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Tetra-μ-acetato-bis{[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]rhodium(II)}(*Rh*—*Rh*) tetrahydrofuran tetrasolvate

Vânia André,[a] M. Teresa Duarte,[a]* Alexandre F. Trindade,[b] Pedro M. P. Góis[c] and Carlos A. M. Afonso[b]

[a]Centro de Química Estrutural, Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal, [b]Centro de Química-Física Molecular, Instituto Superior Técnico, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal, and [c]iMed.UL, Faculdade de Farmácia da Universidade de Lisboa, Avenida Prof. Gama Pinto, 1649-003 Lisboa, Portugal
Correspondence e-mail: teresa.duarte@ist.utl.pt

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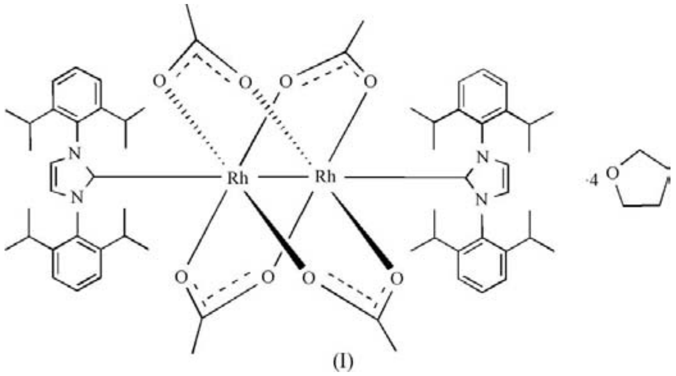
In this paper, we compare and discuss the very different crystal structures and supramolecular arrangements obtained when using different crystallization solvents with the same organometallic moiety. The new title tetrahydrofuran (THF) solvate, $[Rh_2(C_2H_3O_2)_4(C_{27}H_{36}N_2)_2]\cdot 4C_4H_8O$, is compared with the toluene trisolvate reported previously by us [Góis, Trindade, Veiros, Andre, Duarte, Afonso, Caddick & Cloke (2007). *Angew. Chem. Int. Ed.* **46**, 5750–5753]. The molecular structures of the two complex molecules display a similar conformation, but due to the presence of different solvent molecules, the two solvates crystallize in different space groups and exhibit quite diverse supramolecular assemblies. The toluene solvate crystallizes in the triclinic space group $P\overline{1}$, while in the presence of THF, the monoclinic $P2_1/c$ space group is obtained, with the complex molecule residing on an inversion centre. The resulting crystal packing displays no classical hydrogen bonds but different supramolecular synthons give rise to different packing motifs. In this work, we highlight the different supramolecular architectures obtained when organometallic moieties crystallize with different solvent molecules. We compare the novel structure of the THF derivative with that of the toluene solvate of a dirhodium(II) complex belonging to a new family of catalyst compounds exhibiting very high performance in arylation processes.

Comment

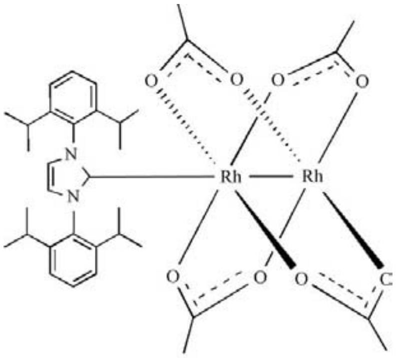
In the last two decades, the family of dirhodium(II) complexes has attracted considerable interest from the organic chemistry community since these complexes are able to catalyse efficiently some remarkable transformations, such as intra- and intermolecular C—H bond activation with Rh^{II} carbenoids (Davies & Beckwith, 2003; Doyle, 2006; Góis & Afonso, 2004), C—H bond amination with Rh^{II} nitrenoids, oxidations, cycloadditions and a variety of ylide-based transformations (see, for example, Catino, Nichols, Choi *et al.*, 2005; Catino, Nichols, Forslund *et al.*, 2005; Liang *et al.*, 2006; Reddy & Davies, 2006; Fiori & Du Bois, 2007; Anada *et al.*, 2004; Forslund *et al.*, 2005; Washio *et al.*, 2005; Wang *et al.*, 2008; Catino, Forslund *et al.*, 2005). More recently, we have been able to prepare and fully characterize stable complexes of $Rh_2(OAc)_4$ with one and two NHCs (N-heterocyclic carbenes, such as imidazol-2-ylidene derivatives) attached at the axial positions. These complexes proved to be excellent catalysts for aldehyde arylation reactions with boronic acids (Góis *et al.*, 2007; Trindade *et al.*, 2008).

