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DUROQUINONERHODIUM(I) COMPLEXES. CRYSTAL STRUCTURE OF $[Rh(DQ)(C_6H_5Me)]PF_6$

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Summary

The preparation of cationic arenerhodium(I) complexes of the type $[Rh(DQ)(arene)]PF_6$ (DQ = duroquinone; arene = $C_6H_{6-n}Me_n$, n = 0,1,2,3,4 or 6) and other duroquinone complexes with Group VB donor ligands are described. The crystal structure of $[Rh(DQ)(C_6H_5Me)]PF_6$ has been determined by X-ray diffraction. The compound crystallizes in the $P2_1/n$ space group, in a unit cell of dimensions a 15.9866(5), b 11.8438(3), c 9.9968(3) Å, β 98.473(4)°. The structure was solved by Patterson and Fourier methods and refined to R and R_w values of 0.062 and 0.076, respectively. The Rh atom is coordinated to a toluene group (η^6) and a duroquinone ligand (η^4), which eclipse each other. Both ligands are distorted to adopt boat-like conformations.

Introduction

Several neutral duroquinone (2,3,5,6-tetramethyl-1,4-benzoquinone; DQ) rhodium complexes have previously been obtained by treating the ligand itself, or in some cases dimethylacetylene, with certain rhodium complexes or salts [1–3]. Several studies, including X-ray structure determinations [4–6], have shown that duroquinone can be regarded as a 1,4-diolefin ligand. Pursuing our interest in cationic arene and/or diolefin rhodium complexes [7–9], we now report a new type of cationic duroquinonerhodium complexes, some related neutral derivatives, and the determination of the crystal structure of $[Rh(DQ)(C_6H_5Me)]PF_6$. Previous studies from these laboratories on cationic arenerhodium complexes have shown a general depar-

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ture from planarity of the coordinated arene ligand [10–13]. In the crystallographically characterized compound both 6-membered rings (arene and duroquinone) display non-planar conformations.

Results and discussion

The $[\mathrm{RhCl(DQ)}]_2$ compound [2] can be used as starting material for the synthesis of new cationic arenerhodium(I) complexes. Thus, an acetone suspension of $[\mathrm{RhCl(DQ)}]_2$ reacts with $\mathrm{AgPF_6}$ to give, as an intermediate, the solvate $[\mathrm{Rh(DQ)(Me_2CO)}_x]\mathrm{PF_6}$, which reacts with arene ligands to give $[\mathrm{Rh(DQ)(arene)}]\mathrm{PF_6}$ complexes (arene = $\mathrm{C_6Me_6}$ (I), 1,2,4,5-$\mathrm{C_6H_2Me_4}$ (II), 1,3,5-$\mathrm{C_6H_3Me_3}$ (III), 1,4-$\mathrm{C_6H_4Me_2}$ (IV), $\mathrm{C_6H_5Me}$ (V) or $\mathrm{C_6H_6}$ (VI)). Attempts to prepare analogous complexes with arene = $\mathrm{C_6H_5F}$, 1,4-$\mathrm{C_6H_4Cl_2}$ or 1,4-$\mathrm{C_6H_4ClMe}$, gave rise to the formation of an uncharacterized red amorphous material. Complexes I–VI can also be prepared by reaction of Rh(acac)(DQ) with perchloric acid in the presence of the corresponding arene.

All the arene complexes are yellow or orange-yellow and behave as 1/1 electrolytes in acetone. Analytical data are listed in Table 1. Their IR spectra show the absorptions due to the uncoordinated anion ($\mathrm{PF_6}^-$: ca. 840 and 560 $\mathrm{cm^{-1}}$, $\mathrm{ClO_4}^-$: ca. 1100 and 620 $\mathrm{cm^{-1}}$), along with weak bands from the arene ligands and strong bands characteristic of coordinated duroquinone. The general splitting of the ν(C=O) bands of the duroquinone ligand (Table 2) suggests that the π-bonded duroquinone molecule is not planar [1]. We have confirmed this by determining the X-ray structure of complex V by X-ray methods (see below). The ^{1}H NMR spectra of $[\mathrm{Rh(DQ)(C_6H_{6-\mathit{n}}Me_\mathit{n})}]^+$ ($n \leqslant 2$) complexes in deuteroacetone reveal the presence of a rapidly established equilibrium with the solvated complex $[\mathrm{Rh(DQ)(\{CD_3\}_2CO)}_x]^+$, but no dissociation was observed for hexamethylbenzene, durene and mesitylene. As expected, the resonance of the arene protons are modified upon coordination (Table 2). Interestingly, the chemical shift of the duroquinone methyl groups is directly related to the donor capacity of the arene. We recently observed similar behaviour

