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Solid state packing of [Rh(β-diketonato)$(CO)_2$] complexes. Crystal structure of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$]

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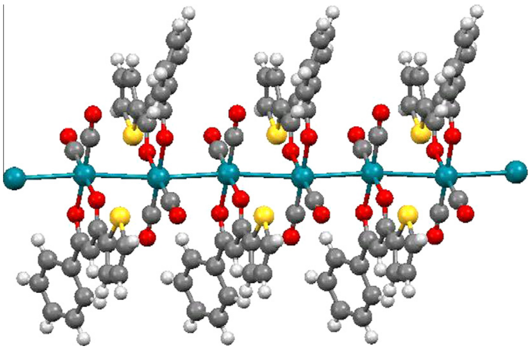
HIGHLIGHTS

- Crystal structure of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$].
- Typical structural parameters of [Rh(β-diketonato)$(CO)_2$] complexes.
- Metal–metal interactions in [Rh(β-diketonato)$(CO)_2$] complexes.

GRAPHICAL ABSTRACT

The structure and solid state packing of complex [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] are compared with those of related [Rh(β-diketonato)$(CO)_2$] complexes.



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ABSTRACT

A neutral columnar stacking of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] molecules was obtained in the crystalline solid state, i.e. the complex forms “molecular wires” in the solid state. The metal–metal interactions of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] and related [Rh(β-diketonato)$(CO)_2$] complexes show, that [Rh(β-diketonato)$(CO)_2$] complexes generally form a dimer-like arrangement, with a Rh^I—Rh^I distance of 3.18–3.54 Å. The dimeric units either stack in infinite chains, or interact with each other via weak Rh—π, or weak hydrogen bond interactions.

1. Introduction

The first square planar [Rh(β-diketonato)$(CO)_2$] complex was reported by Bonati and Wilkinson [1]. Rhodium-dicarbonyl complexes are known for their application in catalysis and catalytic precursors, for example the square planar rhodium(I) $[Rh(CO)_2(I)_2]^-$ complex, which is used for the manufacture of acetic acid, by catalytic carbonylation of methanol [2–6]. Rhodium-dicarbonyl complexes containing a β-diketonato ligand, such as [Rh(acac)$(CO)_2$] (where acac = acetylacetonato), are catalytic precursors for the hydrogenation and for hydroformylation of unsaturated alcohols [7], for the hydrogenation of alkenes [8] and for the hydroformylation of 1-hexene [9]. Square planar 16-electron d^8 rhodium(I) complexes are electron deficient and coordinatively unsaturated, causing these systems to be prone to stacking by allowing the formation of metal–metal bonds [10] and chains [11,12] with weak metal–metal interactions between the rhodium atoms [13,14]. The extended interactions are the result of metal–metal σ-bonding between the square planar d^8 transitional metal complexes [15]. Examples of metal chains with strong metal–metal bonds are known, which are catalytically active in processes, such

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as the water gas shift reaction and CO_2 reduction [16]. One-dimensional stacking of metal centres has led to materials with interesting properties in the crystal phase, such as magnetism and one-dimensional conductivity [15,17]. In this paper we discuss the packing of [Rh(β-diketonato)$(CO)_2$] complexes.

2. Experimental

2.1. Synthesis

[Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] was synthesized as described previously [18].

2.2. Crystallography

Crystals of the [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] complex (where $PhCOCH_2COC_4H_3S$ = benzoylthienylacetone or 1-phenyl-3-(2-thienyl)-1,3-propanedione [19]) were obtained with difficulty by recrystallization from hexane. Only one crystal of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] produced an X-ray diffraction pattern that was deemed suitable for data collection. The red crystal was mounted on a glass fibre and used for the X-ray crystallographic analysis. The X-ray intensity data was measured on a Bruker X8 Apex II 4K Kappa CCD diffractometer area detector system, equipped with a graphite monochromator and a Mo K_α fine-focus sealed tube (λ = 0.71073 Å), operated at 1.5 kW power (50 kV, 30 mA). The detector was placed at a distance of 3.75 cm from the crystal. The crystal temperature during the data collection was kept constant at 100(2) K, using an Oxford 700 series cryostream cooler.

