Journal of Organometallic Chemistry, 276 (1984) 67–77
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

AZULENE AS A LIGAND IN CATIONIC RHODIUM AND IRIDIUM COMPLEXES. CRYSTAL STRUCTURE OF [Rh(TFB)(az)]PF_6

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(Received April 5th, 1984)

Summary

Rhodium or iridium complexes of formula $[M(diolefin)(az)]^+$ have been prepared by treating $[MCl(diolefin)]_2$ complexes with silver salts and azulene, and also by treating $[Rh(diolefin)_2]^+$ with azulene. The reactions of some representative complexes have been studied. Reaction of $[M(C_5Me_5)(Me_2CO)_3]^{2+}$ with azulene appears to give dinuclear diazulene cationic complexes. The crystal structure of compound [Rh(TFB)(az)]PF_6 has been solved by X-ray methods. It crystallizes in the space group $P2_1/c$ with cell constants 8.4241(4), 16.6911(8), 15.0026(7) Å, 95.897(6)°. Refinement gave $R = 0.027$ and $R_w = 0.032$ for 2991 observed reflexions. The Rh atom is coordinated to the five-membered ring, with Rh–C distances shortest for the atoms which are *trans* to the diolefinic double bonds. The bonding scheme within the azulene ligand differs from that in the parent hydrocarbon.

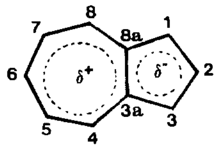
Introduction

The synthesis and crystal structures of cationic rhodium(I) and iridium(I) complexes with arene ligands have been extensively studied [1–9], but few examples involving polycyclic arene ligands have been described [10–12]. In all these arene complexes the benzenoid aromatic ligands are η^6-bonded to the metal atom.

Pursuing our interest in this area, we have studied the coordination ability towards rhodium or iridium of the nonbenzenoid aromatic compound azulene. This

0022-328X/84/$03.00

ligand has a significant dipole moment, with the five-membered ring at the negative end of the dipole



The structure of azulene itself has been determined by both X-ray and electron-diffraction measurements [13,14], and structural studies on azulene carbonyl metal complexes [15,16] have shown that a dominant feature of the azulene–metal bonding is the utilization of the five-membered ring as a π-cyclopentadienyl ligand, along with a general tendency to form dinuclear complexes. We now report the synthesis and reactivity of some cationic rhodium or iridium complexes containing the azulene ligand, and the determination of the crystal structure of $[Rh(TFB)(az)]PF_6$. As far as we know this is the first crystallographic determination of the structure of a mononuclear azulene-metal complex.

Results and discussion

Addition of stoichiometric amounts of the azulene ligand to acetone solutions of $[Rh(diolefin)_2]^+$ (diolefin = tetrafluorobenzobarrelene, 1,5-cyclooctadiene or 2,5-norbornadiene [17]) gives deep red solutions from which red solids can be isolated. An alternative and more direct route involves the treatment with azulene (az) of $[Rh(diolefin)(Me_2CO)_x]^+$ complexes obtained by treating $[RhCl(diolefin)]_2$ with $AgPF_6$ or $AgClO_4$ [1], (eq. 1).

$$1/2[RhCl(diolefin)]_2 \xrightarrow[Me_2Co]{AgA} [Rh(diolefin)(Me_2CO)_x]A \xrightarrow{az} [Rh(diolefin)(az)]A$$

$(A = PF_6^-$, diolefin = TFB (I), COD (II), NBD (III), DQ(duroquinone) (IV)

$(A = ClO_4^-$, diolefin = Me_3TFB (trimethyltetrafluorobenzobarrelene) (V))

The related iridium derivative $[Ir(COD)(az)]ClO_4$ can be prepared similarly by reaction of $[IrCl(COD)]_2$ with $AgClO_4$ and azulene. These azulene complexes are red, except for the duroquinone derivative which is green. Table 1 gives analytical and physical data for the isolated complexes. All of them are air-stable solids and behave as 1/1 electrolytes. Their IR spectra show the absorptions due to the uncoordinated anion (PF_6^-: ca. 840 and 560 cm^{-1}; ClO_4^- 1100 and 620 cm^{-1}), along with the bands characteristics of the coordinated organic ligands.