TABLE 1

ANALYSES, MOLAR CONDUCTIVITIES AND YIELDS OF THE ARENE COMPLEXES

Complex	Analyses (Found (calcd.) (%))		Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
	C	H		
$[\mathrm{Rh(DQ)(C_6Me_6)}]\mathrm{PF_6}$ (I)	45.52	5.22	130	60
	(46.00)	(5.27)		
$[\mathrm{Rh(DQ)(1,2,4,5\text{-}C_6H_2Me_4)}]\mathrm{PF_6}$ (II)	43.32	4.81	134	70
	(43.93)	(4.80)		
$[\mathrm{Rh(DQ)(1,3,5\text{-}C_6H_3Me_3)}]\mathrm{PF_6}$ (III)	42.72	4.82	143	80
	(42.87)	(4.54)		
$[\mathrm{Rh(DQ)(1,4\text{-}C_6H_4Me_2)}]\mathrm{ClO_4}$ (IV)	45.14	4.55	128	60
	(45.73)	(4.69)		
$[\mathrm{Rh(DQ)(C_6H_5Me)}]\mathrm{PF_6}$ (V)	40.41	4.06	145	95
	(40.50)	(4.00)		
$[\mathrm{Rh(DQ)(C_6H_6)}]\mathrm{PF_6}$ (VI)	39.03	3.67	143	85
	(39.20)	(3.70)		

TABLE 2

SPECTROSCOPIC DATA FOR THE ARENE COMPLEXES

Complex	IR (Nujol) ν(CO)	NMR (δ, ppm)		
		Coordinated arene		Coordinated DQ
		aromatic H	methyl H	methyl H
$[Rh(DQ)(C_6Me_6)]PF_6$ (I)	1635,1625	–	2.32	1.80
$[Rh(DQ)(1,2,4,5\text{-}C_6H_2Me_4)]PF_6$ (II)	1660,1640	6.73	2.36	1.95
$[Rh(DQ)(1,3,5\text{-}C_6H_3Me_3)]PF_6$ (III)	1630,1580	7.04	2.46	2.04
$[Rh(DQ)(1,4\text{-}C_6H_4Me_2)]ClO_4$ (IV)	1670,1640	7.09	2.49	2.05
$[Rh(DQ)(C_6H_5Me)]PF_6$ (V)	1660,1640	7.26	2.57	2.13
$[Rh(DQ)(C_6H_6)]PF_6$ (VI)	1655,1635	7.43	–	2.14

for methyl groups linked to doubly-bonded C atoms in $[Rh(Me_3TFB)(arene)]^+$ complexes [12]. As expected, the coordinated arene ligands are readily displaced by related ligands having a higher degree of arene-methyl substitution.

Attempts to prepare $[Rh(DQ)(diolefin)]PF_6$ complexes (diolefin = DQ or TFB) by reaction of $[Rh(DQ)(Me_2CO)_x]PF_6$ with stoichiometric amounts of the corresponding diolefin give uncharacterized red material when diolefin = DQ, but when the diolefin was TFB $[Rh(TFB)_2]PF_6$ was formed as the only isolated product. This complex in the solid state shows bands characteristic of the uncoordinated PF_6^- anion and behaves as 1/1 electrolyte in acetone *. Other cationic complexes with nitrogen donor ligands of the general formula $[Rh(DQ)L_2]^+$ can be isolated after treatment of $[Rh(DQ)(Me_2CO)_x]^+$ with acetonitrile (VII), pyridine (VIII) or 1,10-phenanthroline (IX) or, alternatively, made by reaction of Rh(acac)(DQ) ** with perchloric acid in the presence of the appropriate ligand (Table 3).