The initial unit cell and data collection was achieved by the Apex2 software [20], utilizing COSMO [21] for optimum collection of more than a hemisphere of reciprocal space. A total of 1778 frames were collected, with a scan width of 0.5° in φ and ω, and an exposure time of 40 s frame^{-1}. The frames were integrated using a narrow-frame integration algorithm and reduced with the Bruker SAINT-Plus [22] and XPREP [22] software packages, respectively. The integration of the data, using a monoclinic cell, yielded a total of 25,770 reflections to a maximum θ angle of 28.5°, of which 3596 were independent, with a R_{int} = 0.152. Analysis of the data showed no significant decay during the data collection. Data was corrected for absorption effects, using the multi-scan technique SADABS [23], with minimum and maximum transmission coefficients of 0.620 and 0.937 respectively.

The structure was solved by the direct methods package SHELXS [24] and refined using the X-Seed software package [25] incorporating SHELXL [24]. The final anisotropic full-matrix least-squares refinement on F^2 with 235 variables, converged at R_1 = 0.075 for the observed data and wR_2 = 0.2076 for all data. The GOF was 1.06. The largest peak on the final difference electron density synthesis was 3.49 e Å^{-3}, at 0.5 Å from Rh1, and the deepest hole was −1.60 e Å^{-3}, at 0.77 Å from Rh1.

The aromatic H atoms were placed in geometrically idealized positions (C—H = 0.95 Å) and were constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography, Volume C [26]. The molecular plot was drawn, using the X-Seed programme [25].

3. Results and discussion

3.1. Synthesis

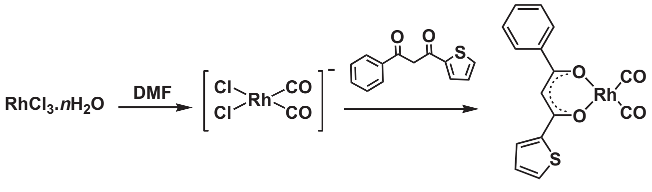
[Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] was synthesized as shown in Scheme 1. Heating a DMF solution of $RhCl_3.nH_2O$, leads to the formation of the salt $[NH_2(CH_3)_2]^+[Rh(CO)_2Cl_2]^-$ [27]. Addition of the β-diketone $PhCOCH_2COC_4H_3S$ to the reaction mixture, with an excess of water, resulted in the precipitation of the red [Rh(β-diketonato)$(CO)_2$] complex.

3.2. Structure of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$]

The atom labelling of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] is shown in Fig. 1. Crystal data of the structure of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] is summarized in Table 1, while selected bond lengths, angles and torsion angles can be found in Table 2. The [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] molecules pack in the $P2_12_12_1$ space group, with Z = 4. The Rh(I) atom has a square planar coordination sphere. The C(1)—O(2) and C(3)—O(1) bonds in the β-diketonato skeleton of the [Rh(β-diketonato)$(CO)_2$] complex are 1.250(9) Å and 1.265(10) Å respectively, and is shorter than the corresponding bonds in the free β-diketone, which are 1.268(3) Å and 1.330(3) Å respectively. The C—O and C—C bonds of intermediate order, indicate a conjugation which forms a pseudo-aromatic system. The 2-thienyl (C_4H_3S) and phenyl (Ph) groups bonded to the β-diketone backbone are both rotated out of the plane formed by the rest of the molecule, by 2° and 15° respectively. The orientation of the 2-thienyl group bonded to a β-diketonato backbone is often flat relative to the plane through the β-diketonato backbone [19,30,28], while the orientation of a Ph group bonded to a β-diketonato backbone is often rotated [29,30]. Although both the side groups phenyl and 2-thienyl are aromatic, the larger angle of the phenyl relative to the plane, compared to the angle between 2-thienyl and the plane, implies that the conjugation between the pseudo-aromatic β-diketonato ring and the 2-thienyl is stronger than the conjugation with the phenyl.

