual electron density in the region trans to Cl. The remote possibility of a hydrogen atom occupying this site is negated by IR and NMR measurements as well as the diamagnetism of **7**. Geometry calculations with dummy atoms in the sixth site and diagrams projected along the missing bond vector suggest that this site is sterically shielded (but *not* occupied) by hydrogens on the methyl groups and on the norbornene residue C. This would discourage this coordinatively unsaturated complex to dimerize or coordinate a sixth ligand, e.g., CO. Indeed the nondistortion toward either a trigonal bipyramid or a more distorted square pyramid is intriguing but has been predicted theoretically by Hoffmann[23] and observed by Turner[24] and co-workers for another d^6 species (i.e., $Cr(CO)_5$) in matrix isolation experiments.

Crystal Structure of 3, $Ir(C_7H_8)_3(acac)$. The molecular structure and atom labeling is shown in Figure 1, and Table I contains a listing of principal bond lengths and angles. There are no unusually close contacts between molecules: Figure 3 shows the crystal packing.

By placement of dummy atoms A and B at the centers of the coordinate C_7H_8 double bonds, C(15)–C(16) and C(18)–C(19), respectively, the molecule can be treated as an octahedral tris-chelate complex of iridium. The acetylacetonate ligand is essentially planar; the distances from iridium to O(1) (trans to Cl) and to O(2) (trans to A) are 2.189 (9) and 2.067 (8) Å. Given that alkyl groups seem to show a much stronger σ-trans influence than olefins, this significant difference is not unexpected. A parallel situation exists in $Ir(allene)_3(acac)(py)$[25] where the analogous distances are 2.13 and 2.08 Å.

The five-membered metallacycle is nonplanar, being folded along the line C(1),C(9) such that C(2) is displaced 0.24 Å out of the plane of the other four atoms toward A. The distance from C(1) [trans to O(1)] to the iridium atom is 2.11 (1) Å, while C(8) (trans to B) is 2.07 (1) Å from the iridium. This small difference presumably reflects the similar and weak σ-trans influences of the oxygen and olefin ligands. In $Ir(allene)_3(acac)(py)$[25] the iridiacycle is twisted about the local twofold axis and the Ir–C distances are 2.11 and 2.07 Å (carbons trans to oxygen and nitrogen, respectively).

The bonding of the π-bonded norbornadiene to iridium is distorted slightly from local C_{2v} symmetry in two ways: the distance Ir–B [A trans to C(8)] is 2.25 Å while Ir–A [trans to O(2)] is 2.01 Å, the difference being in the expected direction. Comparable bond lengths may be found in $Ir(SnCl_3)(C_7H_8)(PPhMe_2)_2$.[26] In the pseudo-trigonal-bipyramidal iridium(I) complex, the distance from the Ir to the pseudoaxial olefin midpoint is 2.245 (6) Å. The second distortion is a slight sideways slip of the norbornadiene away from the metallacyclic norbornadiene C(1)–C(7), so that individual Ir–C distances are 2.10 (1) and 2.31 (1) Å for C(15) and C(19), respectively, and 2.16 (1) and 2.36 (1) Å for C(16) and C(18). The origin of this distortion presumably lies with intramolecular steric effects.

The bites of the three chelating ligands are for the acetylacetonate 2.93 Å, for the norbornadiene (A–B) 2.45 Å, and for the incipient norbornadiene dimer 2.84 Å. The geometries of these ligands show no features deserving of special comment;

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Table I. Distances and Angles in $Ir(C_7H_8)_3(acac)^a$

Distances, Å			
Ir-O(1)	2.189 (9)	Ir-C(15)	2.10 (1)
Ir-O(2)	2.067 (8)	Ir-C(16)	2.16 (1)
Ir-C(1)	2.11 (1)	Ir-C(18)	2.36 (1)
Ir-C(8)	2.07 (1)	Ir-C(19)	2.31 (1)
C(1)-C(2)	1.60 (2)	C(8)-C(9)	1.58 (2)
C(2)-C(3)	1.56 (2)	C(9)-C(11)	1.10 (2)
C(3)-C(4)	1.53 (2)	C(10)-C(11)	1.53 (2)
C(4)-C(5)	1.33 (2)	C(11)-C(12)	1.36 (3)
C(5)-C(6)	1.56 (2)	C(12)-C(13)	1.54 (2)
C(1)-C(6)	1.56 (2)	C(8)-C(13)	1.57 (2)
C(6)-C(7)	1.54 (2)	C(13)-C(14)	1.55 (2)
C(3)-C(7)	1.57 (2)	C(10)-C(14)	1.55 (2)
C(2)-C(9)	1.55 (2)	C(1)···C(8)	2.84 (2)
C(15)-C(16)	1.42 (2)	O(1)-C(23)	1.30 (2)
C(16)-C(17)	1.53 (2)	O(2)-C(25)	1.26 (2)
C(17)-C(18)	1.60 (2)	C(22)-C(23)	1.48 (2)
C(18)-C(19)	1.34 (2)	C(23)-C(24)	1.40 (2)
C(19)-C(20)	1.57 (2)	C(24)-C(25)	1.40 (2)
C(20)-C(15)	1.58 (2)	C(25)-C(26)	1.49 (2)
C(20)-C(21)	1.56 (2)	O(1)···O(2)	2.89 (1)
C(17)-C(21)	1.60 (2)		

Angles, Deg			
O(1)-Ir-O(2)	85.5 (4)	C(1)-Ir-C(15)	114.0 (5)
O(1)-Ir-C(1)	167.9 (5)	C(1)-Ir-C(16)	75.2 (6)
O(1)-Ir-C(8)	85.7 (4)	C(1)-Ir-C(18)	80.4 (5)
O(1)-Ir-C(15)	76.1 (5)	C(1)-Ir-C(19)	113.6 (5)
O(1)-Ir-C(16)	115.1 (5)	C(8)-Ir-C(15)	102.4 (5)
O(1)-Ir-C(18)	109.4 (4)	C(8)-Ir-C(16)	104.5 (5)
O(1)-Ir-C(19)	76.2 (5)	C(8)-Ir-C(18)	163.6 (5)
O(2)-Ir-C(1)	85.5 (5)	C(8)-Ir-C(19)	160.1 (5)
O(2)-Ir-C(8)	85.5 (5)	C(15)-Ir-C(16)	39.0 (5)
O(2)-Ir-C(15)	159.3 (4)	C(15)-Ir-C(18)	76.2 (5)
O(2)-Ir-C(16)	157.3 (4)	C(15)-Ir-C(19)	65.6 (5)
O(2)-Ir-C(18)	101.6 (4)	C(16)-Ir-C(18)	63.9 (5)
O(2)-Ir-C(19)	101.0 (4)	C(16)-Ir-C(19)	76.6 (6)
C(1)-Ir-C(8)	85.5 (5)	C(18)-Ir-C(19)	33.2 (5)
Ir-C(1)-C(2)	111.7 (9)	Ir-C(8)-C(9)	113.7 (8)
Ir-C(1)-C(6)	118.0 (9)	Ir-C(8)-C(13)	118.4 (8)
C(2)-C(1)-C(6)	102 (1)	C(9)-C(8)-C(13)	102 (1)
C(1)-C(2)-C(3)	102 (1)	C(2)-C(9)-C(8)	114 (1)
C(1)-C(2)-C(9)	113 (1)	C(8)-C(9)-C(10)	103 (1)
C(3)-C(2)-C(9)	110 (1)	C(2)-C(9)-C(10)	111 (1)
C(2)-C(3)-C(4)	107 (1)	C(9)-C(10)-C(11)	104 (1)
C(2)-C(3)-C(7)	101 (1)	C(9)-C(10)-C(14)	100 (1)
C(4)-C(3)-C(7)	100 (1)	C(11)-C(10)-C(14)	101 (1)
C(3)-C(4)-C(5)	108 (1)	C(10)-C(11)-C(12)	107 (1)
C(4)-C(5)-C(6)	107 (1)	C(11)-C(12)-C(13)	107 (1)
C(1)-C(6)-C(5)	102 (1)	C(8)-C(13)-C(12)	104 (1)
C(1)-C(6)-C(7)	105 (1)	C(8)-C(13)-C(14)	102 (1)
C(5)-C(6)-C(7)	99 (1)	C(12)-C(13)-C(14)	100 (1)
C(3)-C(7)-C(6)	93 (1)	C(10)-C(14)-C(13)	95 (1)
Ir-O(1)-C(23)	127.1 (9)	C(23)-C(24)-C(25)	127 (2)
Ir-O(2)-C(25)	179.4 (9)	O(2)-C(25)-C(24)	127 (1)
O(1)-C(23)-C(22)	116 (1)	O(2)-C(25)-C(26)	114 (1)
O(1)-C(23)-C(24)	124 (1)	C(24)-C(25)-C(26)	118 (1)
C(22)-C(23)-C(24)	121 (2)	Ir-C(18)-C(19)	71.4 (8)
Ir-C(15)-C(16)	72.6 (8)	C(17)-C(18)-C(19)	107 (1)
Ir-C(15)-C(20)	101.2 (8)	Ir-C(19)-C(18)	75.3 (9)
C(16)-C(15)-C(20)	108 (1)	Ir-C(19)-C(20)	93.0 (9)
Ir-C(16)-C(15)	68.4 (7)	C(18)-C(19)-C(20)	109 (1)
Ir-C(16)-C(17)	103.1 (7)	C(15)-C(20)-C(19)	99 (1)
C(15)-C(16)-C(17)	106 (1)	C(15)-C(20)-C(21)	99 (1)
C(16)-C(17)-C(18)	100 (1)	C(19)-C(20)-C(21)	100 (1)
C(16)-C(17)-C(21)	102 (1)	C(17)-C(21)-C(20)	94 (1)
C(18)-C(17)-C(21)	98 (1)		
Ir-C(18)-C(17)	92.8 (8)		