Bubbling carbon monoxide through dichloromethane solutions of $[Rh(DQ)(MeCN)_2]PF_6$ or $[Rh(DQ)(phen)]PF_6$ leads to the displacement of the coordinated duroquinone and formation of the previously reported *cis*-dicarbonyl derivatives $[Rh(CO)_2(MeCN)_2]PF_6$ [16] and $[Rh(CO)_2(phen)]PF_6$ [17]. On the other hand a neutral dinuclear complex of formula $[Rh(Pz)(DQ)]_2$ (X) was prepared by treating Rh(acac)(DQ) with the binucleating pyrazole ligand. Finally a square planar $RhCl(DQ)(PPh_3)$ (XI) derivative was obtained by adding stoichiometric amounts of triphenylphosphine to $[RhCl(DQ)]_2$. A related pentacoordinated pyridine complex $RhCl(DQ)(py)_2$ was previously reported by Maitlis et al. [2].

Crystal structure of $[Rh(DQ)(C_6H_5Me)]PF_6$

The crystal structure of compound V consists of mononuclear $[Rh(DQ)(C_6H_5Me)]^+$ complexes and octahedral hexafluorophosphate anions. A view of the

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* The related $[Rh(TFB)_2]ClO_4$ [14] complex behaves as 1/1 electrolyte in acetone, gives IR bands in the solid state at 1120, 1040br, 625 and 620 cm^{-1} (C_{3v} symmetry), suggesting that in the solid state it should be formulated as $(TFB)_2RhOClO_3$.

** This Rh(acac)(DQ) [5] precursor, as well as the related *p*-benzoquinone (BQ) derivative Rh(acac)(BQ) [15], can also be prepared in high yield by treating $[RhCl(C_2H_4)_2]_2$ with Tl(acac), filtering off the TlCl, and adding the relevant quinone (DQ or BQ). The duroquinone derivative Rh(acac)(DQ) can also be prepared by reaction of the dimer $[RhCl(DQ)]_2$ with Tl(acac).

TABLE 3

ANALYSES AND PHYSICAL PROPERTIES OF THE RHODIUM(I) COMPLEXES WITH DUROQUINONE AND GROUP VB DONOR LIGANDS

Complex	Colour	Analyses (Found (calcd.) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	ν(CO) (cm^{-1})
		C	H	N			
Rh(DQ)(MeCN)$_2$]PF$_6$ (VII)	red	33.54 (34.00)	3.67 (3.67)	5.57 (5.67)	127	54	1660,1635
[Rh(DQ)(py)$_2$]ClO$_4$ (VIII)	ocre	45.38 (45.78)	4.28 (4.23)	5.85 (5.34)	122	93	1613,1595
[Rh(DQ)(phen)]PF$_6$ (IX)	brown	44.50 (43.90)	3.89 (3.35)	4.65 (4.65)	130	88	1625,1570
[Rh(Pz)(DQ)]$_2$ (X)	red	45.75 (46.72)	4.82 (4.52)	8.41 (8.38)	–	36	1627,1599
RhCl(DQ)PPh$_3$ (XI)	violet	58.70 (59.50)	4.64 (4.84)		–	54	1670,1635

cationic complex with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 4.

The present structure resembles those of the related complexes, of general formula [Rh(arene)(diolefin)]$^+$ [9,11–13], where the duroquinone ligand is acting as a 1,4-diolefin. The Rh atom is coordinated in a "nearly-sandwich" fashion by a toluene group and a duroquinone ligand, interacting η^6- with the arene ring and η^4