The ^1H NMR spectra of complexes I and II in deuteroacetone are rather broad. They show the expected resonances of the coordinated diolefin (e.g., TFB: δ 4.53 (4H, CH=CH) and 6.77 (2H, CH) ppm), and the azulene ligand. The protons of the seven-membered ring show values (ca. 7.5–8.5 ppm) very close to those observed for the free ligand, but there is a significant shift for the H(1)–H(3) protons due to coordination through the electron-rich five-membered ring. Thus, H(1)–H(3) protons appear at δ 5.23 ppm (complex I) or 5.19 ppm (complex II) (free ligand: 7.85 (H(2)) and 7.47 (H(1,3)) ppm).

The $[Rh(diolefin)(az)]^+$ complexes usually react readily with several types of

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, YIELD AND COLOUR FOR THE COMPLEXES

Complex	Analyses (Found(calc.)(%))		Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	Colour
	C	H			
[Rh(TFB)(az)]PF_6 (I)	43.92 (43.88)	2.48 (2.34)	126	73	red
[Rh(COD)(az)]PF_6 (II)	44.32 (44.65)	4.14 (4.16)	127	68	red
[Rh(NBD)(az)]PF_6 (III)	43.21 (43.61)	3.57 (3.44)	123	72	red-violet
[Rh(DQ)(az)]PF_6 (IV)	43.74 (44.46)	3.64 (3.73)	134	87	green
[Rh(Me_3TFB)(az)]ClO_4 (V)	50.00 (50.15)	3.37 (3.20)	139	80	red
[Ir(COD)(az)]ClO_4 (VI)	43.74 (44.46)	3.64 (3.73)	141	80	red-violet
[Rh(CO)(PPh_3)(az)]ClO_4 (VII)	55.34 (56.11)	3.54 (3.73)	123	85	red

ligands with displacement of the coordinated azulene. We report below some representative reactions involving complexes I and II. Addition of the calculated amount of some P-donor or N-donor ligands to solutions of complexes I or II gives the previously described complexes [Rh(diolefin)L_2]PF_6 (L = PPh_3 [18] or py [19]) or [Rh(diolefin)(L–L)]PF_6 (L–L = diphos [20] or phen [21]), but an excess of acetonitrile (or liquid arenes such as mesitylene, or 1,5-cyclooctadiene) is required to displace the coordinated azulene according to the following equilibrium:

$$[Rh(diolefin)(az)]PF_6 + 2L\ (or\ L{-}L) \rightleftarrows [Rh(diolefin)L_2]PF_6 + azulene$$

$$(L = MeCN,\ diolefin = TFB;\ L{-}L = COD\ or\ C_6H_3Me_2,\ diolefin = COD)$$

Treatment of complex II with pyrazole or acetylacetone (in the presence of triethylamine) leads to formation of the neutral complexes $[Rh(pz)(COD)]_2$ [22] or Rh(acac)COD [23].

In contrast, bubbling of carbon monoxide through a dichloromethane solution of I or II does not displace the coordinated azulene. A complex of formula $[Rh(az)(CO)_2]PF_6$ is probably formed in this reaction, and also on treating $[RhCl(CO)_2]_2$ with $AgPF_6$, but the isolated complex was not analytically pure (ν(CO) 2100s and 2040s,br cm^{-1}, Nujol). No further reaction was observed upon addition of triphenylphosphine. However a monocarbonyl complex of formula $[Rh(CO)(PPh_3)(az)]ClO_4$ (ν(CO) 2010 cm^{-1}, Nujol) was prepared by reaction of $[RhCl(CO)(PPh_3)]_2$ [24] with $AgClO_4$.