[a] Estimated deviations are given in parentheses, right justified to the least significant digits of the preceding number.

the bond lengths and angles are all as expected.

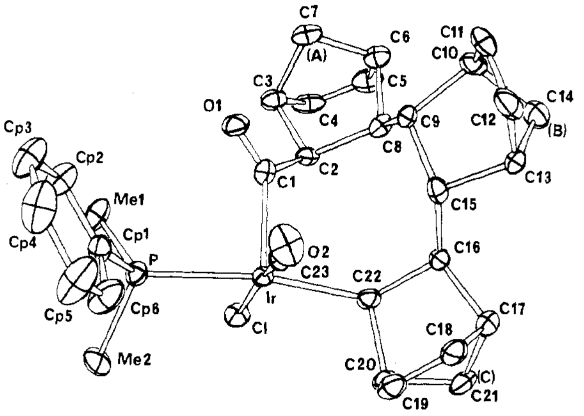

Figure 4. Molecular structure of $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl$.

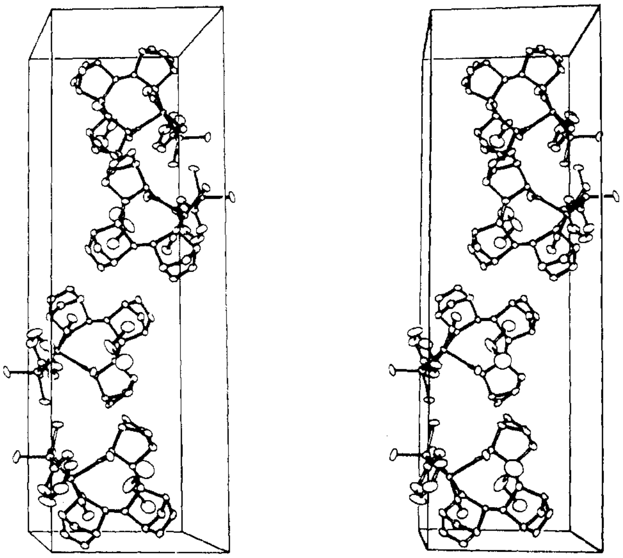

Figure 5. Crystal packing of $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl\cdot CH_2Cl_2$.

Molecular Structure of 7, $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl$. Figure 4 depicts the molecular structure and indicates the method of atom labeling. Figure 5 shows the packing of the four monomeric units of $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl$ and four CH_2Cl_2 molecules, which are separated by normal van der Waals contacts. Table II lists the bond lengths and angles.

The coordination geometry at the iridium atom is found to be the almost perfectly flat square pyramid predicted for a d^6 ion with this geometry.[23] The apical position is occupied by the acyl group with an Ir–Cl bond length of 1.97 (1) Å. This is quite short compared to previously observed bonds between iridium and sp^2-hybridized carbon atoms: 1.99 (1) and 2.10 (1) Å in $Ir(C_3Ph_3)(CO)(PPh_3)_2Cl$,[27] 1.983 (10) and 2.008 (9) Å in $(CO)_3Mn(\mu\text{-}PPh_2)(\mu\text{-}COCH_3)(\mu\text{-}COPh)Ir(\eta^5\text{-}C_5H_5)$,[28] and 2.05 (2) Å in $Ir(COOCH_3)(CO)(bpy)I_2$.[29]

The eight-membered iridiacycle adopts a boat conformation, presumably minimizing steric interactions between the norbornadiene residues. The Ir–C(22) bond, in the basal plane, has a length of 2.14 (1) Å, a little longer than the Ir–C bonds found in $Ir(C_7H_8)_3(acac)$ and comparable with those in a variety of other compounds.[30]

The Ir–P bond length of 2.392 (3) Å is somewhat longer than those found in other square-pyramidal complexes having phosphorus atoms mutually trans, where Ir–P distances range from 2.343 (3) to 2.377 (2) Å.[31] This lengthening can be

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Table II. Distances and Angles in $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl\cdot CH_2Cl_2$[a]

Distances, Å

Ir-P	2.392 (3)	C(5)-C(6)	1.51 (2)
Ir-Cl	2.368 (2)	C(6)-C(7)	1.50 (2)
Ir-C(1)	1.97 (1)	C(6)-C(8)	1.58 (2)
Ir-C(22)	2.14 (1)	C(8)-C(9)	1.55 (2)
Ir-C(23)	1.83 (1)	C(9)-C(10)	1.56 (2)
C(23)-O(2)	1.15 (1)	C(9)-C(15)	1.61 (2)
P-Me(1)	1.82 (1)	C(10)-C(11)	1.50 (2)
P-Me(2)	1.83 (1)	C(10)-C(14)	1.51 (2)
P-Cp(1)	1.77 (1)	C(11)-C(12)	1.29 (2)
Cp(1)-Cp(2)	1.40 (2)	C(12)-C(13)	1.49 (2)
Cp(1)-Cp(6)	1.34 (2)	C(13)-C(14)	1.53 (2)
Cp(2)-Cp(3)	1.40 (2)	C(13)-C(15)	1.54 (2)
Cp(3)-Cp(4)	1.32 (2)	C(15)-C(16)	1.55 (2)
Cp(5)-Cp(6)	1.37 (2)	C(16)-C(17)	1.54 (2)
C(1)-O(1)	1.22 (1)	C(16)-C(22)	1.58 (2)
C(1)-C(2)	1.54 (2)	C(17)-C(18)	1.53 (2)
C(2)-C(3)	1.55 (2)	C(17)-C(21)	1.53 (2)
C(2)-C(8)	1.57 (2)	C(18)-C(19)	1.31 (2)
C(3)-C(4)	1.52 (2)	C(19)-C(20)	1.52 (2)
C(3)-C(7)	1.53 (2)	C(20)-C(21)	1.54 (2)
C(4)-C(5)	1.33 (2)	C(20)-C(22)	1.60 (2)