Dirhodium(II) complexes have an intermetallic bond, two axial ligands (normally solvent molecules) and four bridging ligands which are responsible for controlling the electrophilicity and asymmetry of the complex (Doyle *et al.*, 1998; Lou *et al.*, 2005; Cotton *et al.*, 2002). Unlike bridging ligands, the axial ligands are considered to be labile (weakly bonded) and could easily be displaced by other molecules.

The previously reported $Rh_2(OAc)_4(NHC)_2$ complex (Góis *et al.*, 2007), (II), was obtained as a toluene solvate with a stoichiometry of three molecules of solvent to one molecule of dirhodium(II) (diRh) complex (Fig. 1*a*). More recently, we obtained a new solvate, (I), with tetrahydrofuran (THF). In this case, the asymmetric unit consists of two crystallographically independent THF molecules and half a complex molecule residing on an inversion centre (Fig. 1*b*).



(I)



(III)

In both solvates, no classical hydrogen bonds were found, but the supramolecular arrangements are indeed very

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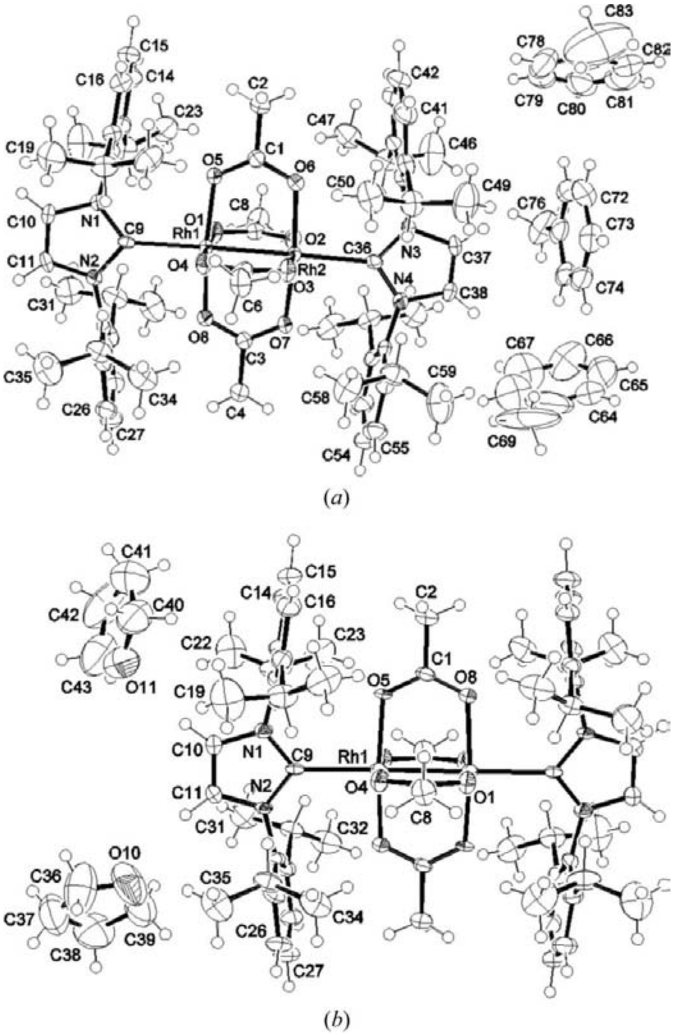

Figure 1
(*a*) The molecular structure of the $Rh_2(OAc)_4(NHC)_2$ toluene trisolvate, (II) (Góis *et al.*, 2007). (*b*) The molecular structure of the title $Rh_2(OAc)_4(NHC)_2$ THF tetrasolvate, (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

