metal-organic compounds

(R,R)-Tricarbonyl{η^6-1-(diphenylphosphino)-2-[1-(diphenylphosphino)-ethyl]benzene}chromium(0), (R,R)-tricarbonyl-1κ^3C-{μ-1(η^6):-2κ^2P,P'-1-(diphenylphosphino)-2-[1-(diphenylphosphino)ethyl]-benzene}[2(η^4)-norbornadiene]-chromium(0)rhodium(I) tetrafluoro-borate methanol 0.75-solvate and (R,R)-tricarbonyl-1κ^3C-{μ-1(η^6):-2κ^2P,P'-1-(diphenylphosphino)-2-[1-(diphenylphosphino)ethyl]-benzene}[2(η^4)-(Z,Z)-cycloocta-1,5-diene]chromium(0)rhodium(I) tetra-fluoroborate methanol 1.5-solvate

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The title mononuclear chromium compound, [Cr(C$_{32}$H$_{28}$P$_2$)-(CO)$_3$], (I), and its rhodium complexes [CrRh(C$_7$H$_8$)-(C$_{32}$H$_{28}$P$_2$)(CO)$_3$]BF$_4$·0.75CH$_4$O, (II), and [CrRh(C$_8$H$_{12}$)-(C$_{32}$H$_{28}$P$_2$)(CO)$_3$]BF$_4$·1.5CH$_4$O, (III), prepared as a ligand and precatalysts, respectively, for application in asymmetric homogeneous hydrogenation, have been studied by single-crystal X-ray diffraction. The structures of the free and com-plexed ligand are compared. It was found that the backbone of the ligand remains rigid on coordination, while only minor conformational changes of its side chains are observed. Both elements of central and planar chirality seem to build a well defined chiral environment for stereoselective catalysis.