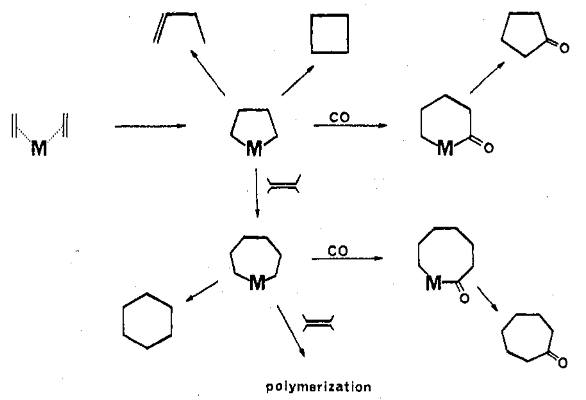
Angles, Deg

P-Ir-C(1)	84.5 (1)	C(1)-C(2)-C(3)	110 (1)
P-Ir-Cl	91.3 (3)	C(1)-C(2)-C(8)	114 (1)
P-Ir-C(22)	167.8 (4)	C(3)-C(2)-C(8)	103 (1)
P-Ir-C(23)	92.5 (4)	C(2)-C(3)-C(4)	104 (1)
Cl-Ir-C(1)	99.2 (3)	C(2)-C(3)-C(7)	101 (1)
Cl-Ir-C(22)	85.7 (3)	C(4)-C(3)-C(7)	99 (1)
Cl-Ir-C(23)	170.4 (4)	C(3)-C(4)-C(5)	108 (1)
Cl-Ir-C(22)	97.6 (5)	C(4)-C(5)-C(6)	107 (1)
Cl-Ir-C(22)	89.9 (5)	C(5)-C(6)-C(7)	101 (1)
C(22)-Ir-C(23)	96.0 (5)	C(5)-C(6)-C(8)	106 (1)
Ir-P-Me(1)	114.3 (5)	C(7)-C(6)-C(8)	99 (1)
Ir-P-Me(2)	112.5 (5)	C(3)-C(7)-C(6)	96 (1)
Ir-P-Cp(1)	114.8 (4)	C(2)-C(8)-C(6)	102 (1)
Me(1)-P-Me(2)	103.3 (7)	C(2)-C(8)-C(9)	117 (1)
Me(1)-P-Cp(1)	106.7 (6)	C(6)-C(8)-C(9)	115 (1)
Me(2)-P-Cp(1)	109.1 (6)	C(8)-C(9)-C(10)	116 (1)
P-Cp(1)-Cp(2)	123.0 (9)	C(8)-C(9)-C(15)	116 (1)
P-Cp(1)-Cp(6)	121 (1)	C(10)-C(9)-C(15)	100 (1)
Cp(2)-Cp(1)-Cp(6)	116 (1)	C(9)-C(10)-C(11)	108 (1)
Cp(1)-Cp(2)-Cp(3)	120 (1)	C(9)-C(10)-C(14)	104 (1)
Cp(2)-Cp(3)-Cp(4)	120 (1)	C(11)-C(10)-C(14)	102 (1)
Cp(3)-Cp(4)-Cp(5)	122 (1)	C(10)-C(11)-C(12)	107 (1)
Cp(4)-Cp(5)-Cp(6)	118 (1)	C(11)-C(12)-C(13)	106 (1)
Cp(1)-Cp(6)-Cp(5)	125 (1)	C(12)-C(13)-C(14)	104 (1)
Ir-C(1)-O(1)	123.9 (9)	C(12)-C(13)-C(15)	108 (1)
Ir-C(1)-C(2)	113.4 (8)	C(14)-C(13)-C(15)	104 (1)
O(1)-C(1)-C(2)	123 (1)	C(10)-C(14)-C(13)	89 (1)
C(9)-C(15)-C(13)	100 (1)	C(18)-C(19)-C(20)	108 (1)
C(9)-C(15)-C(16)	118 (1)	C(19)-C(20)-C(21)	101 (1)
C(13)-C(15)-C(16)	113 (1)	C(19)-C(20)-C(22)	106 (1)
C(15)-C(16)-C(17)	115 (1)	C(21)-C(20)-C(22)	99 (1)
C(15)-C(16)-C(22)	103 (1)	C(17)-C(21)-C(20)	94 (1)
C(17)-C(16)-C(22)	102 (1)	Ir-C(22)-C(16)	129.6 (8)
C(16)-C(17)-C(18)	106 (1)	Ir-C(22)-C(20)	107.4 (7)
C(16)-C(17)-C(21)	101 (1)	C(16)-C(22)-C(20)	102 (1)
C(18)-C(17)-C(21)	101 (1)	Ir-C(23)-O(2)	176 (1)
C(17)-C(18)-C(19)	108 (1)		

attributed to the influence of the Ir–alkyl bond trans to the phosphine ligand. The remaining bonds in the basal plane, iridium to carbonyl carbon [C(23)], 1.83(1) Å, and trans to this Ir–Cl, 2.368 (2) Å, are essentially the same as those in $IrCl_2(CF_2H)(CO)(PPh_3)_2$[32] [1.85, 2.375 (8) Å] and $(CF_2HCOC)(CO)(CF_2H)(PPh_3)_2Ir$ [1.84 (2), 2.393 (4) Å].[33]

The ligand atoms comprising the basal plane of the iridium coordination sphere are coplanar within a 3σ limit, and the Ir atom is situated 0.174 Å above this least-squares plane. The square pyramid in this complex is probably the "flattest" yet observed. The possibility of coordination of a sixth ligand to complete the octahedral coordination of the iridium was investigated by placing a dummy atom 2.0 Å from the iridium trans to the acyl carbon atom. For the observed conformation of the molecule, hydrogen atoms of the methyl group Me(2) and on norbornadiene (C) [C(19) and C(20)] would effectively block this site to all but the smallest of ligands. Dimerization via Cl bridging would be quite out of the question.

Scheme III



Conclusions

The specific reactions described in this paper do not of themselves form part of a catalytic cycle, but each probably has its place in similar known catalytic processes (see Scheme III): coordination of a pair of olefin monomers, metallacycle formation, followed by immediate reductive elimination of an olefin dimer, or carbonyl insertion into a metal–carbon σ bond and then reductive elimination to yield a cyclic ketone. Thus the well-known formation of cyclobutane and/or cyclopentanone derivatives[4] obtained from olefins and carbon monoxide with the use of transition-metal catalysts can be proposed to occur via a series of intermediates analogous to those identified in this paper. By comparison, alternative mechanisms involving concerted processes,[5] although conceptually interesting, appear at present to lack substantive evidence for their support. A further, most interesting aspect of this study is the transformation of **1** to **7** via **5** and **6**. The most important step is the insertion of a coordinated olefin into a metal–carbon bond with cis stereochemistry. This step has often been proposed in catalytic processes, e.g., the Cossee mechanism for polymerization of olefins,[34] but unambiguous examples are lacking. Although the reaction described here is a clear demonstration of such a process, we cannot distinguish between the classic Cossee insertion reaction and the recently suggested carbene mechanism.[35] It is noteworthy that the insertion of the olefin into a metallacycle leads to a seven-membered ring which potentially could serve as a model intermediate for trimerization of olefins. Further non-ring-opened polymers of norbornene could be produced via such a species[36] (Scheme III).

Experimental Section

Materials. All solvents and chemicals used were of reagent grade quality and were used without purification unless stated otherwise. Organic solvents were deoxygenated immediately prior to use either on a vacuum rack or by bubbling N_2 or Ar through them for ca. 5 min.

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Spectra. Infrared spectra were measured on a Perkin-Elmer 337 grating spectrophotometer and calibrated with a polystyrene film. ^{1}H NMR spectra were obtained on Varian A-60 and HA-100 instruments. Mass spectra were measured on an AEI-MS9 mass spectrometer.

