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fac,trans-[(2,2′-Bipyridine-*N*,*N*′)tricarbonylrhenium(I)]-*μ*-(4,4′-bipyridine)-*N*:*N*′-{chlorobis[1,2-phenylenebis(dimethylarsine)]ruthenium(II)} bis(hexafluorophosphate) diacetone solvate

Benjamin J. Coe,[a]* Christopher I. McDonald,[a] Simon J. Coles[b] and Michael B. Hursthouse[b]

[a]Department of Chemistry, University of Manchester, Manchester M13 9PL, England, and [b]EPSRC X-ray Crystallography Service, Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England
Correspondence e-mail: b.coe@man.ac.uk

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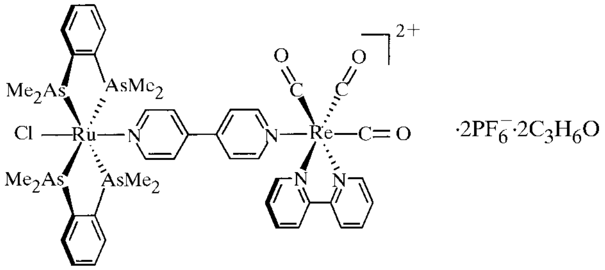
The crystal structure of the heterobimetallic title compound, $[\mathrm{ReRuCl(C_{10}H_{16}As_2)_2(C_{10}H_8N_2)_2(CO)_3](PF_6)_2\cdot 2C_3H_6O}$, is described. Both metal centres have pseudo-octahedral coordination geometries, with a facial arrangement of the carbonyl ligands at $\mathrm{Re^I}$ and a *trans* disposition of the diarsine ligands at $\mathrm{Ru^{II}}$. The dihedral angle between the pyridyl rings of the 4,4′-bipyridine bridging ligand is 13.9 (6)°.

Comment

There is currently great interest in ligand-bridged, di- and polynuclear transition metal complexes. Such compounds are of fundamental importance for the study of intermetallic electronic interactions (Creutz, 1983; Nelsen, 2000), and may also find practical applications in the emerging field of molecular electronics as components of molecular-scale wires or switches (Crutchley, 1994; Ward, 1995).



(I)

We have previously reported a series of symmetrical dinuclear complexes containing *trans*-$[\mathrm{Ru^{II}Cl(pdma)_2}]^+$ [pdma is 1,2-phenylenebis(dimethylarsine)] centres (Coe *et al.*, 1997), and describe here the synthesis and structure of a related hetero-dinuclear complex salt, (I), containing a *fac*-$[\mathrm{Re^I(2,2'\text{-}bpy)(CO)_3}]^+$ (2,2′-bpy is 2,2′-bipyridine) moiety. Such rhenium(I) *α*-diimine centres are of interest for their photoexcitation properties (Schanze *et al.*, 1993). A recent report of particular relevance to the present study described photoinduced electron transfer in the trinuclear complex *fac,trans*-$[\mathrm{Re^I(dmb)(CO)_3}](\mu\text{-}4,4'\text{-bpy})\mathrm{Ru^{III}(en)_2}(\mu\text{-NC})\mathrm{Fe^{III}(CN)_5}]^+$ (dmb is 4,4′-dimethyl-2,2′-bipyridine, 4,4′-bpy is 4,4′-bi-