Comment

One of our main interests lies in the field of the design, synthesis and application of new chiral ligands for asymmetric hydrogenation, including those incorporating an organo-metallic framework. For compound (R,R)-(I), first introduced
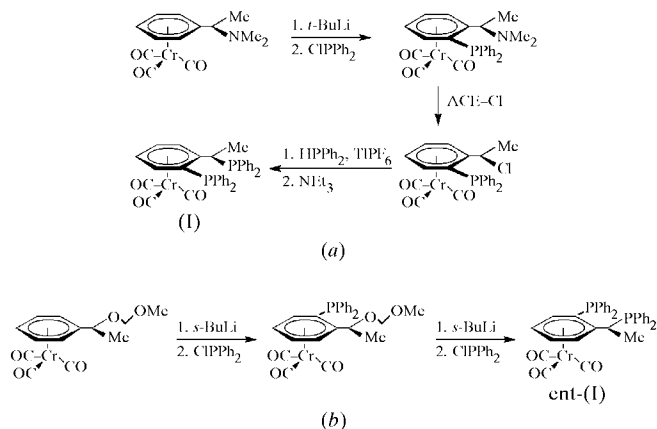
by Uemura (Hayashi *et al.*, 1995) in its enantiomeric form (S,S)-(I), we have recently reported an alternative synthetic route (Vasen *et al.*, 2000; Braun *et al.*, 2003), depicted in Scheme 1 as route (a), together with Uemura's route, *i.e.* (b). Uemura's method starts from the (S)-[1-(methoxymethoxy)-ethyl]benzene–chromium–tricarbonyl complex, which, after deprotonation with s-BuLi and quenching with ClPPh$_2$, gives the *ortho*-substituted product in 50% yield. Subsequent deprotection with boron trifluoride etherate (38%) and nucleophilic substitution of the hydroxy group for PPh$_2$ with tetrafluoroboric acid and diphenylphosphine (80%) leads to the diphosphine in an overall yield of just 15%. In contrast, we employed (R)-[1-(dimethylamino)ethyl]benzene–chromium–tricarbonyl as the starting material. From this, *ortho*-substi-tution by a deprotonation/electrophilic addition sequence with t-BuLi and diphenylphosphine gives the planar chiral product in almost quantitative yield (98%). The dimethylamine group is then substituted for a Cl atom, employing ACE-Cl
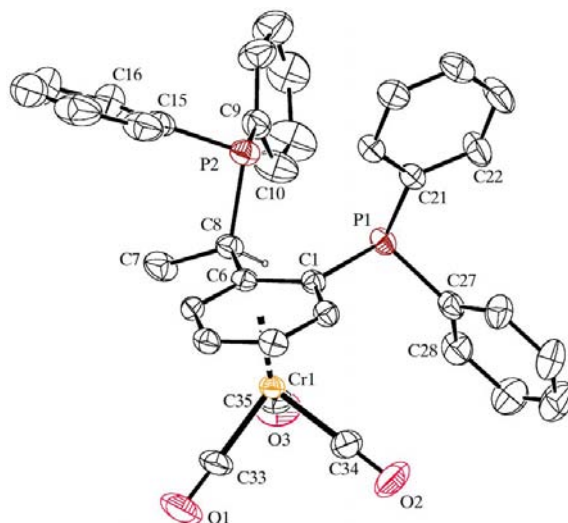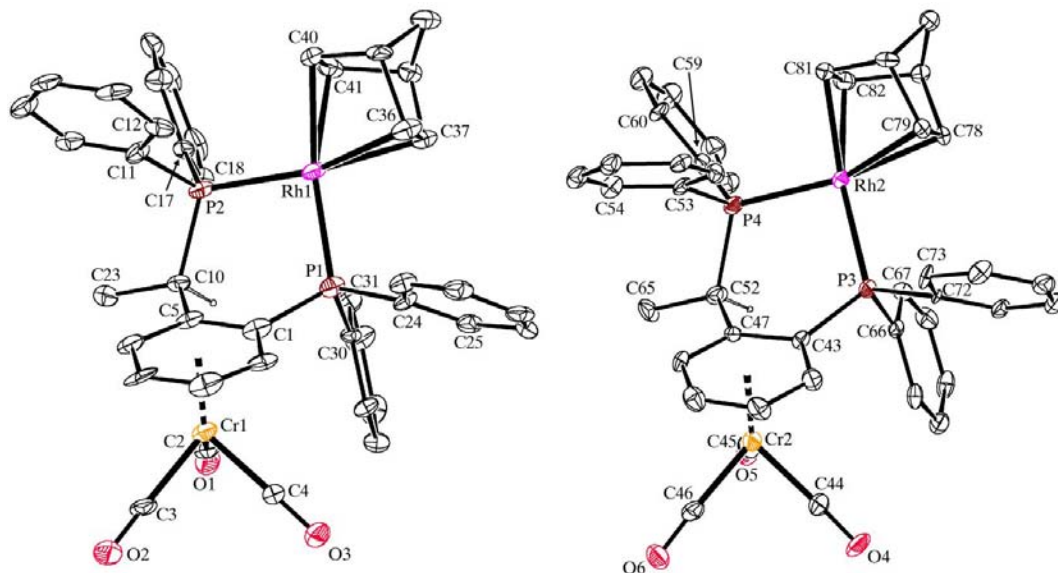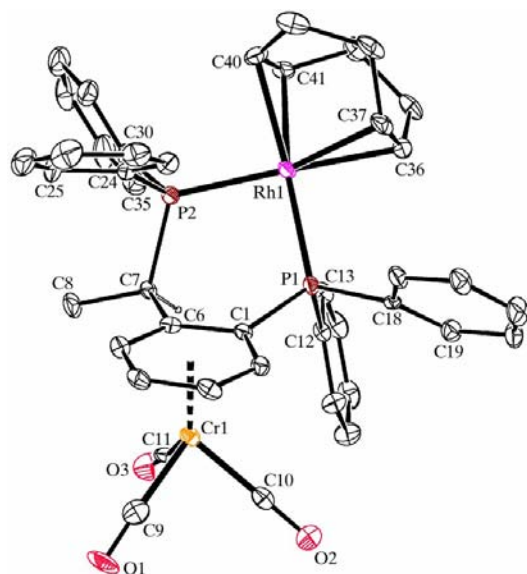
Figure 1
A view of the structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity, apart from that on the α-C atom, which is shown as a small sphere of arbitrary radius.