Preparation of [Ir(1,5-cyclooctadiene)Cl]$_2$. This is a modification of the method of Winkhaus and Singer.[37] Hydrated iridium trichloride (55.16% Ir, Engelhard Industries), 5 g, 50 mL of hydroquinone, and 5 mL of 1,5-cyclooctadiene were heated under reflux with 180 mL of an ethanol/water (2:1) mixture, previously deoxygenated with a vigorous stream of nitrogen for $^1/_2$ h. After 4 h, about 100 mL of solvent was distilled from the reaction vessel, causing crystallization of a yellow-orange solid. After the mixture had cooled, the solid was filtered, washed thoroughly with cold methanol (3 × 10 mL), and dried in vacuo; yield 3.05 g (59%).

Compound 1, $[Ir(C_7H_8)_3Cl]_x$. [Ir(1,5-cyclooctadiene)Cl]$_2$ (1.00 g) was partially dissolved in 15 mL of deoxygenated acetone under N_2. Then 3 mL of norbornadiene, purified by column chromatography on activated alumina, was added and the mixture was stirred for 10 min. The yellow microcrystalline solid which had formed was filtered and washed three times with 10-mL portions of acetone and was dried under vacuum: yield >95%; mp 203 °C dec. Anal. Calcd for $Ir(C_7H_8)_3Cl$: C, 50.05; H, 4.77; Cl, 7.06. Found: C, 49.88; H, 4.77; Cl, 6.92. Mass spectra were obtained at 215 °C and the following showed principal peaks [*m/e* (relative intensity)]: 638 (4.6), $[Ir(C_7H_8)Cl]_2^+$; 184 (42.2), $C_{14}H_{16}^+$; 92 (100), $C_7H_8^+$; 66 (99.2), $C_5H_6^+$.

Compound 2, $Ir(C_7H_8)_3(PMe_3)Cl$. On a vacuum line, 0.4 mL of PMe_3 was condensed into a 50-mL round-bottom flask containing 0.314 g of compound **1**. The flask was removed from the vacuum line under N_2, and 15 mL of deoxygenated $CHCl_3$ was added. The mixture was then refluxed under N_2 for 1 h and cooled to room temperature. All the volatiles were then removed under vacuum. The residue was then extracted with pentane, and the insoluble material was placed under vacuum for 8 h to remove any remaining traces of PMe_3. The solid was dissolved in 20 mL of CH_2Cl_2, and 1 mL of EtOH was also added. On gentle evaporation, small white crystals were formed. These were filtered, washed in EtOH, and dried under vacuum; mp 185 °C. Anal. Calcd for $Ir(C_7H_8)_3(PMe_3)Cl$: C, 49.70; H, 5.70; Cl, 6.12; P, 5.35. Found: C, 49.62; H, 5.59; Cl, 6.53; P, 5.44. The mass spectrum obtained at 200 °C showed the following peaks [*m/e* (relative intensity)]: 638 (2.8), $[Ir(C_7H_8)Cl]_2^+$; 184 (16.8), $C_{14}H_{16}^+$; 76 (66.3), PMe_3^+; 66 (100), $C_5H_6^+$. The ^{1}H NMR spectrum showed the following peaks: τ 3.62 (1 H), 3.98 (1 H), 4.09 (2 H), uncoordinated vinyls; 5.36 (1 H), 5.62 (2 H), 6.07 (1 H), 6.30 (2 H), methine; 6.70 (1 H), 7.05–7.65 (5 H), coordinated vinyls, β-H-Ir; 8.24 (9 H, d, J_{P-H} = 9 Hz), P-CH_3; 8.00–9.40 (8 H, α-H-Ir), methylene.

Compound 3, $Ir(C_7H_8)_3(acac)$. Compound **1** (500 mg) and Na_2CO_3 (200 mg) were suspended in 20 mL of dried, deoxygenated acetone. Acetylacetone (9.20 mL) was then added, the system flushed with N_2, and the mixture refluxed for 1 h and then stirred at room temperature for 2.5 h more. Insoluble material (unreacted compound **1**) was filtered, and 10 mL of EtOH was added to the filtrate. The solution volume was reduced under N_2, and orange crystals formed on standing. These were vacuum dried: yield 57%; mp 189 °C. Mass spectra were obtained at 200 °C and showed the following peaks [*m/e* (relative intensity)]: 568 (48.2), $Ir(C_7H_8)_3(acac)^+$; 502 (55.2), $Ir(C_7H_8)_2(C_2H_2)(acac)^+$; 436 (89.6), $Ir(C_7H_8)(C_2H_2)_2(acac)^+$; 384 (100), $Ir(C_7H_8)(acac)^+$; 66 (69.0), $C_5H_6^+$. The ^{1}H NMR showed the following peaks: τ 3.68 (1 H), 3.98 (1 H), 4.11 (2 H), uncoordinated vinyls; 4.80 (1 H), 5.10 (1 H), 5.32 (1 H), 5.90 (3 H), methines; 4.81 (1 H), acac; 7.34 (2 H), 7.50 (1 H), 7.72 (1 H), coordinated vinyls; 6.26 (1 H), 7.60 (1 H), β-H to Ir; 7.98 (3 H), 8.24 (3 H), acac; 8.3–9.4 (8 H), α-CH_2-Ir.

Compound 4, $Ir(C_7H_8)_2(CO)_2(PPh_3)Cl$. Compound **1** (450 mg) was suspended in 25 mL of CH_2Cl_2, and CO was bubbled through. The vessel was placed in a bath of warm water to prevent cooling of the reaction mixture, and solvent lost by evaporation was periodically replaced. After 2 h, the solid had all dissolved, giving a colorless solution. The CO bubbling was terminated, and 235 mg of solid PPh_3 was then added. The mixture was evaporated to dryness and triturated with pentane to remove unreacted PPh_3. Recrystallization of the solid residue from CH_2Cl_2/EtOH yielded 490 mg of yellow crystals, yield 75%. The material does not melt but chars at about 175 °C. The molecular weight measured osmometrically in $CHCl_3$ was 704 (calculated 729.7). Anal. Calcd for $Ir(C_7H_8)_2(CO)_2(PPh_3)Cl$: C, 56.00; H, 4.24; Cl, 4.87; P, 4.25. Found: C, 56.22; H, 3.46; Cl, 5.06; P, 4.31. ^{1}H NMR: τ 2.6 (15 H), C_6H_5; 3.90 (4 H), uncoordinated vinyls; 6.15–6.70 (4 H), methine; 7.1–7.3 (3 H), β-H-Ir, α-H-CO; 7.9–8.7 (5 H), methylene, α-H-Ir.

Compound 5, $[Ir(C_7H_8)_3(PPhMe_2)Cl]_x$. Compound **1** (540 mg) was suspended in 20 mL of deoxygenated $CHCl_3$, and 148 mg of $PPhMe_2$ was added. After the mixture was refluxed under N_2 for about 5 min, all of the starting material had dissolved to give a red-brown solution. After 10 min, a brick red solid began precipitating. Refluxing was continued for a total of 3 h. Then the system was cooled and the product filtered and washed with $CHCl_3$ and Et_2O until the washings were colorless. The product was dried under vacuum: yield 42%, mp 216 °C. The microanalyses could only be fitted if some $CHCl_3$ of crystallization were present. For example: Anal. Calcd for $Ir(C_7H_8)_3(PPhMe_2)Cl\cdot 0.25CHCl_3$: C, 52.10; H, 5.24; Cl, 9.30; P, 4.64. Found: C, 51.61; H, 5.25; Cl, 8.09; P, 4.46. Mass spectrum (at 210 °C) [*m/e* (relative intensity)]: 642 (0.35), $Ir(C_7H_8)_3(PPhMe_2)Cl^+$; 576 (5.62), $Ir(C_7H_8)_2(C_2H_2)(PPhMe_2)Cl^+$; 510 (2.81), $Ir(C_7H_8)(C_2H_2)_2(PPhMe_2)Cl^+$; 444 (6.14), $Ir(C_2H_2)_3(PPhMe_2)Cl^+$; 366 (4.21), $Ir(PPhMe_2)Cl^+$; 210 (1.93), $[(C_7H_8)_3C_5H_6]^+$; 138 (9.65), $PPhMe_2^+$; 66 (100), $C_5H_6^+$.