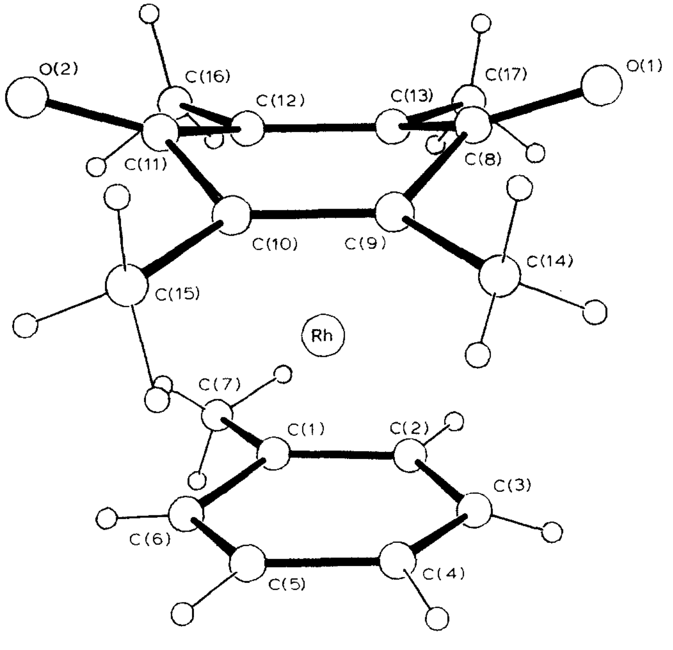

Fig. 1. A view of the studied complex with the atomic numbering.

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

(a) *around the metal atom*			
Rh-C(1)	2.265(9)	Rh-C(8)	2.500(7)
Rh-C(2)	2.259(9)	Rh-C(9)	2.167(7)
Rh-C(3)	2.307(11)	Rh-C(10)	2.183(8)
Rh-C(4)	2.257(9)	Rh-C(11)	2.501(8)
Rh-C(5)	2.263(11)	Rh-C(12)	2.202(8)
Rh-C(6)	2.333(8)	Rh-C(13)	2.189(8)
Rh-C(1G) [a]	1.803(4)	Rh-C(2G) [b]	1.797(3)
C(1G)-Rh-C(2G) [b]	177.8(2)		
(b) *within the duroquinone ligand*			
C(8)-O(1)	1.228(9)	C(10)-C(15)	1.495(11)
C(8)-C(9)	1.490(10)	C(11)-O(2)	1.231(10)
C(8)-C(13)	1.467(11)	C(11)-C(12)	1.471(11)
C(9)-C(10)	1.401(9)	C(12)-C(13)	1.418(11)
C(9)-C(14)	1.519(12)	C(12)-C(16)	1.505(14)
C(10)-C(11)	1.455(10)	C(13)-C(17)	1.503(13)
C(9)-C(8)-O(1)	124.5(7)	C(10)-C(11)-O(2)	122.4(7)
C(13)-C(8)-O(1)	122.8(7)	C(12)-C(11)-O(2)	123.2(7)
C(9)-C(8)-C(13)	111.3(6)	C(10)-C(11)-C(12)	113.0(6)
C(8)-C(9)-C(10)	120.4(6)	C(11)-C(12)-C(13)	119.4(7)
C(8)-C(9)-C(14)	114.6(7)	C(11)-C(12)-C(16)	117.2(7)
C(10)-C(9)-C(14)	124.0(7)	C(13)-C(12)-C(16)	122.4(8)
C(9)-C(10)-C(11)	119.2(7)	C(8)-C(13)-C(12)	119.5(7)
C(9)-C(10)-C(15)	121.6(7)	C(8)-C(13)-C(17)	116.8(8)
C(11)-C(10)-C(15)	118.2(7)	C(12)-C(13)-C(17)	122.7(8)
(c) *within the arene ligand*			
C(1)-C(2)	1.405(12)	C(3)-C(4)	1.367(19)
C(1)-C(6)	1.463(13)	C(4)-C(5)	1.386(15)
C(1)-C(7)	1.514(20)	C(5)-C(6)	1.387(16)
C(2)-C(3)	1.375(15)		
C(2)-C(1)-C(6)	118.1(8)	C(2)-C(3)-C(4)	120.0(9)
C(2)-C(1)-C(7)	122.8(10)	C(3)-C(4)-C(5)	120.6(10)
C(6)-C(1)-C(7)	118.5(9)	C(4)-C(5)-C(6)	122.0(10)
C(1)-C(2)-C(3)	121.6(9)	C(1)-C(6)-C(5)	117.3(8)
(d) *in the hexafluorophosphate anion*			
P-F(1)	1.602(8)	P-F(4)	1.565(10)
P-F(2)	1.568(11)	P-F(5)	1.577(10)
P-F(3)	1.571(8)	P-F(6)	1.545(11)
F(1)-P-F(2)	87.9(5)	F(2)-P-F(6)	87.5(5)
F(1)-P-F(3)	178.6(5)	F(3)-P-F(4)	90.3(5)
F(1)-P-F(4)	90.4(5)	F(3)-P-F(5)	92.1(5)
F(1)-P-F(5)	86.8(4)	F(3)-P-F(6)	87.7(5)
F(1)-P-F(6)	93.4(5)	F(4)-P-F(5)	88.8(5)
F(2)-P-F(3)	91.5(5)	F(4)-P-F(6)	90.8(6)
F(2)-P-F(4)	177.6(6)	F(5)-P-F(6)	179.5(6)
F(2)-P-F(5)	92.9(5)		