Finally, an interesting reaction takes place when $[M(C_5Me_5)(Me_2CO)_3]^{2+}$ (M = Rh, Ir) is treated with azulene. The isolated green (M = Rh) or blue (M = Ir) solids have complex ^1H NMR spectra and analyse as $[(C_5Me_5)_2M_2(C_{10}H_8)_2]A_2$ (A = PF_6^- or ClO_4^-), suggesting the posibility that they involve a cation containing a 4,4'-diazulene ligand in which each of the five-membered rings is bonded to a $M(C_5Me_5)$ group. Related structures have been reported for dinuclear-transition metal complexes [15,16,25]. The proposed dinuclear formulation is supported by conductivity measurements on $[(C_5Me_5)_2Rh_2(C_{10}H_8)_2](PF_6)_2$ in acetone at various concentrations ($10^{-3} - 3 \times 10^{-4}$ M). The value of B in Onsager's equation ($\Lambda_e = \Lambda_\infty - B\sqrt{C}$) [26] is -1370.

Crystal structure of complex I

The structure of complex I involves a mononuclear rhodium(I) cationic complex and hexafluorophosphate counter ion. Selected bond distances and angles and torsion angles are given in Table 2 and 3, respectively. A view of the complex with the atomic numbering is shown in Fig. 1. The rhodium atom is coordinated only to the five-membered ring (see Table 2 and Fig. 2a). The Rh–C distances (five-membered ring) range is 2.229(4)–2.282(5) Å, 9.4σp where $\sigma p = (\sigma 1^2 + \sigma 2^2)^{1/2}$, with Rh–C(21) < Rh–C(23) ~ Rh–C(24) < Rh–C(30) ~ Rh–C(22) a different pattern to that previously reported [16,27,28].

The bonding within the azulene ligand differs from that observed for the parent hydrocarbon [13,14,29]. The C(25)–C(26) and C(27)–C(28) bonds show values greater than corresponding double bonds [28] and shorter than aromatic bonds, while the C(21)–C(30) and C(23)–C(24) bonds are longer than aromatic bonds. The length of the bond shared by the two rings is consistent with a C_{sp^2}–C_{sp^2} (1.465(5) Å) [30] and shorter than that of the corresponding bond in the uncoordinated azulene. The C(21)–C(30) and C(23)–C(24) bonds and the bond shared by the two rings are

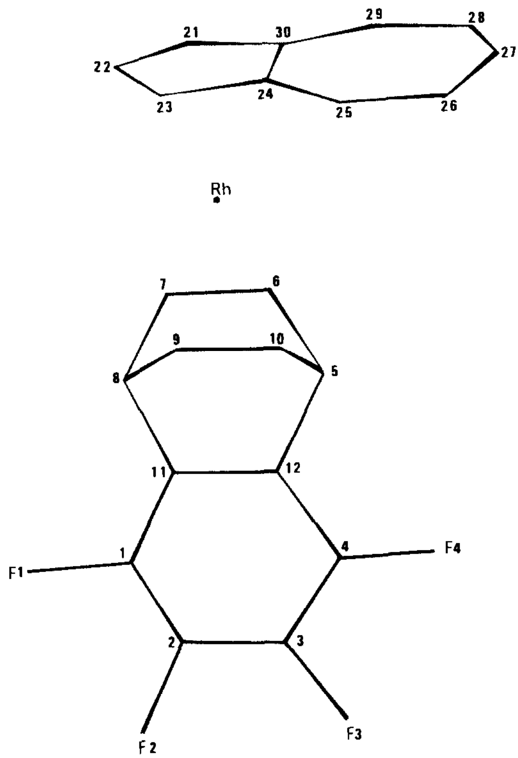


Fig. 1. A perspective view of the complex I showing the atomic numbering.

those associated with the shorter Rh–C lengths, which are *trans* to the diolefinic double bonds (see Fig. 2a), and this implies a change in the bonding within the uncoordinated azulene. In the five- and seven-membered rings the bond angles range are (107.1(3)–109.5(4))° and (127.4(4)–130.3(5))°, respectively, compared with the theoretical values of 108 and 128.47° for regular planar rings.

The distance of the Rh from the five-membered least-squares mean plane is 1.898(2) Å, the same value as the Rh–G, where G is the centroid of this ring.

