metal-organic papers

(Hydridotripyrazolylborato)iodo{(1,2,5,6-η)-1-[(Z)-1-iodo-2-phenylethenyl]cycloocta-1,5-diene}ruthenium(II)–diiodine (2/1)

Christian Slugovc,[a] Karl Kirchner[b] and Kurt Mereiter[c]*

[a]Institute for Chemistry and Technology of Organic Materials (ICTOS), Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria, [b]Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, A-1060 Vienna, Austria, and [c]Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164, A-1060 Vienna, Austria

Correspondence e-mail:
kurt.mereiter@tuwien.ac.at

Key indicators

The title compound, $[\mathrm{Ru}(\mathrm{C}_9\mathrm{H}_{10}\mathrm{BN}_6)\mathrm{I}(\mathrm{C}_{16}\mathrm{H}_{17}\mathrm{I})]\cdot 0.5\mathrm{I}_2$, is a cocrystal of an iodine-bearing neutral ruthenium complex and diiodine. The centrosymmetric diiodine molecule links a pair of Ru complexes *via* halogen bonds to the Ru-bound iodide anions, thus forming a linear $\mathrm{I}\cdots\mathrm{I}-\mathrm{I}\cdots\mathrm{I}$ chain, with $\mathrm{I}\cdots\mathrm{I}$ distances of 2.837 (1) Å for the inner bond and 3.486 (1) Å for the two outer interactions. The C-bound iodine interacts with the π electrons of two pyrazole rings but does not take part in any $\mathrm{I}\cdots\mathrm{I}$ interactions.

Comment

We have shown (Slugovc *et al.*, 1999) that the complex Ru(Tp)(COD)Cl (Tp is hydridotrispyrazolylborate and COD is 1,5-cyclooctadiene) reacts with phenylacetylene, *via* an intermediate cationic vinylidene complex, by C—C coupling between one olefinic C atom of the COD ligand and the terminal alkyne C atom to afford Ru(Tp){(η^4-1,5)-1-[(Z)-2-phenylethenyl]cyclooctadiene}Cl. If this reaction is carried out in the presence of base it leads to Ru(Tp){(η^{3+2}-1,5)-1-[(Z)-2-phenyl-ethenylidene]cyclooctenyl}, a complex with a η^3-bound butadienyl group. An interesting property of this complex and its relatives is the nucleophilicity of the butadienyl group at the enynyl C atom, which can be used to afford by I_2 addition the complex Ru(Tp){(η^4-1,5)-1-[(Z)-1-iodo-2-phenylethenyl]cyclooctadiene}I. This compound crystallized from $\mathrm{CH}_2\mathrm{Cl}_2$/$(\mathrm{C}_2\mathrm{H}_5)_2\mathrm{O}$ in a stable unsolvated form of elongated orange prisms and was studied by X-ray diffraction (Slugovc *et al.*, 1999). When this compound was crystallized from the same solvents in the presence of iodine, the title compound, (I), was obtained in the form of stable dark-red stout prisms. The structure analysis revealed the compound to be a cocrystal of the Ru complex in a general position, with a diiodine molecule on a centre of symmetry. The Ru complex in the diiodine cocrystal (Fig. 1) is very similar in bond lengths and bond angles to that of the parent compound (Slugovc *et al.*, 1999), but differs from it somewhat in conformation. The mean and maximum differences of the corresponding bond lengths of the two complexes are 0.003 and 0.030 Å, respectively. A least squares fit of the two complexes (Fig. 2) gives an r.m.s. deviation of 0.26 Å for corresponding atomic positions excluding H atoms, with minimum and maximum deviations of 0.08 Å for Ru and 0.55 Å for C21, respectively. This result indicates that the complex is fairly rigid, probably because the C-bound atom I2 of the phenylethenyl side chain is locked in a pocket of the Tp ligand and exhibits stabilizing iodine–π interactions with two pyrazole rings by the following four shortest contact distances: $\mathrm{I2}\cdots\mathrm{N6} = 3.416$ (3) Å, $\mathrm{I2}\cdots\mathrm{N2} = 3.623$ (3) Å, $\mathrm{I2}\cdots\mathrm{C23} = 3.637$ (4) Å and $\mathrm{I2}\cdots\mathrm{N5} = 3.681$ (3) Å. In the parent compound these distances are 3.333 (2),
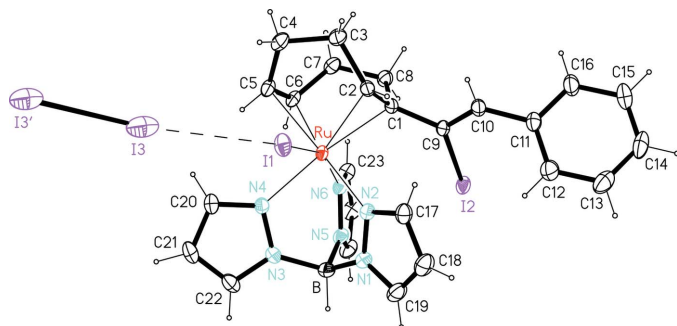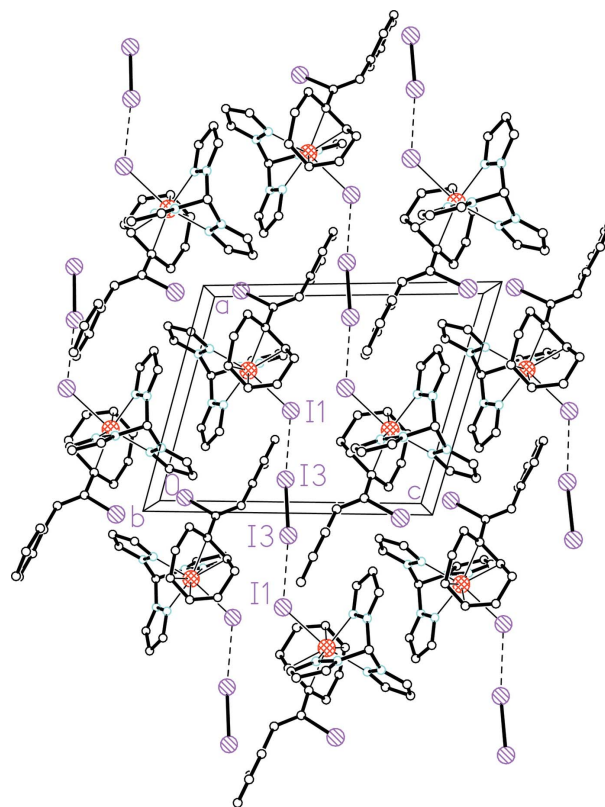
Figure 1
Perspective view of (I). Displacement ellipsoids are shown at the 30% probability level. The prime for I3 corresponds to symmetry code (i) in Table 1.