Compound 6, $Ir(C_7H_8)_3(CO)_2(PPhMe_2)Cl$. Compound **5** (200 mg) was suspended in 25 mL of CH_2Cl_2, and CO was bubbled through slowly until a colorless solution resulted (about 2 h). The solution was then filtered to remove unreacted particles and taken to dryness under vacuum. The resulting residue, recrystallized from $CHCl_3$/EtOH, yielded a white, air-stable, microcrystalline product which is stable in the crystalline form to formation of compound **7**. Anal. Calcd for $Ir(C_7H_8)_3(CO)_2(PPhMe_2)Cl$: C, 53.30; H, 5.03; Cl, 5.10; P, 4.45. Found: C, 52.18; H, 4.97; Cl, 5.27; P, 4.61. Mp: 145 °C dec. ^{1}H NMR: τ 2.5 (5 H), C_6H_5; 3.95 (6 H) uncoordinated vinyls; 6.5–9.0 (ca. 24 H, complex). Mass spectrum (130 °C) [*m/e* (relative intensity)]: 698 (0.02), $[Ir(C_7H_8)_3(PPhMe_2)(CO)_2Cl]^+$; 670 (0.03), $Ir(C_7H_8)_3(PPhMe_2)(CO)Cl^+$; 642 (0.06), $[Ir(C_7H_8)_3(PPhMe_2)Cl]^+$; 604 (0.14), $Ir(C_7H_8)_2(C_2H_2)(PPhMe_2)(CO)Cl^+$; 576 (0.26), $Ir(C_7H_8)_2(C_2H_2)(PPhMe_2)Cl^+$; 532 (5.36), $Ir(C_7H_8)_3(CO)Cl^+$; 504 (7.45), $Ir(C_7H_8)_3Cl^+$; 304 (4.86), $[(C_7H_8)_3 + CO)]^+$; 238 (12.5), $[(C_7H_8)_3 + CO - C_5H_6]^+$; 210 (3.83), $[(C_7H_8)_3 - C_5H_6]^+$; 172 (4.22), $[(C_7H_8)_3 + CO - 2C_5H_6]^+$; 144 (15.6), $[(C_7H_8)_3 - 2C_5H_6]^+$; 138 (31.9), $PPhMe_2^+$; 66 (100), $C_5H_6^+$.

Compound 7, $(C_{22}H_{24}O)(CO)(PPhMe_2)Cl$. Compound **6** was dissolved in $CHCl_3$ and allowed to stand for about 3 h until the solution had turned bright yellow and no further ν_{CO} appeared in the IR spectrum of the reaction mixture at 2065 cm^{-1}. (The absorbance at 2065 cm^{-1} is indicative of the presence of unreacted compound **6**.) This reaction is retarded by maintaining an atmosphere of CO over the solution. The solution was taken to dryness on the rotary evaporator, and the solid was recrystallized from CH_2Cl_2/EtOH by using an absolutely minimum amount of $CHCl_2$ and dried under vacuum. The compound is air stable; mp 160 °C dec. Anal. Calcd for $(C_{22}H_{24}O)(CO)(PPhMe_2)Cl$: C, 53.30; H, 5.03; Cl, 5.10; P, 4.45. Found: C, 52.32; H, 5.02; Cl, 5.25; P, 4.48. The ^{1}H NMR showed the following: τ 2.6 (5 H), C_6H_5; 3.90 (6 H), uncoordinated vinyls; 6.2–9.0 (ca. 24 H, complex). The mass spectrum obtained at 150 °C showed the same peaks as reported in **6** above but of slightly different relative intensities.

Reaction of $[Ir(C_7H_8)_3Cl]_x$ with PPh_3 and Determination of the Amount of Exo-trans-exo Norbornadiene Dimer Liberated. Compound **1** (0.5 g) was refluxed in $CHCl_3$ for 1 h with PPh_3 (1.3 g, fivefold excess). The organic products and PPh_3 were extracted from the reaction mixture with pentane and chromatographed on alumina to remove organometallic impurities. The pentane was removed under reduced pressure. The residue was weighed and then dissolved in $CDCl_3$. The ^{1}H NMR spectrum was identical with that of the exo-trans-exo norbornadiene dimer previously reported [i.e., peaks at τ 4.03 (4 H), 7.38 (4 H), 8.31 (2 H), 8.68 (4 H), and 8.77 (2 H)], only contaminated (but not obscured) by PPh_3. Integration of the phenyl resonances of PPh_3 against the dimer peak at τ 4.03 yielded the relative molar quantities of the dimer and PPh_3 in the NMR sample and hence the overall yield of exo-trans-exo dimer from the reaction (45 mg, ca. 25%). This value represents only a lower limit, since possibly not all of the dimer was extracted into the pentane. Consequently an identical experiment was carried out in which the $CHCl_3$ was removed from the reaction mixture after 1 h of reflux. The residue

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Table III. Experimental Data for X-ray Structure Analysis of $Ir(C_7H_8)_3(acac)$

A. Crystal Data at 18 °C (λ(Mo Kα) = 0.710 69 Å)

	working cell	reduced cell
a, Å	9.239 (2)	9.239
b, Å	14.267 (3)	13.915
c, Å	9.638 (2)	9.638
α, deg	111.95 (1)	108.12
β, deg	65.77 (1)	114.32
γ, deg	106.70 (1)	90.72
V, Å³	1060.9	1060.9

space group $P1$ (C_i^1, No. 2)
mol wt 576.74
$Z = 2$
$\rho_{\mathrm{calcd}} = 1.777\ \mathrm{g{\cdot}cm^{-3}}$
$\rho_{\mathrm{obsd}} = 1.78\ (1)\ \mathrm{g{\cdot}cm^{-3}}$ by flotation in aqueous ZnI_2
cryst dimens: $(100) \rightarrow (\bar{1}00)$, 0.25 mm; $(010) \rightarrow (0\bar{1}0)$, 0.18 mm; $(001) \rightarrow (00\bar{1})$, 0.27 mm
μ: 66.95 $\mathrm{cm^{-1}}$
transmissn factors: 0.21 → 0.38

B. Measurements of Intensity Data

radiation: Mo Kα
monochromator: highly oriented graphite $2\theta_{002} = 12.1°$
cryst–detector dist: 25 mm
detector: scintillation counter and pulse height analyzer set for 100% of Mo Kα peak
attenuators: Ni foil used when counting rate exceeded 10^4 $\mathrm{counts{\cdot}s^{-1}}$
takeoff angle: 3°
detector aperture: 4 × 4 mm
scan type: coupled θ(cryst)–2θ(detector), 1.0° $\mathrm{min^{-1}}$
scan length: $\Delta(2\theta) = (\text{base width} + 0.692 \tan\theta)°$ beginning (base width/2) below the predicted peak
rotation axis: [001]
reflctns measd: $\pm h, \pm k, +l$
min and max 2θ: 4°, 40°
scan base width: 2.4°
stds every 50 cycles: 400, 040, 004
variation of stds: ±2% (random)
no. of intensities collected: 1968
no. with $I > 3\sigma(I)$: 1891

Table IV. Experimental Data for X-ray Structure Analysis of $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl{\cdot}CH_2Cl_2$

A. Crystal Data at 18 °C (λ(Mo Kα) = 0.710 69 Å)

$a = 9.610\ (7)$ Å
$b = 30.81\ (2)$ Å
$c = 10.948\ (7)$ Å
$\beta = 103.52\ (3)°$
$V = 3151.7$ Å³
space group $P2_1/c$ (C_{2h}^5, No. 14)
mol wt 783.18
$Z = 4$
$\rho_{\mathrm{calcd}} = 1.650\ \mathrm{g{\cdot}cm^{-3}}$
$\rho_{\mathrm{obsd}} = 1.64\ \mathrm{g{\cdot}cm^{-3}}$
cryst dimens: $(100) \rightarrow (\bar{1}00)$, 0.30 mm; $(010) \rightarrow (0\bar{1}0)$, 0.47 mm; $(001) \rightarrow (00\bar{1})$, 0.40 mm
$\mu = 48.27\ \mathrm{cm^{-1}}$
transmissn factors: 0.20–0.32

B. Measurements of Intensity Data[a]

rotation axis: [010]
reflctns measd: $+h, +k, \pm l$
min and max 2θ: 4°, 45°
scan base width: 2.2°
stds every 50 cycles: 400; 0,10,0; 004
variation of stds: ±3% random
no. of intensities collected: 4178
no. with $I > 3\sigma(I)$: 3467

[a] See Table III for details of diffractometer configuration.

was redissolved in $CDCl_3$ and the ^1H NMR spectrum measured. The yield calculated by this method was ca. 50%.