The five- and seven-membered rings show small deviations from planarity (see

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°)

Rh–C(6)	2.159(4)	C(5)–C(10)	1.533(5)
Rh–C(7)	2.167(4)	C(5)–C(12)	1.522(6)
Rh–C(9)	2.153(4)	C(6)–C(7)	1.397(6)
Rh–C(10)	2.155(4)	C(7)–C(8)	1.534(5)
Rh–C(21)	2.229(4)	C(8)–C(9)	1.528(6)
Rh–C(22)	2.282(5)	C(8)–C(11)	1.523(6)
Rh–C(23)	2.243(4)	C(9)–C(10)	1.388(6)
Rh–C(24)	2.252(3)	C(11)–C(12)	1.373(7)
Rh–C(30)	2.267(4)	C(21)–C(22)	1.419(6)
Rh–G [a]	1.898(2)	C(21)–C(30)	1.441(6)
C(1)–C(2)	1.404(8)	C(22)–C(23)	1.393(7)
C(1)–C(11)	1.384(7)	C(23)–C(24)	1.435(5)
C(1)–F(1)	1.339(7)	C(24)–C(25)	1.401(6)
C(2)–C(3)	1.365(14)	C(24)–C(30)	1.464(5)
C(2)–F(2)	1.360(9)	C(25)–C(26)	1.371(7)
C(3)–C(4)	1.363(10)	C(26)–C(27)	1.397(7)
C(3)–F(3)	1.342(7)	C(27)–C(28)	1.362(8)
C(4)–C(12)	1.380(6)	C(28)–C(29)	1.389(7)
C(4)–F(4)	1.356(8)	C(29)–C(30)	1.402(6)
C(5)–C(6)	1.529(6)		
C(11)–C(1)–F(1)	122.0(4)	C(5)–C(10)–C(9)	113.1(3)
C(2)–C(1)–F(1)	119.7(5)	C(1)–C(11)–C(8)	125.8(4)
C(2)–C(1)–C(11)	118.3(6)	C(8)–C(11)–C(12)	114.2(4)
C(1)–C(2)–F(2)	117.4(6)	C(1)–C(11)–C(12)	120.0(4)
C(1)–C(2)–C(3)	121.2(5)	C(5)–C(12)–C(11)	113.1(4)
C(3)–C(2)–F(2)	121.5(5)	C(4)–C(12)–C(11)	120.5(4)
C(2)–C(3)–F(3)	119.0(7)	C(4)–C(12)–C(5)	126.5(5)
C(2)–C(3)–C(4)	119.6(5)	C(22)–C(21)–C(30)	107.8(4)
C(4)–C(3)–F(3)	121.5(8)	C(21)–C(22)–C(23)	109.1(4)
C(3)–C(4)–F(4)	118.3(4)	C(22)–C(23)–C(24)	109.5(4)
C(3)–C(4)–C(12)	120.5(6)	C(23)–C(24)–C(30)	106.3(3)
C(12)–C(4)–F(4)	121.2(4)	C(23)–C(24)–C(25)	125.3(4)
C(10)–C(5)–C(12)	108.1(3)	C(25)–C(24)–C(30)	128.3(3)
C(6)–C(5)–C(12)	108.4(3)	C(24)–C(25)–C(26)	127.4(4)
C(6)–C(5)–C(10)	99.8(3)	C(25)–C(26)–C(27)	129.0(5)
C(5)–C(6)–C(7)	113.3(4)	C(26)–C(27)–C(28)	130.3(5)
C(6)–C(7)–C(8)	112.7(3)	C(27)–C(28)–C(29)	129.2(5)
C(7)–C(8)–C(11)	107.8(3)	C(28)–C(29)–C(30)	127.5(4)
C(7)–C(8)–C(9)	100.1(3)	C(24)–C(30)–C(29)	127.5(4)
C(9)–C(8)–C(11)	107.9(3)	C(21)–C(30)–C(29)	125.1(4)
C(8)–C(9)–C(10)	113.3(3)	C(21)–C(30)–C(24)	107.1(3)

[a] G is the centroid of the five-membered ring.