Figure 2
A view of the [(NBD)Rh(PPh₂/PPh₂)]⁺ cation of (II), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity, apart from that on the α-C atom, which is shown as a small sphere of arbitrary radius. The relative orientation of the two molecules in the plot does not reflect their true orientation in the asymmetric unit.


Figure 3
A view of the [(COD)Rh(PPh₂/PPh₂)]⁺ cation of (III), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity, apart from that on the α-C atom, which is shown as a small sphere of arbitrary radius.

(1-chloroethyl chloroformate), in 90% yield, and this can easily be exchanged for the desired diphenylphosphine group in 83% yield. The overall yield of the synthesis of (I) is 73%, significantly higher than the aforementioned compound.

For application in catalysis, we have complexed (I) to NBD-Rh- and COD-Rh- fragments (NBD is norbornadiene and COD is cyclooctadiene) by standard laboratory procedures (Gladiali, 2000), forming the complexes [(NBD)Rh(PPh₂/PPh₂)]BF₄·0.75CH₄O, (II), and [(COD)Rh(PPh₂/PPh₂)]-BF₄·1.5CH₄O, (III). We present here an X-ray crystallographic study of both the ligand and the two rhodium complexes (Figs. 1–3).
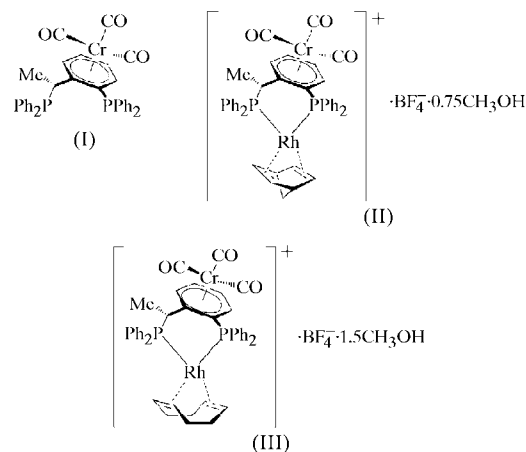
It should be mentioned that the supplementary material associated with Uemura's original report (Hayashi *et al.*, 1995) refers to a compound in the centrosymmetric space group $P2_1/c$, and hence to a racemic crystal rather than enantio-merically pure crystals. In the free ligand, (I), as is typical for piano-stool compounds like these, the Cr tripod is oriented in an eclipsed manner with respect to the arene ring. The three carbonyl ligands are oriented synperiplanar to the respective C atoms of the benzene ring. The bond lengths and angles of

the three title complexes (Tables 1–3) are similar to those of the previously published structures of [(NBD)Rh(PPh$_2$/PCy$_2$)]BF$_4$ and [(NBD)Rh(PCy$_2$/PPh$_2$)]BF$_4$ (Braun *et al.*, 2003). The NBD complex, (II), crystallizes with two complex cations and two anions (BF$_4^-$) per asymmetric unit. The superposition of the two independent complex moieties and an analysis of the torsion angles (Table 4) shows that the geometry of the two molecules is almost the same, except for the phenyl rings on the P atoms, which adopt slightly different conformations, differing by about 9° in the two independent molecules of (II).