3.3. Rh—L bonds and L—Rh—L′ angles in [Rh(β-diketonato)$(CO)_2$] complexes

Selected geometric data of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] is compared with data of the structurally similar [Rh(β-diketonato)$(CO)_2$] complexes, where β-diketonato = $CH_3COCHCOCH_3$ [13], $PhCOCHCOCH_3$ [31], $PhCOCHCOCH_2CH_3$ [32], $PhCOCHCOCH_2CH_2CH_3$ [33], $FcCOCHCOCF_3$ [34] (Fc = ferrocenyl = $(C_5H_5)Fe(C_5H_4)$) and $CF_3COCHCOCH_3$ [35] in Table 2. For all these [Rh(β-diketonato)$(CO)_2$] complexes, the Rh—O bonds of a specific complex is the same within 0.01 Å, except for [Rh($FcCOCHCOCF_3$)$(CO)_2$], where the Rh—O bond nearest to the ferrocenyl group is 0.03 Å longer, than the Rh—O bond nearest to the CF_3 group. The difference in Rh—O bonds in the latter complex is expected, because of the strong electron donating property of the ferrocenyl group (χ_{Fc} = 1.87 [36]), compared to that of CF_3 group (χ_{CF3} = 3.01 [36]) on the β-diketonato ligand $(FcCOCHCOCF_3)^-$. This electronic *trans* influence of the ferrocenyl group, should also lead to a shorter Rh—C′ bond, *trans* to the longer Rh—O bond, but the inaccuracy of the bonds Rh—C = 1.83(2) and Rh—C′ = 1.84(1) Å, prevented clear identification of this effect in [Rh($FcCOCHCOCF_3$)$(CO)_2$]. The observed shorter Rh—C′ bond, *trans* to the Rh—O bond nearest to the electron donating phenyl group in [Rh($PhCOCHCOCF_3$)$(CO)_2$], can be due



Scheme 1. Synthetic route for the synthesis of [Rh($PhCOCHCOC_4H_3S$)$(CO)_2$] from $RhCl_3.nH_2O$.

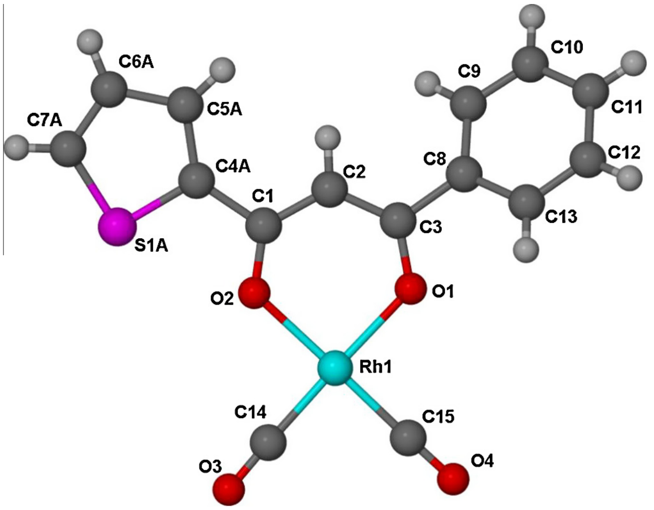


Fig. 1. Molecular plot of [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$], showing atom labelling.

Table 1
Crystal data and structure refinement of [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$].

Empirical formula	$C_{15}H_9O_4RhS$	Theta range for data collection	3.5–40.5°
Formula weight	388.19 g mol^{-1}	Index ranges	$-8 \leqslant h \leqslant 8$ $-15 \leqslant k \leqslant 15$ $-26 \leqslant l \leqslant 26$
Temperature	100(2) K	Reflections collected	25770
Wavelength	0.71073 Å	Independent reflections	3596 [R_{int} = 0.152]
Crystal system	Orthorhombic	Theta maximum	28.5°
Space group	$P2_12_12_1$	Absorption correction	Multi-scan
Unit cell dimensions	a = 6.4610(9) Å b = 11.4245(18) Å c = 19.557(3) Å α = 90° β = 90° γ = 90°	Max. and min. transmission	0.937 and 0.620
Volume	1443.6(4) Å^3	Refinement method	Full-matrix least-squares on F^2
Z	4	Data/restraints/parameters	3596/26/185
Density (calculated)	1.786 Mg m^{-3}	Goodness-of-fit on F^2	1.06
Absorption coefficient (μ)	1.34 mm^{-1}	Final R indices [I > 2sigma(I)]	R_1 = 0.075
F(000)	768	R indices (all data)	R_1 = 0.0747 wR_2 = 0.2076
Crystal size	0.40 × 0.09 × 0.05 mm^3	Largest diff. peak and hole	3.49 and −1.60 e Å^{-3}
–	–	Absolute structure parameter	0.45(10)

to the electronic *trans* influence of the phenyl group (χ_{Ph} = 2.21 [36]), compared to that of the CF$_3$ group (χ_{CF3} = 3.01 [36]) on the β-diketonato ligand (PhCOCHCOCF$_3$)$^-$. The O—Rh—O′ and C—Rh—C′ angles of the [Rh(RCOCHCO′R′)(CO)$_2$] complexes, are the same within 1° and 2° respectively. In summary, the bonds around the rhodium centre of the [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$] molecule and the other [Rh(β-diketonato)(CO)$_2$] molecules, are very similar (Table 2).