[a] C(1G) represents the centroid of the C(1)-C(6) atoms. [b] C(2G) represents the centroid of the duroquinone C(8)-C(13) atoms.

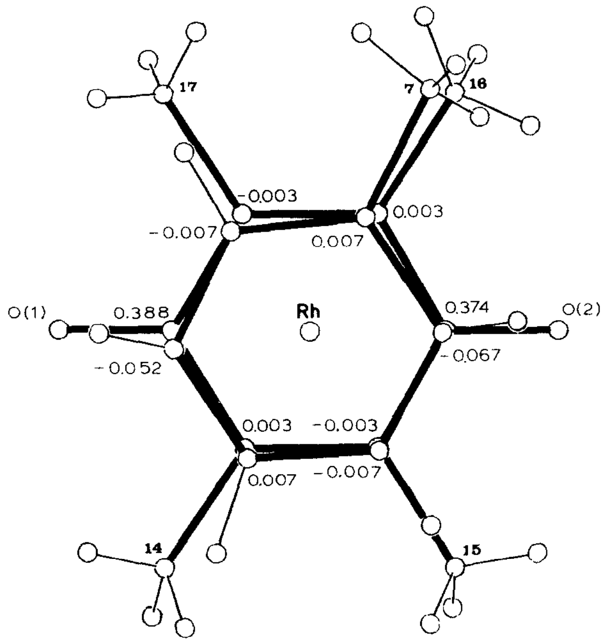

Fig. 2. View of complex perpendicular to the plane defined by C(9), C(10), C(12) and C(13). The deviations (Å) showed are from the least-squares planes through the four C atoms of each ring closer to the Rh atom. (The C atoms of the rings are not numbered for clarity).

with the quinone. As usual for arenerhodium(I) complexes [9–13,18,19], the toluene ring is non planar, adopting a slightly distorted boat-like conformation, as revealed by the Rh–C(arene) distances, the values of the torsion angles within the ring (Table 5), and the deviations of the atoms from the least-squares planes (Fig. 2). The Cremer and Pople puckering parameters [20] have values (q_2 0.070(9) Å, ϕ_2 $-49(8)°$, θ 85(8)°) in accord with this proposal [13]. This conformation is not frequent, but has been previously reported for compounds which also contain phosphite ligands, viz., $Rh\{P(OMe)_3\}_2PhBPh_3$ [18] and $[Rh(C_6H_5Me)\{P(OPh)_3\}_2]ClO_4$ [10]; usually complexes of the type $[Rh(arene)(diolefin)]^+$ prefer an inverted boat [9,13] or a skew conformation [11,12]. The four C atoms closer to the metal are strictly planar, with C(3), C(6) and the methyl C(7) atom out of this plane by −0.052(9), −0.067(9) and −0.122(17) Å, respectively. This plane (π_1) makes

TABLE 5

SELECTED TORSION ANGLES (°)

C(1)–C(2)–C(3)–C(4)	−4.5(15)	C(9)–C(10)–C(11)–C(12)	32.3(10)
C(2)–C(3)–C(4)–C(5)	5.8(16)	C(10)–C(11)–C(12)–C(13)	−31.8(10)
C(3)–C(4)–C(5)–C(6)	−0.7(17)	C(11)–C(12)–C(13)–C(8)	−1.4(11)
C(4)–C(5)–C(6)–C(1)	−5.4(15)	C(12)–C(13)–C(8)–C(9)	32.6(10)
C(5)–C(6)–C(1)–C(2)	6.4(13)	C(13)–C(8)–C(9)–C(10)	−32.3(10)
C(6)–C(1)–C(2)–C(3)	−1.7(13)	C(8)–C(9)–C(10)–C(11)	−0.1(10)
C(1)–C(1G)–C(2G)–C(12)	4.2(5)	C(4)–C(1G)–C(2G)–C(9)	2.3(6)
C(2)–C(1G)–C(2G)–C(13)	4.3(5)	C(5)–C(1G)–C(2G)–C(10)	2.8(6)

similar dihedral angles (4.4(7) and 5.2(7)°) with the two flapping planes π_2 and π_3 *.

