SYNTHESIS AND CRYSTAL STRUCTURE OF [Ir(acac-C^3)(COD)(phen)]

L.A. ORO, D. CARMONA, M.A. ESTERUELAS,

Departamento de Química Inorgánica, Universidad de Zaragoza, Zaragoza (Spain)

C. FOCES-FOCES and F.H. CANO

Departamento de Rayos X, Instituto Rocasolano, C.S.I.C., Serrano 119, Madrid-6 (Spain)

(Received July 5th, 1983)

Summary

The first iridium(I) carbon-bonded diketonate complex [Ir(acac-C^3)(COD)(phen)] has been prepared by two routes. Its reactions with protic acids, [Rh(COD)$_2$]ClO$_4$ and [MCl(COD)]$_2$ (M = Rh, Ir), have been investigated. The crystal structure of [Ir(acac-C^3)(COD)(phen)] has been studied by standard X-ray methods. Final R and R_w factors were 0.043 and 0.047 respectively, for the 3498 independent reflexions. The iridium atom is pentacoordinated, in a distorted pyramidal stereochemistry, with the N atoms of the phenanthroline and the midpoints of the olefin bonds of the cyclooctadiene in the base, and the apex is occupied by a σ-bonded carbon atom of the acac group at a rather long distance (Ir–C 2.420(6) Å).

Introduction

The first examples of β-diketonate complexes containing metal–carbon bonds were established by Swallow and Truter [1] from crystal structure determinations on Pt^{IV} complexes. Since then, other related examples have been reported [2], but to the best of our knowledge, no iridium(I) carbon-bonded diketonate complexes have been previously described.

In the course of our study of cationic diolefin iridium(I) or rhodium(I) complexes [3], we have studied the reaction of [Ir(COD)(phen)]Cl [4] with the acetylacetonate anion. This iridium(I) complex, in equilibrium with [IrCl(COD)(phen)], was selected for study because of its tendency to give pentacoordinated adducts with a variety of small molecules [5]. We now report the isolation and characterization of the pentacoordinated carbon-bonded acetylacetonate complex [Ir(acac-C^3)(COD)-(phen)], which as far as we know is the first example of an iridium(I) carbon-bonded diketonate complex.

Results and discussion

[Ir(COD)(phen)]Cl reacts with an equimolar quantity of thallium acetylacetonate in dichloromethane at room temperature according to eq. 1:

$$[Ir(COD)(phen)]Cl + Tl(acac) \rightarrow [Ir(acac-C^3)(COD)(phen)] + TlCl \quad (1)$$
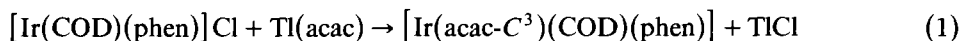
The IR spectrum of the complex shows a pair of $\nu(CO)$ bands at 1615 and 1570 cm^{-1}. Although these frequencies are below the usual 1700–1600 cm^{-1} range found for metal-C^3-bonded acetylacetonate complexes [6], further studies described below confirmed the proposed formulation.

The dark-blue [Ir(acac-C^3)(COD)(phen)] (I) complex reacts with HCl to give the green complex [Ir(COD)(phen)]Cl. A dichloromethane solution of I is initially dark blue, but progressively becomes red-brown. IR observations in the non-conducting solutions suggest the formation of O-bonded acac complexes ($\nu(CO)$ 1550, 1525 cm^{-1}) along with a relatively small amount of a derivative which shows a $\nu(CO)$ at 1711 cm^{-1}. Attempts to isolate these complexes were unsuccesful * but it is possible that the latter compound results from a nucleophilic attack of the acetylacetonyl group at a double bond of the coordinated cyclooctadiene; related nucleophilic reactions have been reported in some complexes of d^8 metal ions [7]. In particular, it has been observed that the [Ir(COD)(phen)]$^+$ complex in methanol, upon coordination of fumaronitrile, undergoes a nucleophilic attack by a methoxy group of the solvent to give the pentacoordinated complex fumaronitrile (8-methoxy-cyclooct-4-enyl)(1,10-phenanthroline)iridium(I) [5b].