3.4. Packing of [Rh(β-diketonato)(CO)$_2$] complexes

The packing diagram of the [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$] molecules, are given in Fig. 2. The main point of interest here, is that the [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$] molecules stack in an infinite chain of rhodium atoms along the *a*-axis, with a Rh···Rh distance of 3.250 Å. Neighbouring units are oriented with an angle of 180° in the opposite direction, due to an inversion symmetry operation (Fig. 2(a)). The rhodium atoms that form the core of a column, are stacked in a zigzag fashion with an angle between Rh···Rh vectors of 167.4°. Typical Rh—Rh single bonds are 2.35–2.45 Å [37]. The typical Rh^I—Rh^I bond length in a dimer with true covalent bonds, and in which there are no supporting bridge ligands between metals, varies from 2.82 to 3.24 Å [11,38]. However, the 3.250 Å distance between the Rh atoms in [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$], fall well within the typical distance between two rhodium(I) molecules in extended metal chains, which have no covalent metal–metal bonds, but still contain meaningful weak metal–metal interactions, which is a distance between 3.25 and 3.68 Å [11,13,14]. The 3.250 Å distance between Rh atoms in [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$], is therefore too long to be considered a true metal–metal bond, but does indicate clearly that interactions between metal atoms do exist.

Similar Rh···Rh interactions resulting in extended metal chains, were also observed for [Rh(β-diketonato)(CO)$_2$] molecules with the β-diketonato ligand = (CH$_3$COCHCOCH$_3$)$^-$, (PhCOCHCOCF$_3$)$^-$ and (PhCOCHCOCH$_3$)$^-$.

The [Rh(CH$_3$COCHCOCH$_3$)(CO)$_2$] molecules consist of weak dinuclear units, with a Rh···Rh distance of 3.253 Å. These [Rh(CH$_3$COCHCOCH$_3$)(CO)$_2$] dimers are stacked along the *a*-axis, with a distance of 3.271 Å between the dimers, in a similar linear fashion than the [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$] dimers. The neighbouring atoms in a dinuclear unit are oriented with an angle of 180° in the opposite direction, due to an inversion symmetry operation. A stereo view of this stacking arrangement is given in Fig. 3. The rhodium atoms which form the core of a column, are not perfectly aligned on top of one another, with an angle between Rh···Rh vectors of 175.28°.

Table 2
Selected geometric and crystallographic data of square planar complexes [Rh(β-diketonato)(CO)$_2$], where β-diketonato = (RCOCHC′O′R′)$^-$, with R and R′ groups as indicated.

R	R′	Rh—O (Å)	Rh—O′ (Å)	Rh—C (Å)	Rh—C′[a]/Å	O—Rh—O′ (°)	C—Rh—C′ (°)	Space group	Stack in	Rh···Rh (Å)	Reference
Ph	C_4H_3S	2.028(6)	2.041(5)	1.866(9)	1.846(9)	90.4(2)	88.1(3)	$P2_12_12_1$	Long chain	3.250	This study
CH_3	CH_3	2.040(4)	2.044(4)	1.831(7)	1.831(7)	90.8(2)	88.9(3)	$P\bar{1}$	Long chain	3.253, 3.271	[13]
Ph	CH_3	2.050(1)	2.035(1)	1.854(2)	1.848(2)	90.61(5)	87.98(7)	P21/c	Long chain	3.308, 3.461	[31]
Ph[b]	CH_2CH_3	2.0288(13)	2.0285(14)	1.849(2)	1.852(2)	90.36(6)	89.14(9)	P21/n	Dinuclear units	3.175	[32]
Ph[b]	$CH_2CH_2CH_3$	2.0300(12)	2.0295(13)	1.851(2)	1.8446(19)	90.72(5)	89.14(8)	$P\bar{1}$	Dinuclear units	3.179	[33]
Fc[c]	CF_3	2.049(8)	2.016(9)	1.83(2)	1.84(1)	90.2(3)	89.1(6)	C2/c	Long chain	3.537	[34]
Ph[b]	CF_3	2.02(2)	2.02(2)	1.82(3)	1.79(3)	89.8(7)	87(1)	Pbca	Dinuclear units	3.346	[35]

[a] Rh—C′ bond is on the side of O′, *trans* to Rh—O.

[b] Ph = phenyl.

[c] Fc = ferrocenyl.