The deviation observed from square-planar towards a tetrahedral coordination sphere is characteristic. The dihedral angles between the planes defined by P/Rh/P and MP1/Rh/MP2 (MP denotes the mid-points of the coordinated double bond) are 3.3 (1) and 6.5 (1)° for (II), and 9.8 (1)° for (III). It is also found for rhodium–diolefin complexes with other bisphosphine ligands that this dihedral angle is larger in COD complexes than in NBD complexes (Drexler *et al.*, 2001, 2004). No substantial change is found for the important bond lengths of the uncoordinated ligand on coordination to rhodium (Tables 1–3).

Selected torsion angles may be used to describe the conformation of the chelate rings of the title complexes. Table 4 shows that these torsion angles do not differ significantly for the NBD complex, (II), and the COD complex, (III). For the group incorporating the α-C atom, as expected, it can be stated that it chooses a conformation in which the small H atom faces down towards the bulky tricarbonylchromium moiety, while the diphenylphosphine group points away from the ring plane. We have calculated in (I) a dihedral angle for P2—α-C8—C6$_{ipso}$—C1$_{ortho}$ of 68.9 (5)°. Since the two P atoms are in close proximity, they can readily coordinate a Rh centre. This dihedral angle does not change significantly on coordination to the Rh centre, as can be seen in Table 4. Nonetheless, a twist of 30° around the P—C$_{asymm}$ bond takes place due to the orientation of the P-atom lone pair towards rhodium.

Within the ligand, the four phenyl rings of both the *ortho* and the α diphenylphosphine groups adopt a conformation that exhibits a sense of helicity, probably induced by the asymmetry of the backbone of the ligand, which might lead to the formation of a chiral cavity for the prochiral substrate in the rhodium complex.

Experimental

The syntheses and complete characterizations of complexes (I) and (II) (including all starting materials) are given by Braun *et al.* (2003). Single crystals were obtained from ethanol for (I) and from methanol for (II). Complex (III) was prepared according to the following procedure. In a Schlenk flask, [(COD)RhCl]$_2$ (104 mg, 0.211 mmol) and AgBF$_4$ (82 mg, 0.423 mmol) were dissolved in tetrahydrofuran (THF; 10 ml) and the solution was stirred vigorously for 30 min at ambient temperature. The AgCl which precipitated was filtered off using a syringe equipped with a filter needle, and the clear liquid dripped into a solution of (I) (258 mg, 0.423 mmol) in THF (5 ml). After stirring for 10 min, the product was precipitated by adding Et$_2$O. The ether solution was discarded and the solid dried *in vacuo*.

Single crystals of (III) were obtained by recrystallization from methanol.

Compound (I)

Crystal data

[Cr(C$_{32}$H$_{28}$P$_2$)(CO)$_3$]
$M_r = 610.51$
Orthorhombic, $P2_12_12_1$
$a = 10.6758$ (12) Å
$b = 13.5533$ (15) Å
$c = 21.255$ (2) Å
$V = 3075.4$ (6) Å^3
$Z = 4$
$D_x = 1.319$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8096 reflections
$\theta = 2.4$–25.2°
$\mu = 0.51$ mm^{-1}
$T = 293$ (2) K
Rod, yellow
$0.70 \times 0.20 \times 0.12$ mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.717$, $T_{max} = 0.941$
33 737 measured reflections
5572 independent reflections

4996 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 25.2$°
$h = -12 \rightarrow 12$
$k = -16 \rightarrow 16$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.098$
$S = 1.01$
5572 reflections
371 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 1.0577P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Absolute structure: Flack (1983), 2430 Friedel pairs
Flack parameter = 0.02 (2)

Table 1
Selected bond distances and angles (Å, °) for (I).