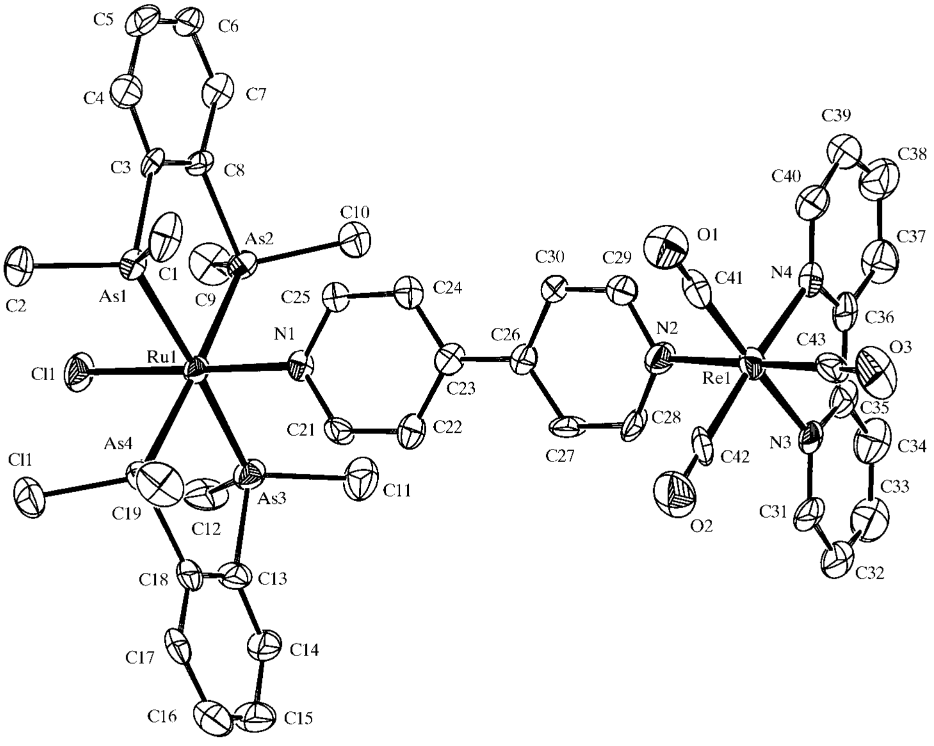


Figure 1
View of the complex cation in (I) with H atoms omitted (50% probability displacement ellipsoids).

pyridine and en is 1,2-diaminoethane; Pfennig *et al.*, 1998). To our knowledge, (I) contains the first hetero-dinuclear transition metal complex featuring a 4,4′-bpy bridging ligand to be structurally characterized. The only other related complex, $[Cd^{II}(4,4'\text{-bpy})_2\{Ag^{I}(CN)_2\}_2]$, has an interpenetrating double-framework structure containing 4,4′-bpy bridges between Cd^{II} and Ag^{I} ions (Soma *et al.*, 1994).

Complex (I) was synthesized by the reaction of *trans*-$[Ru^{II}Cl(pdma)_2(4,4'\text{-bpy})]PF_6$ (Coe *et al.*, 1997) with *fac*-$Re^{I}(CF_3SO_3)(2,2'\text{-bpy})(CO)_3$ (Sullivan & Meyer, 1984). The intense $d\pi(Ru^{II})\rightarrow\pi^*(4,4'\text{-bpy})$ metal-to-ligand charge-transfer absorption band of *trans*-$[Ru^{II}Cl(pdma)_2(4,4'\text{-bpy})]PF_6$ (λ_{max} = 418 nm in acetonitrile; Coe *et al.*, 1997) undergoes a red shift of *ca* 0.2 eV upon coordination of the *fac*-$Re^{I}(2,2'\text{-bpy})(CO)_3$ group to afford (I). However, the $Ru^{III/II}$ $E_{1/2}$ potentials obtained from cyclic voltammetry for (I) and for *trans*-$[Ru^{II}Cl(pdma)_2(4,4'\text{-bpy})]PF_6$ are identical (1.09 V *versus* the saturated calomel electrode in acetonitrile). There is thus minimal electronic communication between the two metal centres in (I).