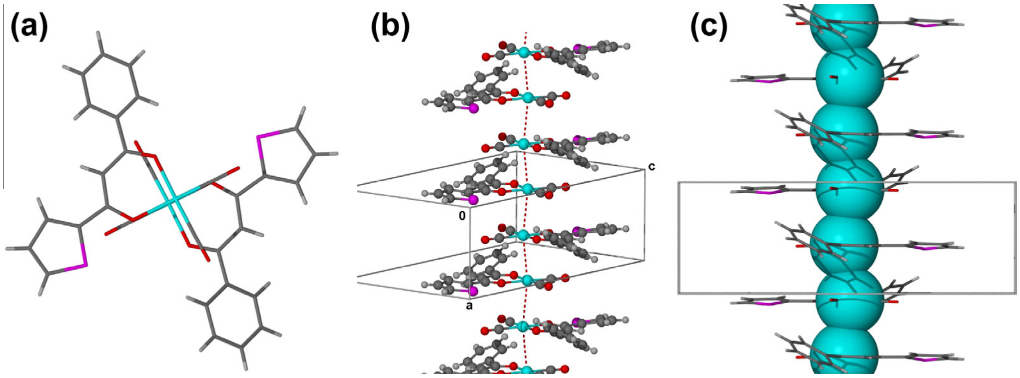


Fig. 2. (a) Orientation of the dinuclear [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$] molecules, viewed perpendicularly to the coordination plane. (b) Packing of the [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$] molecules, resulting in a "molecular wire" along the *a*-axis. (c) Packing accentuated by the blue spheres around the rhodium centre. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