Collection of X-ray Diffraction Data. The crystals were glued on Lindeman glass fibers and subjected to a preliminary photographic survey of all zero and first levels on Weissenberg and precession cameras. These photographs served as a check on the mosaic spread of the crystals and yielded approximate cell dimensions and space group data. More accurate cell dimensions were subsequently obtained with the use of a fully automated Picker-Nuclear FACS-1 diffractometer by a least-squares procedure based on the angular settings for 24 automatically centered reflections. These reflections were chosen to have the highest $|2\theta|$ values consistent with reasonable intensity ($33° < \pm 2\theta < 43°$) and were widely scattered in reciprocal space. The refined unit cell parameters, space groups, and data collection may be found in Tables III and IV.

The following formulas apply to the data processing:

$$I = N - Bt_s/t_b \qquad \sigma(I) = [N + B(t_s/t_b)^2 + (0.02N)^2]^{1/2}$$

where I is the intensity and N and B are the counts accumulated during the scan period t_s and the total background counting period t_b, respectively. Data for which $I < 3\sigma(I)$ were discarded, the remainder were corrected for Lorentz and polarization effects, and a general absorption correction[38] was applied:

$$(Lp)^{-1} = (\sin 2\theta_s)(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$$

where $2\theta_s$ and $2\theta_m$ are the diffraction angles at the sample and the monochromator, respectively.

Solution and Refinement of Structures. The structures were solved by conventional heavy-atom techniques: Patterson syntheses yielded the iridium atom positions, and a sequence of structure factor calculations followed by Fourier syntheses yielded the positions of the remaining atoms.

The scattering factors for neutral atoms were taken from the listings of Cromer and Waber,[39] and the real and imaginary corrections to the scattering factors for anomalous dispersion were taken from the compilations of Ibers.[40]

The function minimized in least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight w was taken as $4F_o^2/\sigma^2(F_o^2)$.

The reliability indices are $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_{wF} = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$. The error in an observation of unit weight (goodness of fit) is $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ where m and n are the number of observations and variables, respectively.

Fourier and Patterson syntheses were performed by using FORDAP by Zalkin. Structure factor and least-squares calculations were performed by using SFLS by Prewitt. The Concordia University CDC 6400 computer was used in these calculations.

Listings of observed and calculated structure factors are available (see the paragraph at the end of the paper regarding supplementary material).

Crystal Structure Determination of $Ir(C_7H_8)_3(acac)$. The photographic data revealed only $\bar{1}$ symmetry and no systematic absences. The choice of space groups $P1$ (C_i^1, No. 1) or $P\bar{1}$ C_i^2, No. 2) was resolved by the successful solution of the structure in the centrosymmetric space group.

The first difference-Fourier map revealed the positions of all nonhydrogen atoms. Refinement with isotropic thermal parameters was terminated at $R_F = 0.104$ and $R_{wF} = 0.119$. Refinement was continued with the use of anisotropic thermal parameters until the shifts in positional variables were less than 0.2 of their esd's. During this phase of the refinement, the atoms were redivided randomly between two matrices for each cycle because of the limited memory of the computer. Refinement converged at $R_F = 0.041$ and $R_{wF} = 0.054$, with a goodness of fit of 3.96. The final atomic positions and thermal parameters are listed in Table V. A final difference-Fourier synthesis revealed no peaks above 0.5 $\mathrm{e{\cdot}Å^{-3}}$.

Crystal Structure Determination of $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl{\cdot}CH_2Cl_2$. A mixture of two different types of crystals was obtained from dichloromethane: while the bulk of the sample consisted of thin elongated plates with an opaque appearance, a few larger blocks remained transparent. The opaque plates failed to give diffraction patterns; presumably loss of solvent had disrupted the crystalline structure. A comparison of infrared spectra indicated that the two forms contained the same iridium compound, and a fragment of a larger block was chosen for the structure analysis. The density measurements suggested the presence of one molecule of dichloromethane per iridium, and the second difference-Fourier synthesis revealed the position of this molecule together with those of a few

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(38) The program GNABS by Barnam, locally modified for the FACS-1 geometry was used: Barnam, C. W. *Am. Mineral.* **1966**, *51*, 159.

(39) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(40) "International Tables of X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, p 216.

Table V. Final Positional and Anisotropic Thermal Parameters for $Ir(C_7H_8)_3(acac)^a$