The most general method [2a,f,h] for the synthesis of metal-C^3-bonded complexes involves treatment of O-bonded bidentate acac with N- or P- Lewis bases. In this way complex I can also be prepared in high yield by reaction of [Ir(acac)(COD)] [8] with 1,10-phenanthroline

$$[Ir(acac)(COD)] + phen \rightarrow [Ir(acac-C^3)(COD)(phen)] \quad (2)$$
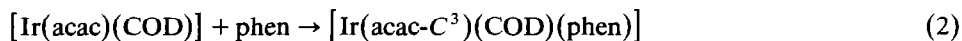
It is of interest to recall that a general route of cationic [M(diolefin)L$_2$]$^+$ (M = Rh, Ir) complexes involves the reaction of [M(acac)(diolefin)] with HBF$_4$, HPF$_6$ or HClO$_4$ in the presence of L (or L–L) [3c]. Thus I reacts with HClO$_4$ to give the previously reported complex [Ir(COD)(phen)]ClO$_4$ [4]. Similarly, with HBF$_4$, gives the analogous [Ir(COD)(phen)]BF$_4$ complex.

Because of the presence in complex I of free carbonyl groups, potentially able to behave as bidentate ligands [9], we studied the reactions of this complex with [Rh(COD)$_2$]ClO$_4$ [10] or [RhCl(COD)]$_2$ [11]. In both cases the Ir–acac-C^3 bond was broken, yielding [Rh(acac)(COD)] [12] and [Ir(COD)(phen)]ClO$_4$ [4] (or [Ir(COD)(phen)]Cl). No phenanthroline-rhodium species were detected. Similarly, the reaction of complex I with [IrCl(COD)]$_2$ [13] gave [Ir(acac)(COD)] and [Ir(COD)(phen)]Cl.

In order to confirm the assumed formulation and to determine the detailed geometry an X-ray structural determination of complex I was undertaken.

---

* Addition of diethyl ether to the solution give a precipitate of the starting dark-blue complex as the main product.

Crystal structure

A perspective ORTEP [14] view of the complex is shown in Fig. 1

The iridium atom is coordinated in a distorted rectangular pyramidal arrangement, with the base of the pyramid formed by the midpoints of the olefin bonds (C(1,2); C(5,6)) and the nitrogen atoms (N(1); N(4)) of the phenanthroline molecule, and the apex occupied by a σ-bonded carbon atom (C(15)) of the acetylacetonate group. Deviations of the points defining the basis from their mean least-squares plane are ±0.099(4) Å, and the angle between the IrN(1)N(4) and IrC(1,2)C(5,6) planes is 152.0(2)°.

Bond distances and angles are given in Table 1.

The Ir–C distances previously reported [15] for pentacoordinated methyl-(1,5-cyclooctadiene)-iridium(I) complexes, range from 2.133 to 2.202 Å. In the present complex, the Ir–C(15) bond length is rather large (2.420(6) Å). However, the C–C distances C(5') ⋯ C(15) 3.068(9), C(2') ⋯ C(15) 3.353 Å and the N–C distances N(1) ⋯ C(15) 3.223(7) and N(4) ⋯ C(15) 3.231(8) Å are less than the sums of the corresponding Van der Waals radii, which are 3.40 and 3.28 Å, respectively [16]. Moreover, if the C(15) atom is placed on the Ir–C(15) line, at 2.20 Å from the metal, these distances become 2.913, 3.187, 3.059 and 3.067 Å, respectively. Thus we think that the long σ-bond distance is mainly due to steric factors.

The acac group is not planar, the angle between the C(15)–C(16)–O(1)–C(17) and C(15)–C(18)–O(2)–C(19) planes (Table 2) being 27.7(3)°. The two carbonyl groups are not parallel, the angle between the C(16)–C(17) and C(18)–O(2) lines being 14.7(6)° (Fig. 1). The two C(sp^3)–C(sp^2) bond distances involving the σ-carbon atom, C(15), are shorter than the reported 1.510(5) Å [17].