The molecular structure of the complex in (I) is as indicated by ^1H NMR spectroscopy, with both metal centres having pseudo-octahedral coordination geometries, a facial arrangement of the carbonyl ligands at rhenium(I) and a *trans* disposition of the diarsine ligands at ruthenium(II). The metal centres are almost perfectly eclipsed with respect to each other, and their geometrical parameters are similar to those found previously in *fac*-$[\{Re^{I}(2,2'\text{-bpy})(CO)_3\}_2(\mu\text{-bpa})](BPh_4)_2\cdot 2C_4H_{10}O$ [bpa is 1,2-bis(4-pyridyl)ethane] (Lin *et al.*, 1992) and in other *trans*-$\{Ru^{II}Cl(pdma)_2\}^+$ complexes (Coe *et al.*, 1997). Also, as observed in related structures (Coe *et al.*, 1997), the Ru-coordinated ring of the 4,4′-bpy ligand approximately bisects the As—Ru—As chelate angles. The dihedral angle between the rings of the 4,4′-bpy bridging ligand in (I) is 13.9 (6)° (ring planes defined by N1/C21/C22/C23/C24/C25 and N2/C26/C27/C28/C29/C30), a little larger than the corresponding angle in the mononuclear precursor *trans*-$[Ru^{II}Cl(pdma)_2(4,4'\text{-bpy})]PF_6$ [10.27 (5)°; Coe *et al.*, 2000]. The close similarity of these dihedral angles is consistent with the lack of intermetallic (π) electronic coupling in (I) shown by cyclic voltammetry (see above). The structure of (I) contains no classical hydrogen bonds, but the following close contacts are worthy of note: C25—H25···O5 with a C···O distance of 3.080 (17) Å and C38—H38···O1 with a C···O distance of 3.22 (2) Å (symmetry code: $1 - x, 1 - y, -\frac{1}{2} + z$).

Experimental

A solution of *fac*-$[Re(CO)_3(2,2'\text{-bpy})(CF_3SO_3)]$ (13 mg, 0.023 mmol) and *trans*-$[RuCl(pdma)_2(4,4'\text{-bpy})]PF_6$ (20 mg, 0.020 mmol) in 2-butanone (10 ml) was heated at reflux in the dark under Ar for 5 h. Addition of aqueous NH_4PF_6 produced an orange precipitate, which was filtered off, washed with water and dried. Reprecipitation from acetone/diethyl ether, followed by several recrystallizations from acetonitrile/diethyl ether afforded a red crystalline solid [yield 7 mg (22%)]. Found: C 32.54, H 3.07, N 3.29%; calculated for $C_{43}H_{48}As_4ClF_{12}N_4O_3P_2ReRu$: C 32.66, H 3.06, N 3.54%. ^1H NMR data (200 MHz, CD_3COCD_3): δ 9.43 (2H, *d*, J = 4.8 Hz, $H^{6,6'}$), 8.67 (2H, *d*, J = 8.2 Hz, $H^{3,3'}$), 8.58 (2H, *d*, J = 6.8 Hz, C_5H_4N), 8.42 (2H, *t*, $H^{4,4'}$), 8.29 (4H, *m*, $2C_6H_2$), 7.95 (2H, *t*, $H^{5,5'}$), 7.83 (4H, *m*, $2C_6H_2$), 7.76 (2H, *d*, J = 6.9 Hz, C_5H_4N), 7.68 (2H, *d*, J = 6.8 Hz, C_5H_4N), 7.41 (2H, *d*, J = 6.9 Hz, C_5H_4N), 1.88 (12H, *s*, 4 × AsMe), 1.74 (12H, *s*, 4 × AsMe). IR υ(C=O) (KBr disc) 2033, 1926 cm^{-1}. Crystals suitable for single-crystal X-ray diffraction measurements were obtained by slow diffusion of diethyl ether vapour into a solution of (I) in acetone at 277 K.

Crystal data

$[ReRuCl(C_{10}H_{16}As_2)_2(C_{10}H_8N_2)_2(CO)_3](PF_6)_2\cdot 2C_3H_6O$
M_r = 1697.35
Orthorhombic, $Pna2_1$
a = 22.736 (5) Å
b = 30.654 (6) Å
c = 8.799 (2) Å
V = 6132 (2) $Å^3$
Z = 4
D_x = 1.838 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15874 reflections
θ = 1.12–25.00°
μ = 4.538 mm^{-1}
T = 150 (2) K
Plate, orange
0.45 × 0.08 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.235, T_{max} = 0.915
15874 measured reflections
7883 independent reflections
6157 reflections with $I > 2\sigma(I)$
R_{int} = 0.109
θ_{max} = 25°
$h = -14 \rightarrow 27$
$k = -36 \rightarrow 36$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R(F)$ = 0.051
$wR(F^2)$ = 0.115
S = 0.989
7883 reflections
852 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 1.55 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.16 e $Å^{-3}$
Absolute structure: Flack (1983)
Flack parameter = 0.066 (10)

Table 1
Selected geometric parameters (Å, °).