atom	*x*	*y*	*z*	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Ir	0.21993 (6)	0.23785 (4)	0.00639 (6)	32.2 (4)	43.6 (4)	32.1 (4)	−0.7 (3)	−10.3 (4)	16.0 (3)
C(1)	0.2468 (15)	0.1570 (10)	0.1375 (15)	49 (11)	43 (9)	39 (7)	0 (6)	−21 (7)	17 (6)
C(2)	0.2642 (16)	0.2318 (10)	0.3032 (15)	56 (11)	61 (9)	36 (7)	11 (6)	−18 (7)	11 (6)
C(3)	0.1501 (17)	0.1697 (11)	0.4218 (16)	70 (11)	52 (9)	47 (11)	11 (6)	−18 (7)	22 (6)
C(4)	0.2161 (18)	0.0693 (12)	0.3676 (16)	77 (11)	61 (9)	36 (7)	11 (11)	−18 (7)	22 (6)
C(5)	0.1866 (18)	0.0111 (12)	0.2339 (18)	70 (11)	69 (9)	54 (11)	0 (11)	−25 (7)	33 (11)
C(6)	0.1044 (16)	0.0730 (10)	0.1928 (16)	60 (11)	52 (9)	54 (11)	6 (6)	−21 (7)	28 (6)
C(7)	0.0031 (17)	0.1283 (11)	0.3618 (16)	56 (11)	61 (9)	39 (11)	0 (6)	−14 (7)	17 (6)
C(8)	0.1946 (15)	0.3603 (9)	0.2120 (14)	49 (11)	43 (9)	25 (7)	6 (6)	−14 (7)	11 (6)
C(9)	0.2084 (16)	0.3360 (10)	0.3530 (16)	49 (11)	35 (9)	43 (7)	6 (6)	−18 (7)	6 (6)
C(10)	0.3373 (19)	0.4290 (12)	0.4098 (17)	74 (11)	52 (9)	54 (11)	−6 (11)	−32 (7)	6 (6)
C(11)	0.2516 (19)	0.5226 (12)	0.4808 (19)	74 (11)	43 (9)	68 (11)	−6 (11)	−32 (11)	11 (6)
C(12)	0.2412 (19)	0.5429 (12)	0.3581 (20)	67 (11)	52 (9)	68 (11)	0 (11)	−25 (11)	11 (11)
C(13)	0.3189 (17)	0.4619 (11)	0.2041 (16)	60 (11)	43 (9)	47 (11)	0 (6)	−25 (7)	11 (6)
C(14)	0.4521 (17)	0.4448 (11)	0.2458 (17)	56 (11)	52 (9)	54 (11)	−11 (6)	−21 (7)	17 (6)
C(15)	0.4830 (15)	0.2902 (11)	−0.1538 (14)	35 (7)	61 (9)	18 (7)	−11 (6)	7 (7)	11 (6)
C(16)	0.4730 (16)	0.2265 (11)	−0.0902 (17)	53 (11)	43 (9)	68 (11)	17 (6)	−16 (7)	28 (11)
C(17)	0.4792 (17)	0.1214 (12)	−0.2136 (17)	49 (11)	61 (9)	47 (11)	0 (6)	−7 (7)	17 (11)
C(18)	0.2940 (16)	0.0869 (11)	−0.1995 (15)	53 (11)	52 (9)	32 (7)	6 (6)	−14 (7)	0 (6)
C(19)	0.2592 (17)	0.1479 (12)	−0.2593 (16)	63 (11)	69 (9)	43 (7)	0 (11)	−21 (7)	28 (6)
C(20)	0.4182 (18)	0.2223 (12)	−0.3186 (17)	63 (11)	69 (9)	47 (7)	0 (11)	0 (7)	28 (11)
C(21)	0.5473 (20)	0.1515 (13)	−0.3767 (18)	77 (11)	78 (9)	50 (11)	17 (11)	4 (7)	22 (11)
O(1)	0.1521 (13)	0.3332 (7)	−0.0826 (10)	77 (7)	52 (9)	47 (7)	11 (6)	−21 (4)	28 (6)
O(2)	−0.0245 (10)	0.1936 (7)	0.1078 (10)	25 (4)	69 (9)	47 (7)	−6 (6)	−7 (7)	17 (6)
C(22)	−0.0029 (24)	0.3972 (14)	−0.1594 (20)	151 (18)	86 (17)	79 (11)	39 (11)	−60 (11)	39 (11)
C(23)	0.0070 (22)	0.3370 (12)	−0.0674 (18)	81 (24)	61 (9)	54 (11)	28 (11)	−35 (11)	0 (11)
C(24)	−0.1328 (21)	0.2899 (12)	0.0292 (19)	81 (14)	69 (9)	75 (11)	17 (11)	−39 (11)	28 (11)
C(25)	−0.1407 (16)	0.2240 (11)	0.1089 (16)	42 (11)	52 (9)	54 (11)	17 (6)	−28 (7)	22 (6)
C(26)	−0.3030 (17)	0.1820 (13)	0.2065 (4)	25 (11)	78 (9)	107 (14)	6 (11)	−4 (11)	33 (11)

[a] The estimated standard deviations in parentheses are right justified to the least significant digit of the preceding number. Anisotropic thermal parameters were applied in the form $\exp(-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots))$.

Table VI. Final Positional and Anisotropic Thermal Parameters for $Ir(C_{22}H_{24}O)(CO)(PPhMe_2)Cl\cdot CH_2Cl_2{}^a$

atom	*x*	*y*	*z*	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Ir	0.13130 (5)	0.37060 (1)	0.62081 (4)	39.4 (3)	35.4 (2)	33.6 (3)	−2.3 (3)	14.5 (2)	7.8 (3)
Cl(1)	0.03851 (36)	0.32531 (10)	0.75750 (28)	64 (2)	56 (2)	44 (2)	−7 (3)	29 (2)	5 (2)
P	−0.01402 (38)	0.32761 (11)	0.45799 (30)	51 (2)	43 (2)	40 (2)	−9 (1)	14 (2)	−3 (2)
Me(1)	0.0306 (16)	0.27006 (37)	0.4666 (12)	115 (13)	29 (10)	60 (10)	−6 (9)	24 (9)	2 (6)
Me(2)	−0.2034 (14)	0.32813 (48)	0.4632 (13)	44 (9)	115 (14)	86 (10)	−31 (9)	33 (5)	−20 (9)
Cp(1)	−0.0149 (14)	0.34482 (40)	0.3032 (11)	57 (9)	43 (10)	45 (10)	−1 (7)	5 (5)	−3 (6)
Cp(2)	0.0456 (16)	0.32032 (40)	0.2197 (12)	106 (13)	53 (10)	55 (10)	3 (9)	33 (9)	3 (8)
Cp(3)	0.0437 (18)	0.33617 (41)	0.0991 (13)	146 (18)	53 (5)	60 (10)	−20 (10)	52 (9)	−9 (8)
Cp(4)	−0.0139 (19)	0.37450 (47)	0.0645 (11)	168 (18)	91 (10)	30 (5)	−20 (13)	9 (9)	23 (8)
Cp(5)	−0.0771 (20)	0.39828 (46)	0.1394 (12)	203 (22)	72 (10)	45 (10)	53 (13)	0 (9)	9 (8)
Cp(6)	−0.0747 (18)	0.38244 (46)	0.2570 (13)	128 (13)	87 (14)	50 (10)	38 (12)	19 (9)	3 (8)
C(1)	0.3027 (13)	0.33670 (31)	0.6123 (11)	57 (9)	10 (5)	65 (10)	−10 (6)	19 (9)	3 (6)
O(1)	0.3370 (9)	0.32812 (27)	0.5148 (7)	53 (4)	82 (5)	40 (5)	10 (6)	19 (5)	−8 (5)
C(2)	0.3916 (12)	0.32268 (35)	0.7418 (10)	35 (9)	38 (10)	50 (5)	4 (6)	19 (5)	3 (6)
C(3)	0.4531 (15)	0.27660 (37)	0.7343 (12)	62 (9)	38 (9)	65 (10)	7 (7)	33 (9)	2 (6)
C(4)	0.5076 (15)	0.26345 (39)	0.8714 (12)	76 (9)	58 (10)	70 (10)	34 (9)	38 (9)	23 (8)
C(5)	0.6226 (15)	0.28712 (41)	0.9200 (12)	75 (9)	67 (10)	65 (10)	31 (9)	19 (9)	19 (8)
C(6)	0.6513 (14)	0.31568 (41)	0.8165 (11)	62 (9)	63 (10)	40 (5)	10 (7)	14 (5)	6 (8)
C(7)	0.5966 (14)	0.28746 (40)	0.7040 (12)	66 (9)	53 (10)	50 (10)	22 (7)	28 (9)	14 (6)
C(8)	0.5290 (13)	0.35120 (34)	0.7918 (11)	66 (9)	38 (5)	40 (5)	4 (6)	19 (5)	0 (5)
C(9)	0.5537 (12)	0.38984 (37)	0.7093 (9)	44 (9)	58 (10)	30 (5)	−4 (7)	9 (5)	−14 (6)
C(10)	0.7078 (13)	0.40890 (39)	0.7393 (12)	40 (9)	48 (10)	70 (10)	9 (7)	14 (5)	8 (6)
C(11)	0.7220 (14)	0.43726 (43)	0.6311 (13)	49 (9)	72 (10)	91 (10)	−28 (9)	28 (9)	−9 (9)
C(12)	0.6464 (14)	0.47151 (39)	0.6358 (15)	44 (9)	53 (10)	126 (15)	−10 (9)	19 (9)	9 (9)
C(13)	0.5884 (14)	0.46628 (40)	0.7501 (13)	49 (9)	43 (10)	101 (10)	−6 (7)	19 (9)	−73 (8)
C(14)	0.7064 (15)	0.44181 (46)	0.8416 (13)	49 (9)	72 (10)	70 (10)	0 (9)	5 (9)	−3 (9)
C(15)	0.4644 (13)	0.43330 (36)	0.7191 (10)	40 (9)	38 (10)	45 (5)	−6 (7)	0 (5)	5 (6)
C(16)	0.3685 (12)	0.43421 (35)	0.8154 (11)	40 (9)	34 (10)	55 (5)	0 (6)	9 (5)	−3 (6)
C(17)	0.3182 (14)	0.47991 (39)	0.8442 (12)	57 (9)	48 (10)	70 (10)	3 (7)	9 (9)	−19 (8)
C(18)	0.2274 (14)	0.49728 (35)	0.7199 (13)	66 (9)	34 (10)	96 (10)	7 (7)	29 (9)	−8 (8)
C(19)	0.1064 (14)	0.47574 (39)	0.6949 (12)	71 (9)	48 (10)	55 (10)	19 (7)	14 (9)	−2 (8)
C(20)	0.1105 (14)	0.44633 (41)	0.8009 (11)	53 (9)	63 (10)	50 (10)	15 (7)	19 (5)	−9 (6)
C(21)	0.2011 (15)	0.46875 (41)	0.9130 (13)	80 (9)	63 (10)	60 (10)	13 (9)	24 (9)	−22 (8)
C(22)	0.2241 (12)	0.40747 (36)	0.7855 (10)	44 (9)	48 (10)	45 (5)	16 (7)	5 (5)	0 (6)
C(23)	0.1731 (12)	0.40955 (39)	0.5082 (10)	40 (9)	67 (10)	40 (5)	7 (7)	−5 (5)	−14 (6)
O(2)	0.1960 (10)	0.43204 (29)	0.4315 (8)	97 (7)	77 (5)	60 (5)	−22 (6)	14 (5)	39 (5)
CS	0.3900 (20)	0.37254 (60)	0.2483 (16)	159 (18)	173 (19)	111 (15)	−101 (16)	80 (14)	−84 (14)
Cl(2)	0.4442 (8)	0.34383 (22)	0.1320 (6)	252 (9)	207 (5)	126 (5)	19 (6)	85 (5)	−11 (5)
Cl(3)	0.5024 (7)	0.41214 (19)	0.3002 (9)	142 (4)	101 (5)	392 (10)	−1 (4)	28 (5)	−33 (6)