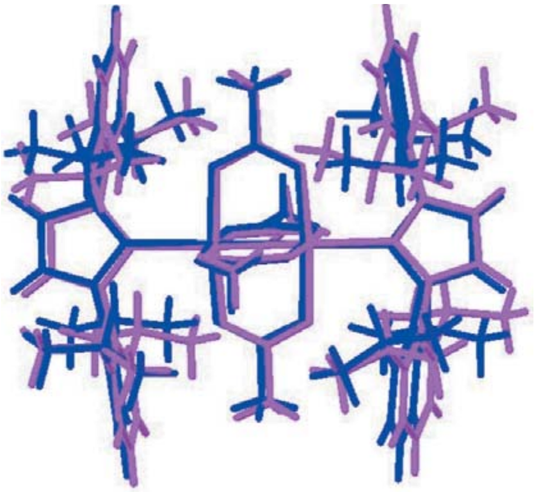

Figure 2
An overlay of the complex molecules of the toluene (light shading) and THF (dark shading) solvates. The solvent molecules have been omitted for clarity.

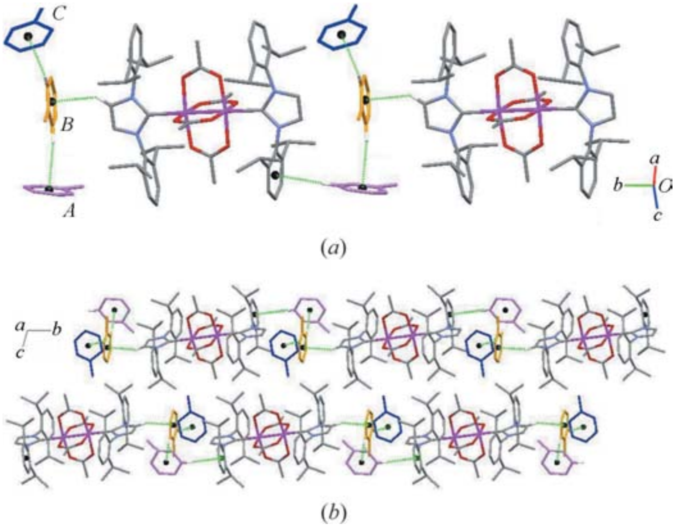

Figure 3
(*a*) The packing of the toluene solvate, (II), showing all the C—H$\cdots\pi$ interactions established in the structure. (*b*) The crystal packing of (II), viewed along *a*.

different due to the distinct interactions with the solvent molecules. On the whole, the two diRh complex molecules retain their conformation, as seen in Fig. 2 and sustained by the small differences in torsion angle values presented in Table 1.

In toluene solvate (II) (Góis *et al.*, 2007), there are no short contacts between the diRh complex molecules; they all interact *via* C—H$\cdots\pi$ interactions with solvent molecules, which behave as linkers. The linking between two complex molecules is achieved through two toluene molecules, denoted *A* and *B* (Fig. 3*a*), which interact further with the remaining solvent molecule, denoted *C*. The diRh complex molecules interact in two different modes with the solvent molecules. Toluene molecule *A* interacts with a neighbouring diisopropylphenyl ring (*Cg*1, defined by atoms C24–C29) [C65—H65$\cdots$*Cg*1^{i}: H65$\cdots$*Cg*1^{i} = 2.79 Å, C65$\cdots$*Cg*1^{i} = 3.716 (8) Å and C65—H65$\cdots$*Cg*1^{i} = 175°; symmetry code: (i) x, $1 + y$, z], while the other interaction is through a C atom of an imidazol-2-ylidene group and the aromatic ring of toluene molecule *B* (*Cg*2, defined by atoms C70–C76) [C37—H37$\cdots$*Cg*2: 2.67 Å, 3.449 (4) Å and 142°].