The duroquinone ring, which is planar in the free ligand molecule [21], becomes distorted on coordination to give a clear boat conformation (Cremer and Pople parameters: q_2 0.440(7) Å, ϕ_2 −0.8(9)°, θ 89(1)° [20]), with C(8) and C(11) furthest from the metal atom. The best plane through the four-coordinated atoms (π_4) forms analogous dihedral angles (27.7(5) and 27.6(6)°) with the π_5 and π_6 planes *. The deviations from these planes of the oxygens of the carbonyl groups towards the Rh atom (0.231(7) and 0.233(7) Å) are noteworthy. Relative to the plane of η^4-coordinated C atoms (π_4), the methyl groups are also bent towards the metal atom by 0.10–0.14(1) Å. In addition to this distortion from planarity, the olefinic C–C bond distances within the duroquinone are also significantly changed by coordination, going from a mean value of 1.341(2) Å in the free ligand [21] to 1.409(10) Å in complex V, the latter value being slightly larger than those previously described (1.36–1.39 Å) [5]. All these facts indicate a greater distortion of the duroquinone ligand in compound V than in previously reported duroquinonerhodium complexes [5,6].

The separations of the Rh atom from the two mean planes π_1 and π_4 are 1.803(4) and 1.797(3) Å. These two planes are practically parallel, the dihedral angle between them being only 2.5(3)°.

In contrast with the observations on the majority of related compounds [13], the two relative positions of the rings practically eclipse each other, in such a way that the methyl group in the toluene ligand nearly eclipses a methyl group of the duroquinone (see Fig. 2). We have previously observed a general tendency of the coordinated diolefin in related $[Rh(diolefin)(C_6H_{6-n}Me_n)]^+$ complexes not to lie opposite to the substituted carbon atoms of the arene, which have a relatively low π-electron density.

Experimental

The C, H and N analyses were carried out with a Perkin–Elmer 240 or a Heraeus Mikro standard 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 ^{1}H NMR spectra were recorded on a Varian XL-100 or XL-200 instruments and shifts are relative to tetramethylsilane.

All reactions were carried out at room temperature and solvents were dried and distilled prior to use. The duroquinone ligand was purchased from Aldrich Chemical Co., TFB and Me_3TFB were prepared by literature procedures [22].

Preparation of complexes of the type [Rh(DQ)(arene)]PF$_6$ (I–VI)

A suspension of the dimer complex $[RhCl(DQ)]_2$ (60.5 mg, 0.10 mmol) [2] in 15 ml of acetone was treated with $AgPF_6$ (50.6 mg, 0.20 mmol). The mixture was stirred for 30 min in the absence of light and the AgCl formed was filtered off through

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* Definition of least-squares planes: π_1: C(1),C(2),C(4),C(5); π_2: C(2),C(3),C(4); π_3: C(1),C(6),C(5); π_4: C(9),C(10),C(12),C(13); π_5: C(9),C(8),C(13); π_6: C(10),C(11),C(12).

kieselguhr. The yellow-orange filtrate containing the solvated complex $[Rh(DQ)(Me_2CO)_x]^+$ was allowed to run into a solution of a large excess of the corresponding arene (C_6H_6 (1 ml); C_6H_5Me (1 ml); 1,3,5-$C_6H_3Me_3$ (1 ml); 1,2,4,5-$C_6H_2Me_4$ (117.4 mg, 0.8 mmol) in acetone (10 ml). After 30 min stirring the solution was concentrated under reduced pressure, and the complex was precipitated with diethyl ether and recrystallized from acetone/diethyl ether.

