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A dinuclear rhenium complex, $\{[(C_{18}H_{24}N_2)Re(CO)_3]_2(\mu\text{-}C_{12}H_{12}N_2)\}(PF_6)_2\cdot 2CH_2Cl_2$

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A new Re^I complex has been synthesized by reflux methods, *viz.* μ-ethylene-1,2-di-4-pyridyl-$\kappa^2N:N'$-bis[*fac*-tricarbonyl-(4,4′-*tert*-butyl-2,2′-bipyridine)rhenium(I)] hexafluorophosphate dichloromethane disolvate, $[Re(\mu\text{-}C_{12}H_{12}N_2)(C_{18}H_{24}N_2)_2(CO)_6](PF_6)_2\cdot 2CH_2Cl_2$. The compound is a centrosymmetric dinuclear complex. The self-assembled structure contains octahedral Re centers, connected by a 1,2-bis(4-pyridyl)ethylene linking group.

Key indicators

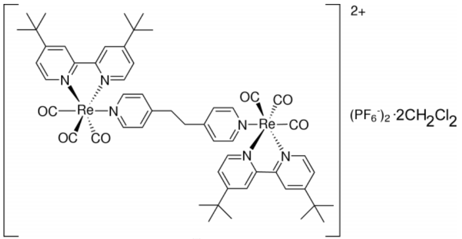
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.007 Å
R factor = 0.035
wR factor = 0.099
Data-to-parameter ratio = 19.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The photochemistry and photophysics of diimine–Re^I–carbonyl complexes are well established (Tapolsky & Meyer, 1990). Many of these complexes exhibit a variety of accessible excited states, including metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT) and intraligand (IL) states. The nature of the lowest energy excited state usually plays a decisive role in the resulting photophysical and photochemical properties (Sun & Lees, 2000*a*).

Diimine–Re^I–carbonyl complexes, in particular, typically possess lowest MLCT excited states, with long-lived excited state lifetimes. They are, therefore, promising candidates for developing highly sensitive luminescent sensing materials (Sun & Lees, 2000*b*). The facial modification of the ancillary and bridging ligands allows the modular design and fine tuning of their ground- and excited-state properties (Sun & Lees, 2002).



(I)

We report here a new centrosymmetric dinuclear Re complex, (I), where the octahedral metal centers are connected by 1,2-bis(4-pyridyl)ethylene (BPA, Fig. 1). For each metal of the cation, a bidentate 4,4′-di-*tert*-butyl-2,2′-bipyridine ligand occupies the *cis* positions relative to the linking sites. Three *trans* carbonyl groups complete the octahedral coordination of the Re atoms.

The complex cations are aligned approximately along [$\bar{1}$01], with hexafluorophosphate anions and dichloromethane molecules residing between them (Fig. 2). The PF_6^- anions charge-balance the divalent cationic charge of the complex. This structure opens up new possibilities in creating oligomeric, cyclic and cage-like organometallic molecules. Such

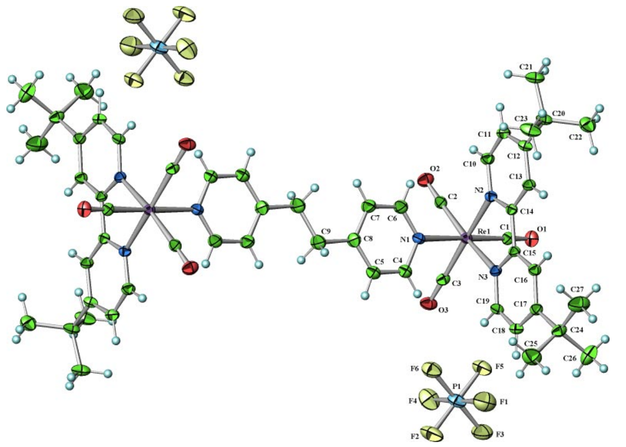


Figure 1
View of the cation and anions, with displacement ellipsoids drawn at the 50% probability level. The CH_2Cl_2 molecules are not shown. The unlabelled part is related to the labeled part by the symmetry operator ($-x$, $-y$, $2 - z$).