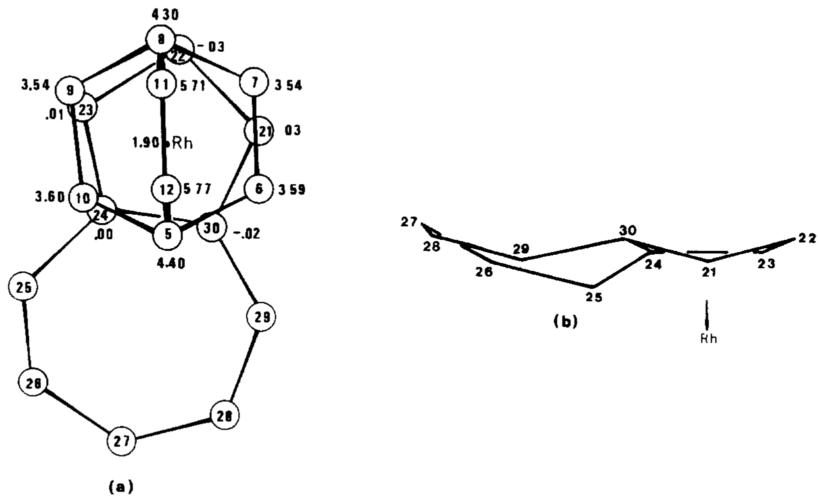


Fig. 2. (a) Complex I projected on the mean squares plane of the five-membered ring, with the distances (Å) of the selected atoms from this plane. (b) Same as 2a but viewed laterally. (Vertical deviations are greatly exaggerated for sake of clarity; the actual distortions are very small).

Fig. 2a and Table 3), they have χ^2 values of 123.9 and 584.1 compared with the tabulated values of 5.99 and 9.49, respectively. The angle between the two mean least-squares planes is 1.5(1)° (see Fig. 2b).

The octahedral PF_6^- anion is disordered between two different orientations, and shows P–F bond distances (range and weighted means) of (1.534(6)–1.616(5)), 1.577(2) Å and (1.339(31)–1.772(30)), 1.613(11) Å for the groups with population parameters pp1 = 0.74(2) and pp2 = 1 − pp1 respectively. The corresponding range of bond angles with weighted means are (86.2(4)–94.3(4)), 89.7(1)°; (173.0(4)–176.0(4)), 175.0(2)° and (80.6(10)–100.6(19)), 93.7(4)°; (166.5(16)–170.7(17)), 168.1(10)°, respectively. The angle formed by the planes (F(11), F(12), F(13), F(14)) and (F(21), F(25), F(23), F(26)) is 33.0(7).

The TFB moiety shows the usual geometry (see Table 2 and 3) [4,5] and the packing in the crystal is wholly due to Van der Waals forces.

Experimental

The C and H analyses were carried out with a Perkin–Elmer 240B microanalyzer. Infrared spectra were recorded on a Perkin–Elmer 567 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets or in dichloromethane solution between NaCl plates. Conductivities were measured in ca. 5×10^{-4} *M* acetone solutions with a Philips 9501/01 conductimeter. The ^1H NMR spectra were recorded on a Varian XL-100 or XL-200 instrument relative to tetramethylsilane.

All reactions were carried out at room temperature and solvents were dried and distilled before use. The ligand azulene (99%) was purchased from Ega-Chemie (W. Germany). Tetrafluorobenzobarrelene (TFB) and its trimethyl derivative (Me_3TFB) were prepared by literature procedures [31].

TABLE 3

SELECTED TORSION ANGLES (°)