3.738 (2), 3.506 (2) and 3.503 (2) Å, showing that I2 in the parent is a little closer to pyrazole ring 3 and more distant from pyrazole ring 1 than in (I). However, unlike (I), the parent compound shows an intermolecular I2···I2 contact of 3.669 (1) Å, which may be compared with the intermolecular distance in solid iodine of ∼3.5 Å (van Bolhuis *et al.*, 1967).
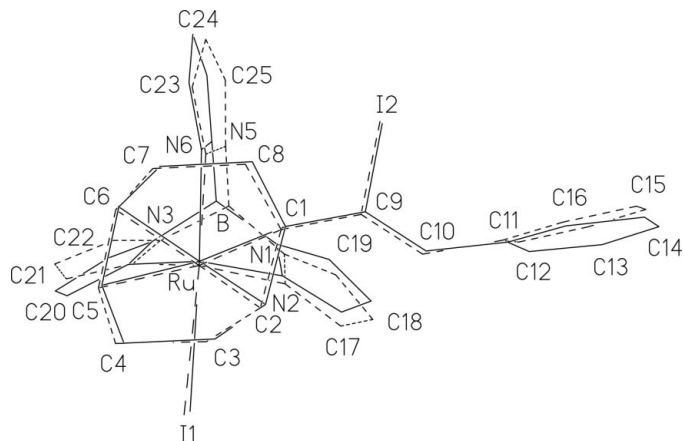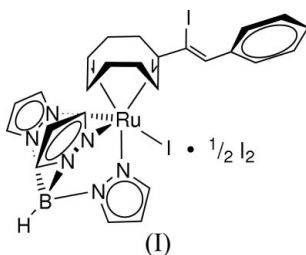
Figure 2
Superposition plot of (I) with full lines and the diiodine-free parent compound with broken lines.