The toluene molecules do not have the same orientation: the dihedral angles between the planes of solvent molecules *A* and *B*, *B* and *C*, and *A* and *C* are 86.1 (3), 78.2 (3) and 32.3 (4)°, respectively. This relative positioning of the solvent molecules is due to the C—H$\cdots\pi$ interactions established among them (Fig. 3*a*): toluene molecules *A* and *B* interact through C75—H75$\cdots$*Cg*3 (where *Cg*3 is the ring defined by atoms C63–C69) [2.77 Å, 3.688 (6) Å and 168°]; molecules *B* and *C* are linked *via* C71—H71$\cdots$*Cg*4 (where *Cg*4 is the ring defined by atoms C77–C83) [2.73 Å, 3.587 (6) Å and 154°].

In a view along *a* (Fig. 3*b*), it is possible to see that, along *b*, the diRh complex molecules are intercalated by groups of the

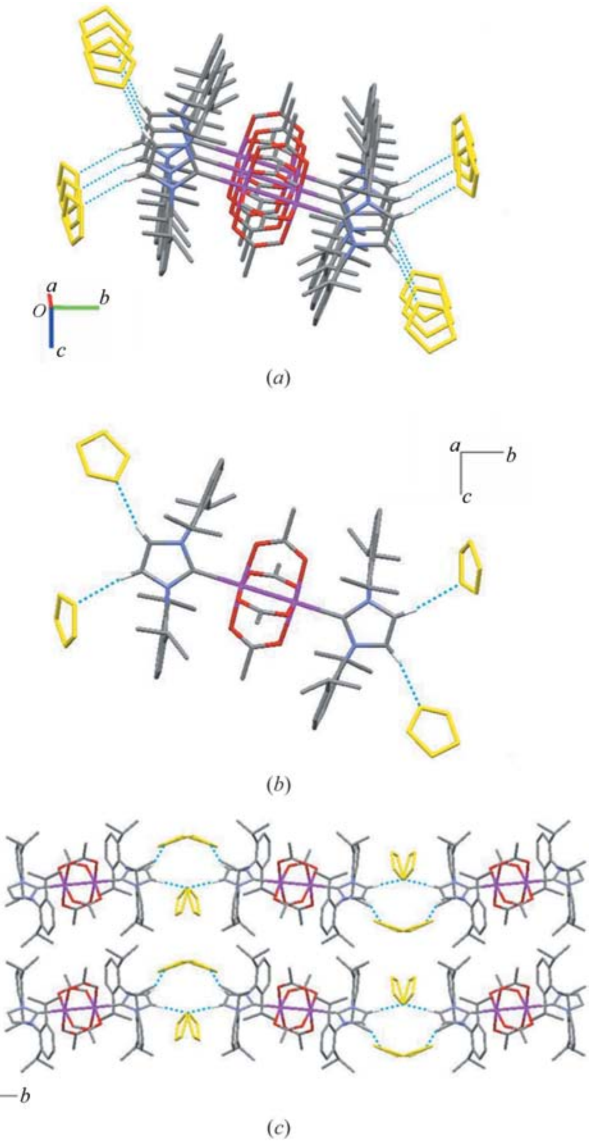

Figure 4

(*a*) The packing of the THF solvate, (I), showing its bidimensionality. (*b*) The packing of (I), viewed along *a*; THF molecules are rotated by 86.7° relative to each other. (*c*) The packing of (I), viewed along *c*.

three independent toluene molecules, forming chains with a repeat motif of (diRh complex molecule)–(group of toluene molecules)–(diRh complex molecule). On the other hand, diRh complex molecules align along the *bc* diagonal.

The THF solvate (I) presents a very different supramolecular arrangement compared with the toluene solvate, resulting in very different crystal packing for the two structures. In this new derivative, not only do the solvent molecules interact differently with the organometallic moieties, but they also do not interpose with the diRh complex molecules, resulting in a 'pseudo-polymer' array of diRh complex molecules aligning along *a* (Fig. 4*a*). However, even though the diRh complex molecules do not interact with each other directly, they are much closer to each other (shortest intermolecular distance of 2.34 Å) than in the crystal packing of toluene solvate (II) (2.77 Å).