C(21)–C(22)–C(23)–C(24)	−4.0(5)
C(22)–C(23)–C(24)–C(30)	0.9(5)
C(23)–C(24)–C(30)–C(21)	2.4(4)
C(24)–C(30)–C(21)–C(22)	−4.8(5)
C(30)–C(21)–C(22)–C(23)	5.5(5)
C(24)–C(25)–C(26)–C(27)	4.2(8)
C(25)–C(26)–C(27)–C(28)	5.0(10)
C(26)–C(27)–C(28)–C(29)	−4.4(10)
C(27)–C(28)–C(29)–C(30)	−4.9(9)
C(28)–C(29)–C(30)–C(24)	7.8(7)
C(29)–C(30)–C(24)–C(25)	0.7(7)
C(30)–C(24)–C(25)–C(26)	−8.4(7)
C(5)–C(6)–C(7)–C(8)	−0.6(5)
C(6)–C(7)–C(8)–C(9)	−59.0(4)
C(7)–C(8)–C(9)–C(10)	59.7(4)
C(8)–C(9)–C(10)–C(5)	−0.3(5)
C(9)–C(10)–C(5)–C(6)	−59.4(4)
C(10)–C(5)–C(6)–C(7)	59.8(4)
C(5)–C(6)–C(7)–C(8)	−0.6(5)
C(6)–C(7)–C(8)–C(11)	53.6(5)
C(7)–C(8)–C(11)–C(12)	−54.0(5)
C(8)–C(11)–C(12)–C(5)	0.2(5)
C(11)–C(12)–C(5)–C(6)	53.5(4)
C(12)–C(5)–C(6)–C(7)	−53.1(4)
C(8)–C(9)–C(10)–C(5)	−0.3(5)
C(9)–C(10)–C(5)–C(12)	53.8(4)
C(10)–C(5)–C(12)–C(11)	−53.8(5)
C(5)–C(12)–C(11)–C(8)	0.2(5)
C(12)–C(11)–C(8)–C(9)	53.3(4)
C(11)–C(8)–C(9)–C(10)	−52.8(4)

Preparation of complexes of the type [Rh(diolefin)(az)]PF_6 (diolefin = TFB (I), COD (II), NBD (III), DQ (IV))

A suspension of 0.2 mmol of the dimer [RhCl(diolefin)]$_2$ [31–34] in ca. 15 ml of acetone was treated with 0.4 mmol of $AgPF_6$. After 20 min stirring, the solution which contained complex [Rh(diolefin)(Me_2CO)$_x$]PF_6, was filtered through kieselguhr into a solution of 0.4 mmol of azulene in ca. 10 ml of acetone. The deep red (green for IV) solution obtained was stirred for 30 min, the solvent was removed in vacuo to ca. 3 ml, and diethyl ether was added. The solid was filtered off, washed with diethyl ether, and vacuum-dried. The complexes were recrystallized from acetone/diethyl ether.

Preparation of the complex [Rh(Me_3TFB)(az)]ClO_4

A suspension of 81.4 mg (0.1 mmol) of the dimer [RhCl(Me_3TFB)]$_2$ [31] in acetone (15 ml) was treated with 41.5 mg (0.2 mmol) of $AgClO_4$ and 28.2 mg (0.22 mmol) of azulene. The mixture was stirred for 30 min in absence of light and then filtered through kieselguhr. The filtrate was concentrated under vacuum and diethyl ether was added to crystallize the complex.

TABLE 4

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	$[Rh(TFB)(az)]PF_6$
Crystal habit	Red, prismatic
Crystal size (mm)	0.14×0.20×0.32
Symmetry	2/*m* Monoclinic. $P2_1/c$
Unit cell determination:	
least-squares fit to	
θ(Cu) < 45°	41 reflexions
Unit cell dimensions (Å)	8.4241(4), 16.6911(8), 15.0026(7)
	β 95.897(6)°
Packing: $V(Å^3)$, Z	2098.3(2), 4
$D(g\ cm^{-3})$, M, $F(000)$	1.906, 602.22, 1184
$\mu(cm^{-1}$; min − Mx, transmissions.	83.95; 0.119–0.444 (applied to data)
Experimental data	
Radiation and technique	Cu-K_α, PW1100 Philips Diffractometer
	Bisecting geometry
Monochromator	Graphite oriented
Collection mode	$w/2\theta$, 1×1 deg. det. apertures, θ < 65°,
	1 min/refl, scan width of 1.5 deg.
Total independent data	3692
Observed data $I > 3\sigma(I)$	2991
Stability	Two reflexions every 90 min. no variation
Solution and refinement	
Solution mode	Patterson. X-Ray 70 System [37]
	VAX 11/750
Refinement mode	Least-squares on F's.
	Observed reflexions only.
	1 blocks in the final cycles.
Final shift/error	0.55
Parameters:	
no. of variables	418 (See text: extinction factor)
degrees of freedom	1873
ratio of freedom	7.2
Weighting scheme	Empirical as to give no trends in
	$\langle w\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin\theta/\lambda \rangle$.
Max. thermal values ($Å^2$)	$U_{22}(F_{24}) = 0.36(6)$
Final ΔF-peaks	0.44 $eÅ^{-3}$
Final R, R_w	0.027, 0.032
Atomic factors	International Tables for X-Ray
	Crystallography [38].