P1—C1	1.854 (3)	P2—C8	1.878 (3)
⟨Cr1—C(C$_6$H$_4$ ring)⟩	2.213 (4)	⟨Cr1—C(CO)⟩	1.840 (4)
C33—Cr1—C34	88.3 (2)	C34—Cr1—C35	88.8 (2)
C35—Cr1—C33	88.6 (2)		

Compound (II)

Crystal data

[CrRh(C$_7$H$_8$)(C$_{32}$H$_{28}$P$_2$)(CO)$_3$]·BF$_4$·0.75CH$_4$O
$M_r = 916.40$
Tetragonal, $P4_32_12$
$a = 14.3886$ (6) Å
$c = 76.056$ (4) Å
$V = 15746.0$ (13) Å^3
$Z = 16$
$D_x = 1.546$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8096 reflections
$\theta = 1.5$–25.0°
$\mu = 0.84$ mm^{-1}
$T = 110$ (2) K
Fragment, red
$0.16 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.878$, $T_{max} = 0.921$
72 654 measured reflections
13 552 independent reflections

9225 reflections with $I > 2\sigma(I)$
$R_{int} = 0.105$
$\theta_{max} = 25.0$°
$h = -17 \rightarrow 16$
$k = -16 \rightarrow 17$
$l = -85 \rightarrow 70$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.071$	$+ 29.8752P]$
$wR(F^2) = 0.174$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
13 552 reflections	$\Delta\rho_{max} = 1.77$ e Å^{-3}
983 parameters	$\Delta\rho_{min} = -0.90$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983),
	5780 Friedel pairs
	Flack parameter = -0.01 (4)

Table 2
Selected bond distances and angles (Å, °) for molecules 1 and 2 in (II).

MP1 and MP2 denote the mid-points of the olefinic bonds C36—C37/C78—C79 and C39—C40/C81—C82, respectively.

	Molecule 1	Molecule 2
Rh1—P1	2.277 (3)	2.288 (3)
Rh1—P2	2.273 (3)	2.253 (3)
Rh1—MP1	2.0974 (8)	2.1141 (6)
Rh1—MP2	2.1242 (7)	2.0962 (7)
⟨Rh1—C=C(diolefin)⟩	2.221 (10)	2.215 (9)
P1—C1	1.846 (11)	1.827 (9)
P2—C10	1.851 (10)	1.865 (10)
P1—C24	1.810 (10)	1.823 (9)
P2—C11	1.810 (11)	1.807 (10)
P1—C30	1.812 (9)	1.793 (10)
P2—C17	1.808 (10)	1.816 (10)
⟨Cr1—C(C$_6$H$_4$ ring)⟩	2.214 (11)	2.226 (10)
⟨Cr1—C(CO)⟩	1.826 (11)	1.843 (11)
P1—Rh1—P2	91.60 (10)	91.42 (9)
MP1—Rh1—MP2	68.26 (3)	69.23 (2)
P1—Rh1—MP1	99.02 (8)	101.11 (7)
P2—Rh1—MP2	101.03 (7)	98.53 (7)
C2—Cr1—C3	87.5 (5)	85.9 (5)
C3—Cr1—C4	86.4 (5)	87.1 (5)
C4—Cr1—C2	90.4 (5)	88.2 (5)

Compound (III)

Crystal data

[CrRh(C$_8$H$_{12}$)(C$_{32}$H$_{28}$P$_2$)(CO)$_3$]··	$D_x = 1.475$ Mg m^{-3}
BF$_4$·1.5CH$_4$O	Mo $K\alpha$ radiation
$M_r = 956.47$	Cell parameters from 5000
Monoclinic, $P2_1$	reflections
$a = 11.262$ (2) Å	$\theta = 4$–20°
$b = 14.116$ (3) Å	$\mu = 0.77$ mm^{-1}
$c = 14.226$ (3) Å	$T = 200$ (2) K
$\beta = 107.81$ (3)°	Prism, red
$V = 2153.2$ (7) Å^3	$0.50 \times 0.30 \times 0.30$ mm
$Z = 2$	