The second constituent of (I) is an I_2 molecule that lies across a centre of inversion and exhibits an I—I bond length of 2.837 (1) Å. This molecule is not free but halogen-bonded [designation for non-covalent halogen–X interactions in analogy to hydrogen-bond, *cf.* Ouvrard *et al.* (2003)] to the iodide I1 of the Ru complex at an I1···I3 distance of 3.486 (1) Å. It links thereby two inversion-related Ru complexes *via* a chain of four I atoms (Fig. 3). The angles Ru—I1···I3 = 122.67 (2)° and I1···I3—I3 = 172.44 (2)° are typical for such assemblies. A closely related example of a cocrystal between two iodo[phthalocyaninato(2+)]manganese(III) complexes and a bridging neutral I_2 molecule of symmetry C_i [I—I = 2.783 (1) Å, I···I = 3.424 (1) Å, Mn—I···I = 102.2° and I···I—I = 179.0°] was recently reported by Janczak (2004). This reference also discusses the structures of cocrystals between mononuclear metal complexes and neutral I_2 molecules having a metal to I_2 ratio of 1:1 instead of 1:0.5 as in (I).

Figure 3
Packing diagram of (I), viewed down *b*, showing the I1···I3—I3[i]···I1[i] groups [symmetry code: (i) $-x, -y + 1, -z + 1$]. All other intermolecular I···I distances are larger than 4.2 Å.

Experimental

The Ru complex of the title compound was synthesized as described by Slugovc *et al.* (1999). This complex (90 mg) was dissolved in CH_2Cl_2 (5 ml), iodine (about 50 mg) was added, and (I) was obtained within one day in the form of well developed stout prisms by crystallization using vapour diffusion of diethyl ether at room temperature.

Crystal data

[Ru(C9H10BN6)I(C16H17I)]·0.5I2	$Z = 2$
$M_r = 904.11$	$D_x = 2.107$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.716$ (3) Å	Cell parameters from 702
$b = 10.979$ (3) Å	reflections
$c = 13.307$ (4) Å	$\theta = 2.4$–29.8°
$\alpha = 75.67$ (1)°	$\mu = 3.83$ mm^{-1}
$\beta = 71.87$ (1)°	$T = 299$ (2) K
$\gamma = 77.49$ (1)°	Block, dark red
$V = 1424.9$ (7) Å^3	$0.32 \times 0.22 \times 0.20$ mm

Data collection

Bruker SMART CCD diffractometer	8224 independent reflections
	6949 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.020$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 30.0°$
	$h = -15 \rightarrow 15$
$T_{min} = 0.35$, $T_{max} = 0.47$	$k = -15 \rightarrow 15$
19965 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 2.9155P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.002$
8224 reflections	$\Delta\rho_{max} = 2.48$ e Å^{-3}
326 parameters	$\Delta\rho_{min} = -1.86$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.00149 (15)

Table 1
Selected geometric parameters (Å, °).

Ru—N2	2.130 (3)	C1—C2	1.401 (4)
Ru—N4	2.130 (3)	C5—C6	1.385 (5)
Ru—N6	2.176 (3)	C1—C9	1.505 (4)
Ru—C1	2.268 (3)	C9—C10	1.339 (4)
Ru—C2	2.212 (3)	I2—C9	2.128 (3)
Ru—C5	2.266 (3)	I1—I3	3.486 (1)
Ru—C6	2.245 (3)	I3—I3^{i}	2.837 (1)
Ru—I1	2.7899 (7)		
Ru—I1—I3	122.67 (2)	I1—I3—I3^{i}	172.44 (2)

Symmetry code: (i) $-x, -y + 1, -z + 1$.

All H atoms are unambiguously defined by stereochemistry. They were placed in calculated positions and constrained to ride on their parent atoms with C—H = 0.95–0.98 Å, B—H = 1.10 Å, and $U_{iso}(H) = 1.2U_{eq}(C,B)$. The maximum and minimum residual electron densities are located 0.73 and 0.83 Å from atom I3.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

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