Preparation of the complex [Ir(COD)(az)]ClO₄

To a solution of 100.8 mg (0.15 mmol) of the dimer $[IrCl(COD)]_2$ [35] in 50 ml of dichloromethane was added 62.2 mg (0.3 mmol) of $AgClO_4$ and 38.5 mg (0.3 mmol) of azulene under argon. The mixture was stirred for 2 h under argon then filtered through kieselguhr. The red solution obtained was concentrated under reduced pressure and the complex was precipitated with diethyl ether and recrystallized from dichloromethane/diethyl ether.

TABLE 5

FINAL ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Rh	0.10640(3)	0.15192(2)	0.19559(2)
C(1)	0.4673(7)	−0.0469(3)	0.3945(3)
C(2)	0.4362(12)	−0.1033(3)	0.4600(4)
C(3)	0.2860(12)	−0.1133(3)	0.4848(3)
C(4)	0.1630(9)	−0.0695(3)	0.4436(3)
C(5)	0.0649(5)	0.0379(2)	0.3258(3)
C(6)	0.0771(5)	0.0266(2)	0.2256(3)
C(7)	0.2313(5)	0.0382(2)	0.2015(3)
C(8)	0.3512(5)	0.0604(3)	0.2815(3)
C(9)	0.2741(4)	0.1369(2)	0.3127(2)
C(10)	0.1210(5)	0.1250(2)	0.3367(2)
C(11)	0.3407(6)	−0.0032(2)	0.3535(3)
C(12)	0.1895(6)	−0.0152(2)	0.3773(3)
F(1)	0.6173(4)	−0.0354(2)	0.3752(2)
F(2)	0.5620(7)	−0.1461(3)	0.4990(3)
F(3)	0.2628(8)	−0.1668(2)	0.5489(2)
F(4)	0.0146(5)	−0.0816(2)	0.4686(2)
C(21)	0.0360(5)	0.1812(3)	0.0520(3)
C(22)	0.1659(5)	0.2324(3)	0.0806(3)
C(23)	0.1247(5)	0.2796(3)	0.1513(3)
C(24)	−0.0379(4)	0.2641(2)	0.1662(3)
C(25)	−0.1173(5)	0.2980(2)	0.2347(3)
C(26)	−0.2741(6)	0.2879(3)	0.2491(4)
C(27)	−0.3897(6)	0.2387(3)	0.2037(4)
C(28)	−0.3768(5)	0.1839(3)	0.1376(4)
C(29)	−0.2455(5)	0.1651(3)	0.0927(3)
C(30)	−0.0960(4)	0.2028(2)	0.1011(2)
P	0.64053(13)	−0.09744(7)	0.11524(7)
F(11)[a]	0.6058(9)	−0.1880(3)	0.0835(5)
F(12)[a]	0.8191(6)	−0.1176(5)	0.1359(5)
F(13)[a]	0.6630(12)	−0.0108(4)	0.1484(6)
F(14)[a]	0.4512(6)	−0.0822(5)	0.0933(4)
F(15)[a]	0.6012(8)	−0.1266(5)	0.2116(3)
F(16)[a]	0.6634(9)	−0.0764(5)	0.0157(4)
F(21)[b]	0.7772(33)	−0.1671(14)	0.1208(13)
F(22)[b]	0.7690(32)	−0.0460(12)	0.0596(15)
F(23)[b]	0.5372(46)	−0.0247(22)	0.1154(23)
F(24)[b]	0.5555(47)	−0.1341(31)	0.1783(29)
F(25)[b]	0.7666(26)	−0.0618(18)	0.2086(13)
F(26)[b]	0.5760(39)	−0.1339(22)	0.0406(20)
H(5)	−0.034(6)	0.029(3)	0.340(3)
H(6)	0.006(6)	0.004(3)	0.186(3)
H(7)	0.267(6)	0.019(3)	0.150(4)
H(8)	0.454(7)	0.067(3)	0.266(3)
H(9)	0.333(5)	0.182(3)	0.328(3)
H(10)	0.050(5)	0.161(3)	0.360(3)
H(21)	0.042(5)	0.139(3)	0.005(3)
H(22)	0.266(8)	0.233(4)	0.054(5)
H(23)	0.193(6)	0.319(3)	0.186(3)
H(25)	−0.051(6)	0.332(3)	0.274(4)
H(26)	−0.304(7)	0.321(4)	0.306(4)
H(27)	−0.493(8)	0.246(4)	0.223(4)
H(28)	−0.479(8)	0.152(4)	0.116(5)
H(29)	−0.253(6)	0.122(3)	0.052(4)