Data collection

Stoe IPDS image-plate	$R_{int} = 0.035$
diffractometer	$\theta_{max} = 24.4°$
φ scans	$h = -12 \rightarrow 12$
Absorption correction: empirical	$k = -16 \rightarrow 15$
(*ABSCOR*; Stoe & Cie, 1995)	$l = -16 \rightarrow 16$
$T_{min} = 0.700$, $T_{max} = 0.802$	50–200 standard reflections
11 684 measured reflections	frequency: 360 min
6454 independent reflections	intensity decay: none
5511 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	$(\Delta/\sigma)_{max} = 0.009$
$S = 0.95$	$\Delta\rho_{max} = 0.63$ e Å^{-3}
6454 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}
532 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	2773 Friedel pairs
	Flack parameter = 0.00 (2)

Table 3
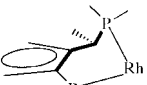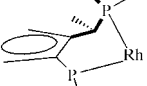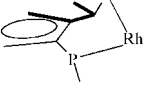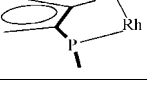Selected distances and angles (Å, °) for (III).

MP1 and MP2 denote the mid-points of the olefinic bonds C36—C37/C78—C79 and C39—C40/C81—C82, respectively.

Rh1—P1	2.290 (2)	Rh1—P2	2.279 (2)
Rh1—MP1	2.135 (5)	Rh1—MP2	2.149 (5)
⟨Rh1—C=C(diolefin)⟩	2.249 (6)		
P1—C1	1.852 (5)	P2—C7	1.871 (5)
P1—C12	1.832 (5)	P2—C24	1.815 (5)
P1—C18	1.823 (5)	P2—C30	1.818 (5)
⟨Cr1—C(C$_6$H$_4$ ring)⟩	2.217 (5)	⟨Cr1—C(CO)⟩	1.835 (7)
P1—Rh1—P2	90.0 (1)	MP1—Rh1—MP2	84.2 (1)
P1—Rh1—MP1	94.4 (1)	P2—Rh1—MP2	92.2 (1)
C9—Cr1—C10	86.5 (2)	C10—Cr1—C11	88.9 (2)
C11—Cr1—C9	87.1 (2)		

Table 4
Comparison of characteristic torsion angles (°) in (I)–(III).

Torsion angle		Compound	
	(I)	(II) Molecule 1/Molecule 2	(III)
	−68.9 (5)	−68.6 (11)/−68.5 (10)	−68.9 (5)
	−92.3 (2)	−66.3 (8)/−56.8 (7)	−54.1 (3)
	−17.9 (4)	−19.5 (13)/−21.4 (13)	−20.0 (6)
	−61.6 (2)	−75.9 (9)/−83.6 (8)	−75.1 (4)

H atoms were placed in calculated positions and refined using a riding model, with C—H distances of 0.98 Å and with $U_{iso}(H) = 1.3U_{eq}(C)$. The BF$_4^-$ anion in complex (III) is disordered; two sets of F atoms were refined isotropically, each set with near half occupancy. For complexes (II) and (III), the final structure models show several peaks of relatively high electron density. In agreement with the ^{1}H NMR data, this electron density was interpreted as MeOH molecules (solvent of crystallization). In the case of (II), both solvent molecules are disordered and were treated as isotropic. For one solvent molecule, the position of the hydroxyl H atom attached to atom O8 was refined using a riding model, with O—H = 0.95 Å. The choice of the H-atom position was determined by the best hydrogen bond that could be created (O8···F6). For the second MeOH molecule, no hydrogen-bond acceptor was found in the neighbourhood of atom O7 and the maximum electron density was taken as the starting position for the H atom, and it was also treated as riding, with O—H = 0.95 Å. For both hydroxy H atoms, $U_{iso}(H) = U_{eq}(O)$. For (III), the position of one solvent molecule was only half occupied. For both MeOH molecules, the maximum electron density was taken as the starting position for the hydroxy H atom and these were treated as riding, with O—H = 0.95 Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

metal-organic compounds

For compounds (I) and (II), data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

For compound (III), data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1995); cell refinement: *CELL* in *IPDS*; data reduction: *INTE-GRATE* in *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXL*97.

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