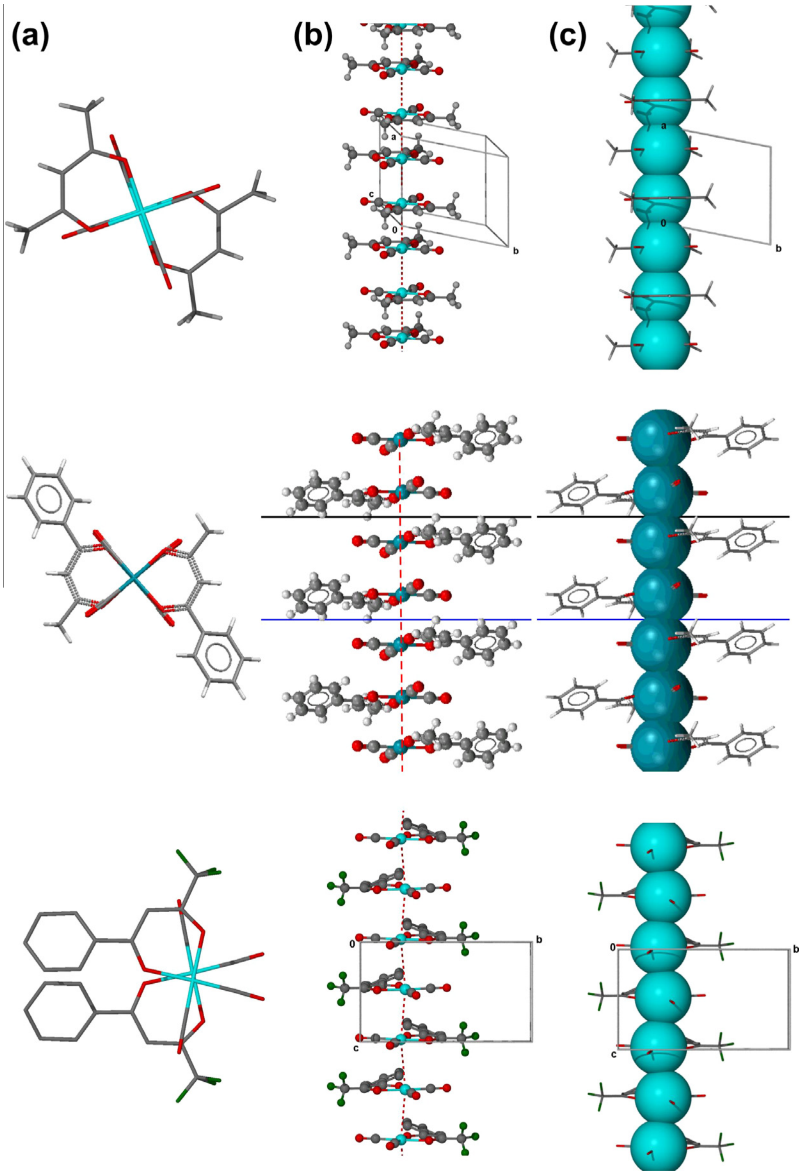


Fig. 3. (a) Orientation of three different dinuclear [Rh(β-diketonato)(CO)$_2$] molecules, viewed perpendicularly to the coordination plane. (b) Packing of the three [Rh(β-diketonato)(CO)$_2$] molecules, resulting in an infinite chain. (c) Packing accentuated by the blue spheres around the rhodium centre. The three β-diketonato ligands pictured are: (CH$_3$COCHCOCH$_3$)$^-$ (top), (PhCOCHCOCH$_3$)$^-$ (middle) and (PhCOCHCOCF$_3$)$^-$ (bottom). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

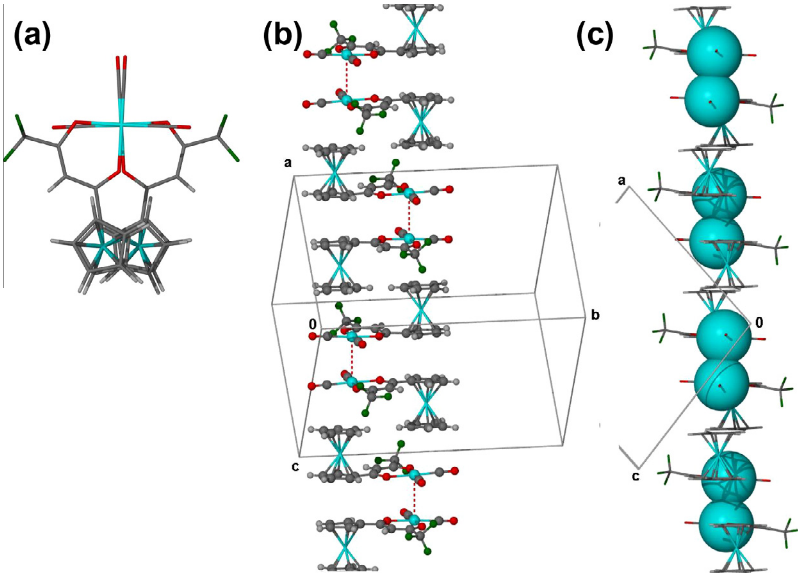


Fig. 4. (a) Orientation of the dinuclear [Rh(FcCOCHCOCF$_3$)(CO)$_2$] units, viewed perpendicularly to the coordination plane. (b) Packing of the dinuclear [Rh(FcCOCHCOCF$_3$)(CO)$_2$] units, with weak Rh—π interactions shown and (c) accentuated by the blue spheres around the rhodium centres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