The C(1')–C(2') and C(5')–C(6') lengths are 1.447(10) and 1.408(10) Å, and there is a relationship between these lengths and those of Ir–C, the greater C(sp^2)–C(sp^2) bond the shorter being the Ir–C bond. The C(sp^2)–C(sp^3) and C(sp^3)–C(sp^3) cyclooctadiene bond lengths in I are 1.494(12) and 1.505(5) Å, compared with the
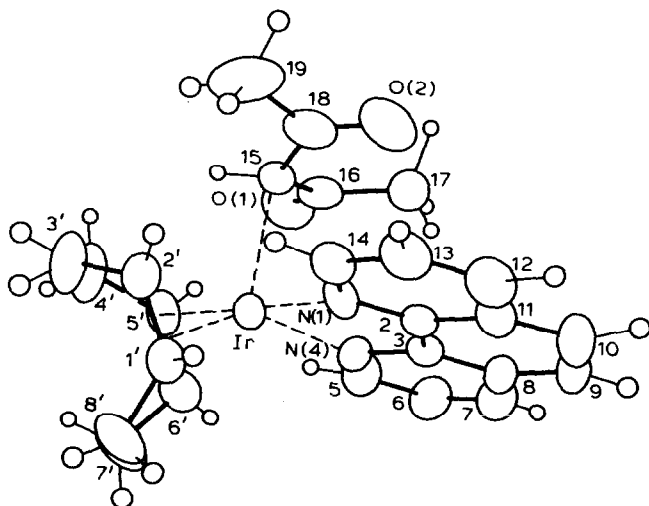

Fig. 1. An ORTEP view of the studied complex with the atom numbering scheme.

accepted values of 1.510(5) and 1.537(5) Å [17]. The ring shows a twisted boat conformation (Table 2) with only a binary axis perpendicular to the ring plane.

The two Ir–N distances are significantly different, and this can be explained in

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°)

Ir–N(1)	2.085(4)	C(10)–C(11)	1.422(9)
Ir–N(4)	2.122(4)	C(11)–C(12)	1.407(8)
Ir–C(15)	2.420(6)	C(12)–C(13)	1.379(10)
Ir–C(1')	2.108(6)	C(13)–C(14)	1.380(9)
Ir–C(2')	2.116(6)	C(15)–C(16)	1.472(8)
Ir–C(5')	2.144(6)	C(15)–C(18)	1.439(9)
Ir–C(6')	2.138(7)	C(16)–C(17)	1.498(10)
Ir–C(1,2) [a]	1.984(4)	C(16)–O(1)	1.227(8)
Ir–C(5,6) [a]	2.022(5)	C(18)–C(19)	1.503(14)
N(1)–C(2)	1.340(7)	C(18)–O(2)	1.235(12)
N(1)–C(14)	1.352(7)	C(1')–C(2')	1.447(10)
C(2)–C(3)	1.447(7)	C(1')–C(8')	1.511(10)
C(2)–C(11)	1.403(8)	C(2')–C(3')	1.507(9)
C(3)–N(4)	1.362(7)	C(3')–C(4')	1.508(11)
C(3)–C(8)	1.405(8)	C(4')–C(5')	1.491(10)
N(4)–C(5)	1.338(7)	C(5')–C(6')	1.408(10)
C(5)–C(6)	1.392(10)	C(6')–C(7')	1.513(11)
C(6)–C(7)	1.370(10)	C(7')–C(8')	1.483(10)
C(7)–C(8)	1.399(9)	N(1)–N(4)	2.640(6)
C(8)–C(9)	1.428(9)	N(1)–C(1,2) [a]	2.972(6)
C(9)–C(10)	1.366(10)	N(4)–C(5,6) [a]	3.079(7)
		C(1,2)–C(5,6) [a]	2.735(6)
C(1,2)–Ir–C(5,6) [a]	86.1(2)	C(8)–C(9)–C(10)	121.1(6)
C(15)–Ir–C(5,6) [a]	102.4(2)	C(9)–C(10)–C(11)	120.6(6)
C(15)–Ir–C(1,2) [a]	114.7(2)	C(2)–C(11)–C(10)	120.1(6)
N(4)–Ir–C(5,6) [a]	96.0(2)	C(10)–C(11)–C(12)	123.4(6)
N(4)–Ir–C(15)	90.5(2)	C(2)–C(11)–C(12)	116.5(5)
N(1)–Ir–C(1,2) [a]	93.8(2)	C(11)–C(12)–C(13)	118.8(6)
N(1)–Ir–C(15)	91.1(2)	C(12)–C(13)–C(14)	120.7(6)
N(1)–Ir–N(4)	77.7(2)	N(1)–C(14)–C(13)	121.9(6)
Ir–N(1)–C(14)	126.6(4)	Ir–C(15)–C(18)	106.2(4)
Ir–N(1)–C(2)	116.0(3)	Ir–C(15)–C(16)	105.0(4)
C(2)–N(1)–C(14)	117.3(5)	C(16)–C(15)–C(18)	121.6(6).
N(1)–C(2)–C(11)	124.8(5)	C(15)–C(16)–O(1)	120.8(6)
N(1)–C(2)–C(3)	116.1(5)	C(15)–C(16)–C(17)	120.8(5)
C(3)–C(2)–C(11)	119.1(5)	C(17)–C(16)–O(1)	118.4(6)
C(2)–C(3)–C(8)	119.8(5)	C(15)–C(18)–O(2)	126.3(6)
C(2)–C(3)–N(4)	116.2(5)	C(15)–C(18)–C(19)	115.5(8)
N(4)–C(3)–C(8)	123.9(5)	C(19)–C(18)–O(2)	118.2(7)
Ir–N(4)–C(3)	113.9(3)	C(2')–C(1')–C(8')	124.4(6)
C(3)–N(4)–C(5)	116.8(5)	C(1')–C(2')–C(3')	121.1(6)
Ir–N(4)–C(5)	129.2(4)	C(2')–C(3')–C(4')	115.2(6)
N(4)–C(5)–C(6)	122.8(6)	C(3')–C(4')–C(5')	114.1(6)
C(5)–C(6)–C(7)	120.1(6)	C(4')–C(5')–C(6')	123.1(6)
C(6)–C(7)–C(8)	119.3(7)	C(5')–C(6')–C(7')	123.5(7)
C(3)–C(8)–C(7)	117.0(6)	C(6')–C(7')–C(8')	112.3(7)
C(7)–C(8)–C(9)	123.7(6)	C(7')–C(8')–C(1')	113.4(6)
C(3)–C(8)–C(9)	119.3(6)		