Re1—C42	1.928 (15)	Ru1—N1	2.117 (9)
Re1—C41	1.937 (16)	Ru1—As1	2.4162 (16)
Re1—C43	1.947 (14)	Ru1—As3	2.4206 (17)
Re1—N4	2.169 (11)	Ru1—As2	2.4215 (17)
Re1—N3	2.176 (11)	Ru1—As4	2.4243 (17)
Re1—N2	2.185 (10)	Ru1—Cl1	2.424 (3)
C42—Re1—C41	86.8 (6)	N1—Ru1—As1	93.4 (3)
C42—Re1—C43	84.0 (6)	N1—Ru1—As3	91.8 (3)
C41—Re1—C43	86.0 (6)	As1—Ru1—As3	174.67 (6)
C42—Re1—N4	174.2 (5)	N1—Ru1—As2	92.0 (3)
C41—Re1—N4	98.9 (5)	As1—Ru1—As2	84.65 (5)
C43—Re1—N4	97.6 (5)	As3—Ru1—As2	94.31 (6)
C42—Re1—N3	98.2 (5)	N1—Ru1—As4	92.9 (3)
C41—Re1—N3	173.5 (5)	As1—Ru1—As4	96.10 (6)
C43—Re1—N3	98.6 (5)	As3—Ru1—As4	84.49 (6)
N4—Re1—N3	76.1 (4)	As2—Ru1—As4	175.01 (6)
C42—Re1—N2	95.4 (5)	N1—Ru1—Cl1	178.5 (3)
C41—Re1—N2	93.2 (5)	As1—Ru1—Cl1	86.41 (9)
C43—Re1—N2	179.0 (6)	As3—Ru1—Cl1	88.31 (9)
N4—Re1—N2	83.1 (4)	As2—Ru1—Cl1	86.51 (10)
N3—Re1—N2	82.2 (4)	As4—Ru1—Cl1	88.61 (10)

Geometrical and thermal restraints were applied to the two PF_6^- anions in order to accurately model the disorder present, whilst the absolute structure configuration was tested using the Flack parameter (Flack, 1983).

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1004). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Coe, B. J., Beyer, T., Jeffery, J. C., Coles, S. J., Gelbrich, T., Hursthouse, M. B. & Light, M. E. (2000). *J. Chem. Soc. Dalton Trans.* pp. 797–803.

Coe, B. J., Hayat, S., Beddoes, R. L., Helliwell, M., Jeffery, J. C., Batten, S. R. & White, P. S. (1997). *J. Chem. Soc. Dalton Trans.* pp. 591–599.

Creutz, C. (1983). *Prog. Inorg. Chem.* **30**, 1–73.

Crutchley, R. J. (1994). *Adv. Inorg. Chem.* **41**, 273–325.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Lin, R., Fu, Y., Brock, C. P. & Guarr, T. F. (1992). *Inorg. Chem.* **31**, 4346–4353.

Nelsen, S. F. (2000). *Chem. Eur. J.* **6**, 581–588.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Pfennig, B. W., Goertz, J. K., Wolff, D. W. & Cohen, J. L. (1998). *Inorg. Chem.* **37**, 2608–2611.

Schanze, K. S., MacQueen, D. B., Perkins, T. A. & Cabana, L. A. (1993). *Coord. Chem. Rev.* **122**, 63–89.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Soma, T., Yuge, H. & Iwamoto, T. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1665–1666.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Sullivan, B. P. & Meyer, T. J. (1984). *J. Chem. Soc. Chem. Commun.* pp. 1244–1245.

Ward, M. D. (1995). *Chem. Soc. Rev.* **24**, 121–134.

Acta Cryst. (2000). C**56**, 963–965 Benjamin J. Coe *et al.* • $[ReRuCl(C_{10}H_{16}As_2)_2(C_{10}H_8N_2)_2(CO)_3](PF_6)_2\cdot 2C_3H_6O$ **965**