When the arene C_6Me_6 (129.8 mg; 0.8 mmol) was used, the solution was evaporated to dryness and dichloromethane added to precipitate a yellow-orange solid. Diethyl ether was added and the solid was filtered off, washed with diethyl ether, and air-dried. The product crystallized with a molecule of solvent $[Rh(DQ)(C_6Me_6)]PF_6 \cdot CH_2Cl_2$. (Analysis: Found: C, 41.11; H, 4.69. $C_{23}H_{32}Cl_2F_6O_2PRh$ calcd.: C, 41.89; H, 4.92%). The solvent was removed in vacuo at 60°C for 4 h.

An alternative route was used for the preparation of the complex $[Rh(DQ)(1,4\text{-}C_6H_4Me_2)]ClO_4$. To the starting complex Rh(acac)(DQ) [5] (30 mg, 0.08 mmol) in acetone (10 ml) was added a large excess of 1,4-$C_6H_4Me_2$ (0.5 ml) and ca. 0.05 ml of aqueous perchloric acid (60%; d: 1.54). The mixture was stirred for 15 min, evaporated to a small volume, and crystallized by addition of diethyl ether.

Reaction of $[Rh(DQ)(Me_2CO)_x]PF_6$ with diolefins

A solution of $[Rh(DQ)(Me_2CO)_x]PF_6$ (0.2 mmol) in acetone (prepared as above), was added to a solution of the diolefin (DQ or TFB) in the same solvent. After 30 min stirring, the solution was vacuum-concentrated to ca. 2–3 ml. Addition of diethyl ether gave a precipitate of a red (DQ) or orange (TFB) solid. The latter was identified as $[Rh(TFB)_2]PF_6$. (Analysis: Found: C, 40.83; H, 1.97. $C_{24}H_{12}F_{14}PRh$ calcd: C, 41.10; H, 1.73%. Λ_M 131 $ohm^{-1} cm^2 mol^{-1}$ (acetone)). The red duroquinone complex was not characterized.

Preparation of complexes of the type $[Rh(DQ)L_2]A$ ($L = py$, $A = ClO_4^-$; $L = MeCN$, $L_2 = phen$, $A = PF_6$)

A solution of $[Rh(DQ)(Me_2CO)_x]^+$ (0.2 mmol) in acetone (prepared as above) was added to a solution containing the appropriate ligand (py (0.1 ml), MeCN (0.5 ml), phen (39.7 mg, 0.2 mmol)) in acetone (10 ml). The solution obtained was stirred for 30 min and then concentrated in vacuo to a small volume. Addition of diethyl ether gave a solid, which was filtered off, washed with diethyl ether, air-dried, and recrystallized from acetone/diethyl ether.

Preparation of the dinuclear complex $[(Rh(Pz)(DQ)]_2$ (X)

To a solution of the neutral complex Rh(acac)(DQ) (73.2 mg, 0.20 mmol) in dichloromethane (10 ml) was added a solution of pyrazole (13.8 mg, 0.20 ml) in the same solvent (5 ml). The initially red solution became darker during stirring (1 h). The solution was concentrated to a small volume and pentane was added. The dark red amorphous precipitate was filtered off, washed with pentane, and vacuum-dried.

Preparation of the neutral complex $RhCl(DQ)PPh_3$ (XI)

To a solution of the dimer complex $[RhCl(DQ)]_2$ (60.5 mg, 0.1 mmol) in dichloromethane (15 ml) was added the stoichiometric amount of PPh_3 (52.5 mg, 0.2

mmol). The violet solution formed was stirred for 15 min and concentrated to small volume. The complex was precipitated by addition of diethyl ether and recrystallized from acetone/diethyl ether.

X-ray analysis

The crystal structure data and procedures are indicated in Table 6. When the refinement had converged, $R = 0.064$ and $R_w = 0.078$, the extinction parameter was refined [23] to a value of $G = 0.0019(1)$, giving rise to a significant decrease in the R values at low $\sin(\theta/\lambda)$ (0.0–0.2) and at high F values (128–256).

Fractional atomic coordinates for the non-hydrogen atoms are given in Table 7. Lists of structure factors, hydrogen coordinates, and thermal parameters can be obtained from the authors on request.