[a] C(1,2) and C(5,6) are the midpoints of the 1'–2' and 5'–6' bonds.

terms of the different location of the Ir atom with respect to the two halves of the phenanthroline molecule. This ligand is significantly not planar, as shown by the angles between the three rings listed in Table 2. The molecule has a pseudo mirror plane perpendicular to the central ring and passing through the midpoints of C(2)–C(3) and C(9)–C(10) (C(2,3); C(9,10)). The angle between the Ir–C(2,3) and C(2,3)–C(9,10) lines is 1.3(2)°. The N–N distance of 2.640(6) Å is within the range reported for these molecules (2.63–2.78 Å) [18]. The two halves of the molecule show different bond distances patterns: that involving the C(3),C(4) ⋯ C(9) atoms has bond lengths in good agreement with those given by Frenz and Ibers [18] and the delocalization seems to be lower than that in the other half, formed by the N(1), C(2), C(10) ⋯ C(14) atoms. The reason may be that two atoms in the first half are involved in the following short intermolecular contacts [16] C(12) ⋯ O(2(i)) 3.223(9), H(12) ⋯ O(2(i)) 2.30(8) Å, C(12)–H(12) ⋯ O(2(i)) 138(6)°, C(14) ⋯ O(1(ii)) 3.200(8), H(14) ⋯ O(1(ii)) 2.35(8) Å, C(14)–H(14) ⋯ O(1(ii)) 145(7)° [$i = 1 - x, -y, 1 - z$; $ii = 1/2 + x, 1/2 - y, 1/2 + z$]. These intermolecular contacts, are probably responsible for the low ν(CO) frecuencies observed in the IR spectrum.

TABLE 2

MAIN TORSION ANGLES AND ANGLES BETWEEN THE LEAST SQUARES SETS (PLANES OR LINES(+) BY THE REFERRED ATOMS (°)