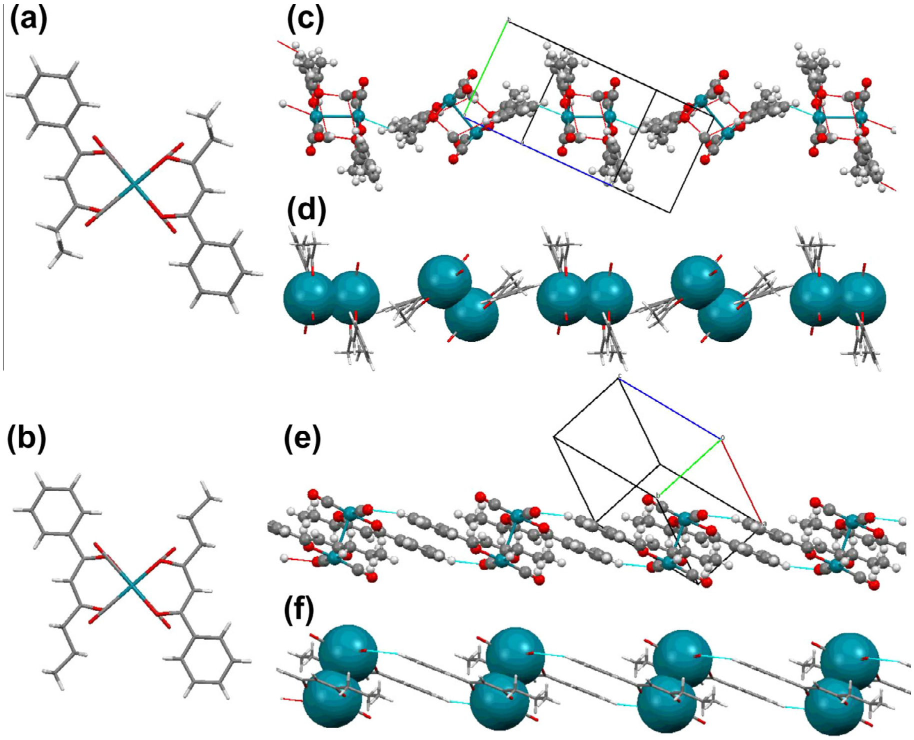


Fig. 5. Orientation of the following two dinuclear units, viewed perpendicularly to the coordination plane: (a) [Rh(PhCOCHCOCH$_2$CH$_3$)(CO)$_2$] and (b) [Rh(PhCOCHCOCH$_2$CH$_2$CH$_3$)(CO)$_2$]. (c) Packing of the first dinuclear [Rh(PhCOCHCOCH$_2$CH$_3$)(CO)$_2$] units, comprising of weak Rh···H interactions and (d) the same [Rh(PhCOCHCOCH$_2$CH$_3$)(CO)$_2$] packing, accentuated by the blue spheres around the rhodium centre. (e) Packing of the second dinuclear [Rh(PhCOCHCOCH$_2$CH$_2$CH$_3$)(CO)$_2$] units, comprising of weak C—H···O═C interactions and (f) the same [Rh(PhCOCHCOCH$_2$CH$_2$CH$_3$)(CO)$_2$] packing, accentuated by the blue spheres around the rhodium centre. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The [Rh(PhCOCHCOCH$_3$)(CO)$_2$] molecules also form dinuclear units, which are oriented with an angle of 180° in the opposite direction, due to an inversion symmetry operation. The Rh···Rh distance between the rhodium atoms within the dinuclear unit is 3.308 Å, and slightly longer (3.461 Å) between the different dinuclear units. The [Rh(PhCOCHCOCH$_3$)(CO)$_2$]$_2$ dinuclear units stack in infinite arrays along the *b*-axis, see Fig. 3.

The [Rh(PhCOCHCOCF$_3$)(CO)$_2$] molecules stack in infinite arrays along the *c*-axis, with a Rh···Rh distance of 3.537 Å between the molecules. Different from the [Rh(PhCOCHCOC$_4$H$_3$S)(CO)$_2$] and

$[Rh(CH_3COCHCOCH_3)(CO)_2]$ complexes, the neighbouring $[Rh(PhCOCHCOCF_3)(CO)_2]$ molecules in a dinuclear unit are staggered with an O—Rh···Rh—O torsion angle of 114.2° between them. The β-diketonato ligands in neighbouring molecules of this dinuclear unit, are orientated in opposite directions, i.e. the neighbouring molecules are anti-eclipsed. The angle between the Rh···Rh vectors forming the core of a column, is 170.0°. The phenyl (Ph) group bonded to the β-diketonato backbone in $[Rh(PhCOCHCOCF_3)(CO)_2]$, is rotated out of the plane, formed by the rest of the molecule by 22°, which is slightly more than the 15° rotation of the phenyl group in the $[Rh(PhCOCHCOC_4H_3S)(CO)_2]$ complex.

In the case of the $[Rh(\beta\text{-diketonato})(CO)_2]$ molecules with the β-diketonato ligands = $(PhCOCHCOCH_2CH_3)^-$, $(PhCOCHCOCH_2CH_2CH_3)^-$ and $(FcCOCHCOCF_3)^-$, no extended metal chains were observed in the solid state, however, the packing of the $[Rh(\beta\text{-diketonato})(CO)_2]$ molecules does result in dinuclear units.

The $[Rh(FcCOCHCOCF_3)(CO)_2]$ molecules form weak dinuclear units, with a Rh···Rh distance of 3.346 Å. As with $[Rh(PhCOCHCOCF_3)(CO)_2]$, the two units of a $[Rh(FcCOCHCOCF_3)(CO)_2]$ dimer are staggered, with an O—Rh···Rh—O torsion angle of 96.2° between the units (Fig. 4(a)), and with the orientation of the neighbouring molecules again being anti-eclipsed. The dinuclear units are further supported by π–π interactions, which exist between the neighbouring cyclopentadienyl rings of the ferrocenyl (Fc) groups. The cyclopentadienyl rings are displaced from each other, in a slipped or offset alignment [39], with a centroid–centroid separation of 3.585 Å. One main difference between $[Rh(FcCOCHCOCF_3)(CO)_2]$ and the $[Rh(\beta\text{-diketonato})(CO)_2]$ complexes with β-diketonato = $(CH_3COCHCOCH_3)^-$, $(PhCOCHCOCF_3)^-$ and $(PhCOCHCOCH_3)^-$, which are illustrated in Fig. 3, is that the dinuclear units do not stack with the rhodium as a central axis. In this case, the dinuclear unit additionally rotates a further 180°, so that the rhodium centre of the one pair stacks on the β-diketonato backbone of the adjacent pair. Such an arrangement allows Rh-π interactions between the Rh of one dinuclear unit and the cyclopentadienyl ring of another unit. The Rh-centroid separation is 3.599 Å. The stacking is illustrated by the blue spheres in Fig. 4(c).