[a] See footnote to Table V.

other atoms which had not been unambiguously located in the first map.

Isotropic refinement for four cycles converged at $R_F = 0.082$ and $R_{wF} = 0.089$. Continued refinement, with anisotropic thermal motion allowed for all atoms, and subdividing the atoms among three matrices, converged after seven cycles with $R_F = 0.050$, $R_{wF} = 0.048$, and a goodness of fit of 2.43. A difference-Fourier map calculated after the fifth anisotropic cycle had revealed all hydrogen atoms except those on the methyl groups and three others. Peak heights ranged from 0.2 to 0.7 e·Å^{-3}. Those hydrogen atoms whose positions could be calculated, except those on the methylene chloride, were located 0.98 Å from either carbon atom and included in the structure factor calculations of the last two cycles of refinement. They were assigned isotropic thermal parameters equal to the final isotropic values of the carbons to which they were attached. A final difference-Fourier map was featureless.

The refined atomic positions and thermal parameters are listed in Table VI.

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Registry No. 1, 74466-65-2; **2**, 41612-45-7; **3**, 41612-46-8; **4**, 40964-31-6; **5**, 74482-42-1; **6**, 74482-43-2; **7**, 74482-45-4; [Ir(1,5-cyclooctadiene)Cl]$_2$, 12112-67-3.

Supplementary Material Available: Tables of observed and calculated structure amplitudes (16 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of Acyl Chlorides to Diphenylmethylphosphine Complexes of Iridium(I). Formation of Five-Coordinate Acyliridium(III) and Six-Coordinate Alkyliridium(III) Complexes Containing Cis Phosphine Ligands

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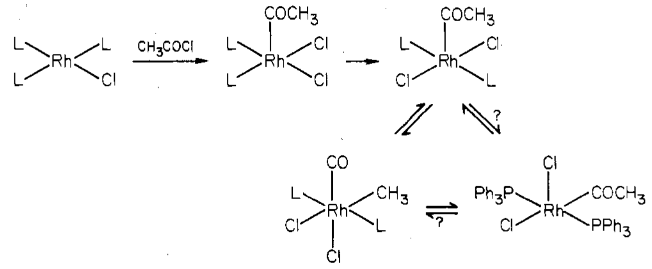
Acyl chlorides RCOCl react either with IrCl(PMePh$_2$)$_3$ or with a solution containing the cyclooctene complex [IrCl(C$_8$H$_{14}$)$_2$]$_2$ and diphenylmethylphosphine in a 1:4 mole ratio to give six-coordinate alkyliridium(III) complexes containing mutually cis PMePh$_2$ groups, *cis*-IrCl$_2$R(CO)(PMePh$_2$)$_2$ (R = CH$_3$ (**1a**), C$_2$H$_5$ (**1b**), *n*-C$_3$H$_7$ (**1c**)). In solution **1b** and **1c** equilibrate rapidly (<1 min) with five-coordinate acyliridium(III) complexes IrCl$_2$(COR)(PMePh$_2$)$_2$ (R = C$_2$H$_5$ (**2b**), *n*-C$_3$H$_7$ (**2c**)) which also have cis PMePh$_2$ ligands and are probably square pyramidal with apical acyl groups. The equilibrium constants for the acyl–alkyl equilibrium in chloroform at 32 °C are 3.3 (**2b** $\rightleftharpoons$ **1b**) and 4.2 (**2c** $\rightleftharpoons$ **1c**). At ambient temperature in chloroform/methanol **1a–c** isomerize by a first-order process to complexes containing mutually trans PMePh$_2$ ligands, *trans*-IrCl$_2$R(CO)(PMePh$_2$)$_2$ (**3a–c**: R = CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$), the rates being in the order R = C$_2$H$_5$ ≈ *n*-C$_3$H$_7$ > CH$_3$. Isomerization is suggested to proceed by rapid rearrangement of intermediate five-coordinate alkyliridium(III) cations [IrClR(CO)(PMePh$_2$)$_2$]$^+$ formed by rate-determining loss of Cl$^-$ from **1a–c**. Complexes **1b** and **1c** also isomerize to **3b** and **3c** on heating in benzene, but **1a** is stable under these conditions. In contrast with **1b** and **1c**, solutions of **1a** and of **3a–c** do not contain spectroscopically detectable amounts of iridium(III) acyls. The *n*-propyl complex **3c** is the final product isolated from reaction of 2-methylpropanoyl chloride (CH$_3$)$_2$CHCOCl with [IrCl(C$_8$H$_{14}$)$_2$]$_2$ + 4PMePh$_2$ and presumably is formed by isomerization of an undetected intermediate isopropyliridium(III) complex. ^{1}H and ^{31}P NMR data are reported, and the fact that the alkyl group proton resonances of **3a–c** are consistently to higher field than those of **1a–c** is attributed to diamagnetic shielding by phenyl rings of the mutually trans PMePh$_2$ ligands. Oxidative addition of acyl chlorides to IrCl(PMePh$_2$)$_3$ is compared with literature reports of similar additions to RhCl(PPh$_3$)$_3$, IrCl(N$_2$)(PPh$_3$)$_2$, and IrCl(PPh$_3$)$_3$.

Introduction

The oxidative addition of acyl chlorides RCOCl to RhCl(PPh$_3$)$_3$ has been widely studied in view of its potential application to the decarbonylation of acyl halides catalyzed by rhodium(I) and iridium(I) complexes.[1-10] The first product is a five-coordinate acylrhodium(III) complex, RhCl$_2$(COR)(PPh$_3$)$_2$, which undergoes alkyl group migration to give a six-coordinate rhodium(III) complex, RhCl$_2$R(CO)(PPh$_3$)$_2$. Finally, reductive elimination of alkyl or aryl halide, or of alkene and HCl, gives the rhodium(I) carbonyl complex RhCl(CO)(PPh$_3$)$_2$. A recent ^{1}H and ^{31}P NMR study of the reaction of acetyl chloride with RhCl(PPh$_3$)$_3$ has shown[10] that

Scheme I



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