[a] Means population parameters pp1 = 0.0.74(2) and [b] pp2 = 1 − pp1.

Preparation of the complex $[Rh(az)(CO)(PPh_3)]ClO_4$

A suspension of 85.8 mg (0.1 mmol) of the dimer $[RhCl(CO)(PPh_3)]_2$ [24] in 15 ml of acetone was treated under argon with 41.5 mg (0.2 mmol) of $AgClO_4$ in acetone. The solution was filtered, then added to a solution of 26.5 mg (0.2 mmol) of azulene in acetone. The solution obtained was stirred for 20 min, then solvent was removed in vacuo to a small volume, and diethyl ether was added. The solid which separated was filtered off, washed with diethyl ether, and vacuum-dried.

Reaction of $[M(C_5Me_5)(Me_2CO)_3]^{2+}$ (M = Rh or Ir) with azulene

The general method used is illustrated for the reaction of $[Rh(C_5Me_5)$-$(Me_2CO)_3]A_2$ ($A = PF_6^-$ or ClO_4^-).

A suspension of 123.6 mg (0.2 mmol) of the dimer complex $[RhCl_2(C_5Me_5)]_2$ [36] in acetone (55 ml) was treated with 0.8 mmol of the silver salt ($AgClO_4$ or $AgPF_6$). The yellow solution containing the solvated complex $[Rh(C_5Me_5)(Me_2CO)_3]A_2$ was filtered into a solution of 51.3 mg (0.4 mmol) of azulene in acetone (10 ml). The mixture was stirred for 20 min and, the solvent was removed in vacuo, and diethyl ether was added to precipitate a green microcrystalline solid.

Analyses: $[(C_5Me_5)_2Rh_2(C_{10}H_8)_2]A_2$. ($A = PF_6^-$. Found: C, 47.50; H, 4.35. $C_{40}H_{46}F_{12}P_2Rh_2$ calcd.: C, 47.00; H, 4.53%. $A = ClO_4^-$. Found: C, 52.07; H, 4.73. $C_{40}H_{46}Cl_2O_8Rh_2$ calcd.: C, 51.60; H, 4.97%.)

Reactions of complexes I and II

About 0.05 mmol of the azulene complex was treated with the appropriate ligand in acetone or dichloromethane. The reactions were carried out at room temperature with vigorous stirring for 5 min. The displacement of the azulene ligand was indicated by the blue colour of the solution, and the formed diolefin complexes were precipitated by adding diethyl ether. The products were characterized mainly by comparison of their IR and NMR spectra with those of pure samples made by published methods.

X-ray analysis

Table 4 lists the crystal data and the refinement parameters. When the refinement had converged $R = 0.031$ and $R_w = 0.033$, the extinction parameter was refined [37] to a value of $G = 0.0034(1)$, giving rise to a significant decrease in the R values at low $\sin \sigma/\lambda$ [0.0–0.2] and at high F values [128–256].

The final atomic coordinates are listed in Table 5. Thermal parameters and structure factors tables can been obtained from the authors on request.

Acknowledgements

The authors thank "Programa de Cooperación con Iberoamérica, Ministerio de Educación y Ciencia, España", for financial support.

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