C(1')–C(2')–C(3')–C(4')	−81.2(9)	
C(2')–C(3')–C(4')–C(5')	15.9(11)	
C(3')–C(4')–C(5')–C(6')	58.5(10)	
C(4')–C(5')–C(6')–C(7')	5.7(10)	
C(5')–C(6')–C(6')–C(7')	−88.4(9)	
C(6')–C(7')–C(8')–C(1')	15.8(10)	
C(7')–C(8')–C(1')–C(2')	62.1(9)	
C(8')–C(1')–C(2')–C(3')	−3.0(9)	
N(1)–Ir–C(15)–C(16)	104.7(4)	
N(4)–Ir–C(15)–C(16)	27.0(4)	
N(1)–Ir–C(15)–C(18)	−25.2(5)	
N(4)–Ir–C(15)–C(18)	−103.0(5)	
C(1,2)–Ir–C(15)–C(16)	−160.6(4)	
C(5,6)–Ir–C(15)–C(16)	−69.2(4)	
C(1,2)–Ir–C(15)–C(18)	69.4(5)	
C(5,6)–Ir–C(15)–C(18)	160.8(4)	
Ir–C(15)–C(16)–O(1)	87.2(6)	
Ir–C(15)–C(16)–C(17)	−96.7(6)	
Ir–C(15)–C(18)–O(2)	88.6(8)	
Ir–C(15)–C(18)–C(19)	−90.6(7)	
C(15)–C(16)–O(1)–C(17)	C(15)–C(18)–O(2)–C(19)	27.7(3)
N(1)–N(4)–Ir	C(1,2)[a]–C(5,6)[a]–Ir	152.0(2)
N(1)–N(4)–Ir	Ir–C(15(+))	18.1(5)
C(1,2)[a]–C(5,6)[a]–Ir	Ir–C(15(+))	23.9(3)
C(2)–C(3)–C(8)–C(9)–C(10)–C(11)	C(3)–N(4)–C(5)–C(6)–C(7)–C(8)	2.3(2)
C(2)–C(3)–C(8)–C(9)–C(10)–C(11)	N(1)–C(2)–C(11)–C(12)–C(13)–C(14)	1.3(2)
N(1)–N(4)–Ir	C(2)–C(3)–C(8)–C(9)–C(10)–C(11)	1.5(2)

[a] C(1,2) and C(5,6) are the midpoints of the C(1')–C(2') and C(5')–C(6') bonds.

Experimental

C,H and N analysis were carried out with a Perkin–Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets or dichloromethane solutions between sodium chloride windows, and calibrated with polyethylene. Conductivities were measured at 20°C in ca. 4×10^{-4} M acetone solutions using a Philips 9501/01 conductimeter. All reactions were carried out under dry nitrogen, and the solvents were dried by standard methods and distilled before use.

Preparation of [Ir(acac-C^3)(COD)(phen)] (I)
The two routes are described below.

(i) Addition of phen (259.8 mg, 1.44 mmol) to a solution of [Ir(acac)(COD)] (575.8 mg, 1.44 mmol) in 10 ml of ether led to immediate precipitation of a dark-blue solid. After 1 h stirring, the solid was filtered off, washed with ether, and vacuum-dried. Yield: 700 mg (84%). Analysis: Found: C, 51.66; H, 4.51; N, 5.21. $C_{25}H_{27}N_2O_2Ir$N$_2$O$_2$ calcd.: C, 51.80; H, 4.69; N, 4.83%.

(ii) Tl(acac) (58.0 mg, 0.19 mmol) was added to a solution of [Ir(COD)(phen)]Cl (96.6 mg, 0.19 mmol) in 10 ml of dichloromethane. After 1 h stirring the TlCl was filtered off, the dark-blue filtrate was vacuum-concentrated to ca. 1 ml, and 10 ml of pentane was added. The solid was filtered off, washed with ether, and vacuum-dried. Yield: 60 mg (58%). Its IR spectrum was identical to that of the sample described in (i) above.

Reaction of I with protic acids
(i) Reaction with HCl. Aqueous HCl (12.9 µl, 0.15 mmol) in 5 ml of ethanol was added to a solution of complex I (87.3 mg, 0.15 mmol) in 5 ml of ethanol. After 1 h stirring along with the green solution there was a green solid in suspension. Addition of 20 ml of ether led to the complete precipitation of the green complex, which was filtered off, washed with ether and vacuum-dried. It was identified as [Ir(COD)(phen)]Cl Yield: 58.0 mg (75%).

(ii) Reaction with HBF$_4$. Addition of 14.7 µl of HBF$_4$ (54% in ether) to a suspension of complex I (61.1 mg, 0.10 mmol) in 20 ml of ether gave a green solid. After 8 h stirring the formed solid was filtered off, washed with ether, and vacuum-dried. It was identified as [Ir(COD)(phen)]BF$_4$. Yield: 33.1 mg (55%). Analysis: Found: C, 41.26; H, 3.61; N, 4.45. $C_{20}H_{20}N_2IrBF_4$ calcd.: C, 42.33; H, 3.55; N, 4.94%.

(iii) Reaction with HClO$_4$. Addition of aqueous HClO$_4$ (30.0 µl, 0.28 mmol) in 5 ml of ether to a solution of complex I (162.0 mg, 0.28 mmol) in 5 ml of dichloromethane caused immediate precipitation of a green solid, which were filtered off, washed with ether, and vacuum-dried. It was identified as [Ir(COD)(phen)]ClO$_4$. Yield: 151 mg (93%).