TABLE 6

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	$C_{17}H_{20}F_6O_2PRh$
M.W.	504.213
Crystal habit	Yellow Transparent. Prismatic.
Size	0.08 × 0.38 × 0.46 mm
Symmetry	Monoclinic; $P2_1/n$
Unit cell determination	Least-squares fit to 59 reflexions [θ(Cu) $\leqslant$ 45°]
Unit cell dimensions	15.9866(5), 11.8438(3), 9.9968(3) Å; β 98.473(4)°
Packing: V (Å^3), Z	1872.2(2), 4
D (g cm^{-3}) (F(000))	1.79, 1008
Experimental data	
Radiation and technique	Cu-K_α; 4-Circle PW 1100 Philips diffractometer; Bisecting geometry
Monochromator	Graphite oriented
Orientation	$hk0$: $\chi \sim -11°$, $\phi \sim 291°$; $00l$: $\chi \sim 32°$; $\phi \sim 8°$.
Collection mode	$\theta \leqslant 65°$
($\omega/2\theta$, 1° × 1° det. apertures)	1.50° scan width, 1.5 min/reflex
Total independent data	3181
Observed data: $3\sigma_c(I)$	2514
Stability	Two reflexions every 90 min. No variation detected
Absorptions faces	$\pm(100)$, $\pm(10\bar{1})$, $\pm(2\bar{3}1)$
μ-Min. and Mx. transmission	90.15 cm^{-1}, 0.118–0.618
Solution and refinement	[23] X-Ray 80 system. Computer: VAX 11/750
Solution mode	Patterson
Refinement mode	Least-squares on F's. Observed reflexions only
Final shift/error	0.084
Parameter: no. variables	316
Degrees of freedom	2198
w-scheme	Empirical as to give no trends in $\langle w\Delta^2 \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin\theta/\lambda \rangle$
ΔF final	2.6 e Å^{-3} in the surroundings of Rh atom
Max. thermal values (Å^2)	$U_{11}(F_2) = 0.19(1)$
R, R_w	0.062, 0.076
Atomic factors	International Tables for X-ray Crystallography; Neutral atoms [24]; Anomalous dispersion applied for Rh, P and F.

TABLE 7

FRACTIONAL ATOMIC COORDINATES FOR THE NON-HYDROGEN ATOMS FOR $[Rh(DQ)(C_6H_5Me)]PF_6$

Atom	x/a	y/b	z/c
Rh	0.08090(3)	0.18523(4)	0.25498(5)
P	0.71558(12)	0.10470(19)	0.28847(20)
F(1)	0.77788(46)	0.15887(82)	0.41207(80)
F(2)	0.77629(75)	0.00015(79)	0.29738(77)
F(3)	0.65412(50)	0.04917(88)	0.16955(76)
F(4)	0.65833(65)	0.21242(80)	0.27994(87)
F(5)	0.66388(66)	0.05531(86)	0.39784(84)
F(6)	0.76560(63)	0.15367(92)	0.18084(100)
O(1)	0.00161(44)	0.16916(57)	−0.09482(66)
O(2)	0.21111(40)	0.42373(52)	0.22218(67)
C(1)	0.02689(53)	0.19100(68)	0.45204(77)
C(2)	−0.02212(50)	0.11597(82)	0.36405(89)
C(3)	0.01317(82)	0.02361(79)	0.31039(93)
C(4)	0.09869(87)	0.00732(75)	0.33486(99)
C(5)	0.14974(66)	0.07737(104)	0.42307(100)
C(6)	0.11707(60)	0.16667(95)	0.48868(79)
C(7)	−0.01151(117)	0.28442(139)	0.52663(178)
C(8)	0.04525(47)	0.21018(63)	0.00474(71)
C(9)	0.12993(43)	0.16686(55)	0.06534(63)
C(10)	0.18567(43)	0.23569(62)	0.15071(76)
C(11)	0.15989(49)	0.34995(61)	0.17914(74)
C(12)	0.06836(49)	0.36038(64)	0.18086(79)
C(13)	0.01177(49)	0.29020(63)	0.09548(83)
C(14)	0.15498(77)	0.05568(81)	0.00659(102)
C(15)	0.27622(53)	0.20363(86)	0.19210(118)
C(16)	0.03873(72)	0.46029(81)	0.25429(124)
C(17)	−0.08229(61)	0.30824(95)	0.07367(134)

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