Each solvent molecule establishes a short-contact interaction involving different H atoms from the five-membered ring of the imidazol-2-ylidene group of the diRh complex, resulting in its association with two THF molecules through C10—H10···O11 [2.37 Å, 3.313 (9) Å and 169°] and C11—H11···O10 [2.39 Å, 3.322 (9) Å and 165°] interactions (Fig. 4*b*).

In Fig. 4(*c*), chains of alternating diRh complex and THF molecules are visible along *b*. The diRh complex pseudo-polymer array aligned along *a* is once again observed, as well as an interesting THF motif intercalating consecutive complex molecules.

As discussed above, the supramolecular assemblies in both solvates compared in this paper are completely different and the space filling is achieved in two distinct modes, even though they both result in similar packing efficiencies, with a slightly higher value (64.8%) in the THF solvate than in the toluene solvate (62.8%).

Experimental

Complex (III) (see scheme in *Comment*) (43 mg, 0.051 mmol) was suspended in dry tetrahydrofuran (THF; 1 ml) and phenyl lithium (27 µl, 0.051 mmol) was added at 193 K. The colour changed instantaneously from purple to orange. The mixture was stirred at room temperature for 12 h. After filtration, the solvent was removed under vacuum and fresh THF was added (1 ml). The solution was kept at 253 K to induce crystallization. X-ray diffraction analysis of the crude crystals formed allowed the identification of the bis-complex presented in this paper and the mono-complex, with a molecule of THF attached to the vacant coordination site, previously reported by Trindade *et al.* (2008).

Crystal data

$[Rh_2(C_2H_3O_2)_4(C_{27}H_{36}N_2)_2]\cdot 4C_4H_8O$
$M_r = 1507.56$
Monoclinic, $P2_1/c$
$a = 10.509$ (4) Å
$b = 33.708$ (6) Å
$c = 11.967$ (3) Å
$\beta = 111.388$ (6)°
$V = 3947.2$ (19) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.48$ mm^{-1}
$T = 150$ (2) K
0.30 × 0.15 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.870$, $T_{max} = 0.932$
38595 measured reflections
9028 independent reflections
6488 reflections with $I > 2\sigma(I)$
$R_{int} = 0.082$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.071$
$wR(F^2) = 0.151$
$S = 1.17$
9028 reflections
438 parameters
96 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.92$ e Å^{-3}

Distance restraints were applied to the C—C bonds of the solvent molecules, while similarity and pseudo-isotropic restraints were applied to the atomic displacement parameters of these atoms. H atoms were placed in calculated positions and allowed to ride on their parent C atoms, with C—H = 0.93 Å for aromatic, 0.97 Å for methylene, 0.98 Å for methine and 0.96 Å for methyl H atoms, and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C).

Table 1
Comparison of torsion angles (°) in the two solvates.

	THF solvate (this work)	Toluene solvate (Góis *et al.*, 2007)
C9—N1—C12—C17	−92.5 (6)	−98.3 (4)
C9—N1—C12—C13	91.3 (6)	85.3 (4)
C9—N2—C24—C25	101.9 (6)	99.8 (4)
C9—N2—C24—C29	−82.0 (6)	−84.0 (4)
C36—N3—C39—C40	101.9 (6)†	93.7 (4)
C36—N3—C39—C44	−82.0 (6)†	−89.8 (4)
C36—N4—C51—C52	91.3 (6)†	87.5 (4)
C36—N4—C51—C56	−92.5 (6)†	−96.7 (4)
N1—C12—C13—C21	−8.2 (7)	−8.1 (5)
N1—C12—C17—C18	7.6 (7)	9.9 (5)
N2—C24—C25—C33	−11.4 (7)	−10.1 (5)
N2—C24—C29—C30	8.8 (7)	8.4 (5)
N3—C39—C40—C48	−11.4 (7)†	−7.1 (5)
N3—C39—C44—C45	8.8 (7)†	6.9 (5)
N4—C51—C56—C57	7.6 (7)†	9.9 (5)
N4—C51—C52—C60	−8.2 (7)†	−8.9 (5)

† Values obtained by symmetry.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3.2* (Farrugia, 1997) and *Mercury* (Version 1.4; Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3081). Services for accessing these data are described at the back of the journal.

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