Reaction of I with [Rh(COD)$_2$]ClO$_4$
Addition of I (70.5 mg, 0.12 mmol) in 10 ml of dichloromethane to a solution of [Rh(COD)$_2$]ClO$_4$ (50.9 mg, 0.12 mmol) in 20 ml of dichloromethane gave a green precipitate. After 2 h stirring 20 ml of ether were added, and the solid was filtered off, washed with ether, and vacuum-dried. It was identified as [Ir(COD)(phen)]ClO$_4$.

TABLE 3

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formulae	[Ir(acac-C^3)(COD)(phen)]
Crystal habit	Prismatic. Trapezium basis
size (mm)	$0.09 \times 0.14 \times 0.30$
Symmetry	$2/m$. Monoclinic $P2_1/n$
Unit cell determination	θ(Cu) < 45°
least-squares fit	63 reflexions
Unit cell determination (Å)	9.4347(2), 16.0895(4), 13.8334(4), β 99.749(2)°
Packing: V(Å^3), Z	2069.58(9), 4
D(g cm^{-3}), (F(000))	1.861, 1136
Diffraction data	
Radiation & technique	Cu-K_α. 4-Circle PW 1100 Philips Diffractometer
	Bisecting geometry
Monochromator	Graphite oriented
Orientation	h-h0: $\chi \sim 60°$, $\phi \sim 205°$; 0-kk: $\chi \sim 4°$, $\phi \sim 165°$
Collection mode	θ < 65°
($w/2\theta$, 1° × 1° det. apertures)	1.40° scan width, 1 min/reflex
Total independent data	3498
Observed data: $3\sigma(I)$	3281
Stability	Two reflexions every 90 min. No variation
Absorption: faces	$\pm$(0 5 −6), $\pm$(2 −1 −1), (0 5 2), (−1,12,10)
μ, Min-max transmission	124.45 cm, 0.154–0.450
Solution and refinement	[19] XRAY 70 System. Univac 1100/80
Solution mode	Patterson
Refinement mode	Least-squares on F's. Observed reflexions
	only. 4 blocks for the final.
Final shift/error	0.18
Parameters: no. variables	370
degrees of freedom	2911
ratio of freedom	8.9
w-scheme	Empirical, so as to give no trends in $\langle w\Delta^2 \rangle$ vs.
	$\langle F_o \rangle$ or $\langle \sin\theta/\lambda \rangle$
ΔF final	Some maxima up to 1.4 eÅ^{-3} near the Ir
	position
Max. thermal values	U_{22}(C19) = 0.14(1) Å^2
R, R_w	0.043, 0.047
Atomic factors	[20] International Tables for X-Ray Crystallo-
	graphy. Neutral atoms. Real part of anomalous
	dispersion applied for Ir.

TABLE 4

NORMAL PROBABILITY RESULTS

Type	$|F_o|$ vs. $|F_c|$
Total points	3498
Excluded from fit	41
Total R	0.045
Slope	0.975(1)
Intercept	0.106(1)
Correlation	0.997
D_p max.	± 3.0