The $[Rh(PhCOCHCOCH_2CH_3)(CO)_2]$ molecules also form dinuclear units that do not pack in extended metal–metal chains. The two $[Rh(PhCOCHCOCH_2CH_3)(CO)_2]$ molecules in a dinuclear unit are oriented with an angle of 180° in the opposite direction, due to an inversion symmetry operation. The Rh···Rh distance of 3.175 Å in $[Rh(PhCOCHCOCH_2CH_3)(CO)_2]_2$, is shorter than that observed in any other dinuclear $[Rh(\beta\text{-diketonato})(CO)_2]$ unit to date, see Table 2. The angle between Rh···Rh vectors of the dinuclear units, is 50.0°. Weak Rh···H interactions [40] exist between the different dinuclear units (C13—H11···Rh Symmetry code $1/2 - x$, $-1/2 + y$, $1/2 - z$, with H11···Rh = 3.146 Å and C13···Rh = 3.933 Å), see Fig. 5.

Similarly to $[Rh(PhCOCHCOCH_2CH_3)(CO)_2]$, the $[Rh(PhCOCHCOCH_2CH_2CH_3)(CO)_2]$ molecules also form dinuclear units that do not pack in extended metal–metal chains, with the two $[Rh(PhCOCHCOCH_2CH_2CH_3)(CO)_2]$ molecules in a dinuclear unit, oriented with an angle of 180° in the opposite direction. The Rh···Rh vectors of the dinuclear units are parallel to each other, with a similar short Rh···Rh distance of 3.179 Å. Weak C—H···O═C interactions (2.659 Å) exist between the different dinuclear units (C12—H11···O1 Symmetry code $1 - x$, $1 - y$, $-1 - z$, with H11···O1 = 2.659 Å and C12···O1 = 3.641 Å), see Fig. 5.

Square planar rhodium(I) complexes that form dinuclear units, which interact with another similar dinuclear unit either *via* weak metal–metal interactions [13,14,41], metal and ligand interactions [42,43], metal and aromatic π-interactions [43] or π–π interactions [11], are known. In these cases, the typical distance between the metals in the dinuclear unit varies from 3.23 to almost 4.00 Å [43,44]. The short Rh···Rh distance observed in $[Rh(PhCOCHCOCH_2CH_3)(CO)_2]$ and $[Rh(PhCOCHCOCH_2CH_2CH_3)(CO)_2]$ (3.175 Å and 3.179 Å), is thus shorter than generally observed in dinuclear units, and falls within the range of the typical Rh^I—Rh^I bond length of a dimer with true covalent bonds, 2.82–3.24 Å [11,38].

4. Conclusions

We have presented here the comparative study of the packing of $[Rh(\beta\text{-diketonato})(CO)_2]$ dinuclear units. The rhodium(I) metal ion in $[(Rh(PhCOCHCOC_4H_3S)(CO)_2]$ forms Rh···Rh interactions in the solid state, resulting in the formation of molecular wires. Similar Rh···Rh interactions are observed for $[Rh(CH_3COCHCOCH_3)(CO)_2]$, $[Rh(PhCOCHCOCF_3)(CO)_2]$ and $[Rh(PhCOCHCOCH_3)(CO)_2]$. The $[Rh(PhCOCHCOCH_2CH_3)(CO)_2]$, $[Rh(PhCOCHCOCH_2CH_2CH_3)(CO)_2]$ and $[Rh(FcCOCHCOCF_3)(CO)_2]$ complexes, however, do not form infinite metal–metal chains, but form dinuclear $[Rh(\beta\text{-diketonato})(CO)_2]$ units in the solid state.

Supplementary material

CCDC 943069 contains the supplementary crystallographic data for this paper.

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