TABLE 5. FRACTIONAL ATOMIC COORDINATES

Atom	X	Y	Z
Ir	0.09693(2)	0.23173(1)	0.39589(1)
N(1)	0.20824(47)	0.13077(28)	0.46640(31)
C(2)	0.15690(53)	0.05541(34)	0.43789(37)
C(3)	0.02974(55)	0.05393(36)	0.36288(39)
N(4)	−0.02315(47)	0.12923(29)	0.32916(32)
C(5)	−0.13562(62)	0.12868(42)	0.25585(45)
C(6)	−0.20204(72)	0.05571(48)	0.21766(51)
C(7)	−0.15137(75)	−0.01974(46)	0.25423(53)
C(8)	−0.03008(69)	−0.02256(37)	0.32800(44)
C(9)	0.03504(85)	−0.09792(41)	0.36795(55)
C(10)	0.15607(82)	−0.09676(39)	0.43790(53)
C(11)	0.21748(67)	−0.02007(36)	0.47519(40)
C(12)	0.34114(71)	−0.01466(42)	0.54777(45)
C(13)	0.39559(72)	0.06283(46)	0.57585(46)
C(14)	0.32953(60)	0.13385(42)	0.53423(40)
C(15)	0.24601(61)	0.22965(34)	0.26972(42)
C(16)	0.15443(58)	0.19330(43)	0.18334(42)
C(17)	0.16379(86)	0.10270(47)	0.16040(57)
C(18)	0.37973(71)	0.19170(57)	0.31326(47)
C(19)	0.49387(97)	0.25050(101)	0.36166(77)
O(1)	0.07422(66)	0.23724(39)	0.12561(36)
O(2)	0.40766(66)	0.11670(45)	0.31504(44)
C(1')	0.11340(62)	0.29011(36)	0.53377(43)
C(2')	0.21160(75)	0.32885(39)	0.47768(46)
C(3')	0.18018(95)	0.41319(43)	0.43161(57)
C(4')	0.07773(95)	0.41336(47)	0.33526(60)
C(5')	−0.00608(73)	0.33495(39)	0.31462(48)
C(6')	−0.09666(70)	0.30332(48)	0.37700(48)
C(8')	−0.02253(79)	0.33031(55)	0.55547(53)
C(7')	−0.12888(84)	0.34910(58)	0.46634(59)
H(5)	−0.166(8)	0.186(5)	0.224(5)
H(6)	−0.280(13)	0.058(8)	0.167(9)
H(7)	−0.193(9)	−0.061(6)	0.231(6)
H(9)	−0.013(8)	−0.152(5)	0.339(6)
H(10)	0.204(8)	−0.156(6)	0.450(6)
H(12)	0.391(8)	−0.074(6)	0.578(6)
H(13)	0.479(10)	0.065(6)	0.629(7)
H(15)	0.370(9)	0.189(6)	0.551(6)
H(16)	0.247(7)	0.290(5)	0.277(5)
H(17A)	0.265(9)	0.087(6)	0.138(6)
H(17B)	0.083(10)	0.088(6)	0.104(7)
H(17C)	0.118(25)	0.073(16)	0.198(18)
H(19A)	0.467(9)	0.307(6)	0.360(6)
H(19B)	0.570(21)	0.229(10)	0.322(13)
H(19C)	0.510(15)	0.256(8)	0.443(11)
H(1')	0.171(11)	0.258(7)	0.579(8)
H(2')	0.310(7)	0.312(4)	0.501(4)
H(3'A)	0.247(12)	0.456(7)	0.456(7)
H(3'B)	0.157(11)	0.454(6)	0.468(7)
H(4'A)	0.134(0)	0.427(0)	0.279(0)
H(4'B)	0.029(8)	0.461(6)	0.333(5)
H(5')	−0.024(13)	0.319(8)	0.236(10)
H(6')	−0.161(10)	0.274(5)	0.361(6)
H(7'A)	−0.023(0)	0.367(0)	0.602(0)
H(7'B)	−0.038(14)	0.289(9)	0.596(9)
H(8'A)	−0.230(14)	0.344(9)	0.473(9)
H(8'B)	−0.116(19)	0.420(13)	0.441(13)

Yield: 37.4 mg (53%). The filtrate was evaporated to dryness, the residue was treated with pentane (10 ml) and the resulting suspension was filtered. The yellow filtrate was vacuum-concentrated to ca. 0.5 ml and 10 ml of methanol were added. The solid was filtered off, washed with methanol, and vacuum-dried. It was identified as [Rh(acac)(COD)]. Yield: 24.6 mg (65%).

Reaction of I with [MCl(COD)]₂

(i) M = Rh. A mixture of [RhCl(COD)]₂ (101.4 mg, 0.20 mmol), complex I (238.4 mg, 0.40 mmol) and 30 ml of dichloromethane was stirred for 12 h and 20 ml of ether were added. The resulting green solid was filtered off, washed with ether, and vacuum-dried. It was identified as [Ir(COD)(phen)]Cl. Yield: 144.0 mg (68%). The filtrate was vacuum-evaporated to dryness and the residue was treated with 10 ml of pentane. The resulting suspension was filtered, the yellow filtrate vacuum-concentrated to ca. 0.5 ml and 10 ml of methanol were added. The formed solid was filtered off, washed with methanol, and vacuum-dried. It was identified as [Rh(acac)(COD)]. Yield: 25.0 mg (19%).

(ii) M = Ir. Addition of [IrCl(COD)]₂ (84.6 mg, 0.125 mmol) in 5 ml of dichloromethane to a solution of complex I (146.0 mg, 0.25 mmol) in 5 ml of dichloromethane led to immediate precipitation of a green solid. After 1 h stirring the suspension was vacuum-concentrated to ca. 5 ml and 20 ml of hexane were added. The solid was filtered off, washed with hexane, and vacuum-dried. It was identified as [Ir(COD)(phen)]Cl. Yield: 105.0 mg (80%). The yellow filtrate was vacuum-concentrated until a yellow precipitate separated. Methanol was added and the solid was filtered off, washed with methanol, and vacuum-dried. It was identified as [Ir(acac)(COD)]. Yield: 45.0 mg (45%).

X-Ray analysis

Crystal analysis details are given in Table 3. The consistency of the weighting scheme used in the last cycles of refinement was tested by mean of a δR_w plot [21] (Table 4). Table 5 shows the final atomic coordinates with the numbering system given in Fig. 1. A list of structure factors and thermal parameters can be obtained from the authors on request.

References

1 (a) A.G. Swallow and M.R. Truter, Proc. Roy Soc., A, 254(1960)205; (b) A.G. Swallow and M.R. Truter, Proc. Roy Soc., A, 266(1962)527.
2 (a) D. Gibson, Coord. Chem. Rev., 4(1969)225; (b) G. Hulley, B.F.G. Johnson and J. Lewis, J. Chem. Soc., (1970)1732; (c) S. Baba, T. Ogura and S. Kawaguchi, Inorg. Nucl. Chem. Letters, 7(1971)1195; (d) G. Ingrosso, A. Immirzi and L. Porri, J. Organomet. Chem., 60(1973)C35; (e) M. Morike, Y. Kai, N. Yasuoka and N. Kasai, J. Organomet. Chem., 72(1979)441; (f) M.A. Bennett and T.R.B. Mitchell, Inorg. Chem., 15(1976)2936; (g) W. Rigby, H.-B.Lee, P.M. Bailey, J.A. McCleverty and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1979)387; (h) B.K. Sahu and B.K. Mohapatra, J. Indian Chem. Soc., (1982)732.
3 (a) R. Usón, L.A. Oro and M.J. Fernández, J. Organomet. Chem., 193 (1980)127; (b) R. Usón, L.A. Oro, D. Carmona and M.A. Esteruelas, Inorg. Chim. Acta, 73(1983)275; (c) M.A. Garralda and L.A. Oro, Transition Met. Chem., 5(1980)65.
4 G. Mestroni, A. Camus and G. Zassinovich, J. Organomet. Chem., 73 (1974)119.
5 (a) G. Mestroni, G. Zassinovich and A. Camus, Inorg. Nuclear Chem. Letters, 11(1975)359; (b) N. Bresciani-Pahor, M. Calligaris, G. Nardin and P. Delise, J. Chem. Soc., Dalton Trans., (1976)762.

6 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd. Edn., Wiley, Int. Sc. New York, 1970, p. 247.

7 B.F.G. Johnson in J.C. Bailar, H.J. Emeléus, R. Nyholm and A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Pergamon Press, Oxford, 1973, Vol. 4, p. 751.

8 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1965)4997.

9 (a) J. Lewis and C. Oldman, J. Chem. Soc., A, (1966)1456; (b) N. Yanase, Y. Nakamura and S. Kawaguchi, Inorg. Chem., 17(1978)2874.

10 R. Usón, L.A. Oro and F. Ibáñez, Rev. Acad. Ciencias, Zaragoza, 31(1975)169.

11 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957)4735.

12 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 3156.

13 J.L. Herde, J.C. Lambert and C.V. Senoff, Inorg. Synth., 15 (1974)19.

14 C.K. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).

15 M.R. Churchill and S.A. Bezman, Inorg. Chem., 11(1972)2243; 12(1973) 260; 12(1973)531.

16 B.K. Vainshtein, V.M. Fridkin and V.L. Indenbom, Modern Crystallography II, Structure of Crystals, Springer-Verlag, Berlin, 1972.

17 Chem. Soc., Spec. Publ. no. 18 S14s(1965).

18 B.A. Frenz and J.A. Ibers, Inorg. Chem., 11(1972)1109.

19 J.M. Stewart, F.A. Kundell and J.C. Baldwin. The X-Ray System. Computer Science Center, Univ. of Maryland, College Park, Maryland, 1970.

20 International Tables for X-Ray Crystallography. Vol. IV. Kynoch Press, Birmingham, 1974.

21 S.C. Abrahams and E.T. Keve, Acta Cryst., A27(1971)157.