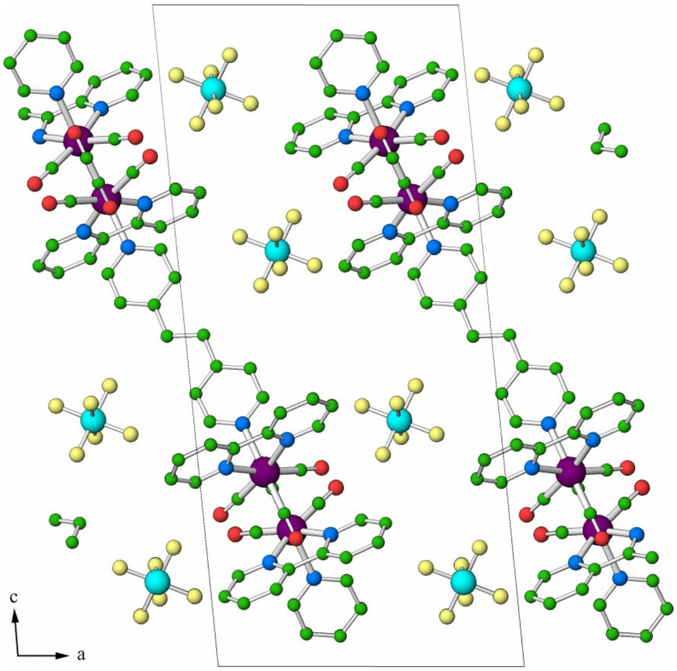


Figure 2
The crystallographic b-projection, showing PF_6 ions and CH_2Cl_2 molecules between the cations (colour scheme: Re purple, N dark blue, C green, Cl green, O red, F yellow, and P light blue).

structures, with accessible well-defined voids, may lead to various host–guest applications, such as sensing or catalysis.

Experimental

To a 100 ml flask containing (4,4′-^{t}Bu$_2$bpy)Re(CO)$_3$(CH$_3$CN)(PF$_6$) (100 mg, 0.14 mmol) and 1,2-bis(4-pyridyl)ethane (BPA, 12 mg, 0.065 mmol) was added 30 ml of tetrahydrofuran. The resulting mixture was refluxed for 16 h. Subsequently, the solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was dissolved in 20 ml CH_2Cl_2 and filtered to remove any undissolved material. The filtrate was layered with 100 ml hexane and allowed to stand for 2 d to afford yellow microcrystals (yield: 86%). IR ($\nu_{C=O}$, CH_2Cl_2): 2033, 1929; ^{1}H NMR (300 MHz, acetone-d_6): δ 9.28 (d, 4H, $^3J_{H-H}$ = 5.9 Hz, $H_{6,6'}$–Bu$_2$bpy), 8.72 (d, 4H, $^4J_{H-H}$ = 1.7 Hz, $H_{3,3'}$–Bu$_2$bpy), 8.37 (d, 4H, $^3J_{H-H}$ = 6.5 Hz, Hα-py), 7.95 (d, 4H, $^3J_{H-H}$ = 5.9 Hz, $^4J_{H-H}$ = 1.9 Hz, $H_{5,5'}$–Bu$_2$bpy), 7.35 (d, 4H, $^3J_{H-H}$ = 6.5 Hz, Hβ-py), 2.90 (s, 4H, $-CH_2-$), 1.42 (s, 72H, $-CH_3$); ^{13}C NMR (acetone-d_6): δ 196.8, 192.9, 167.1, 156.9, 155.8, 154.5, 152.8, 127.7, 127.0, 123.1, 36.8, 34.9; ES–MS: m/z = 1407.5 (calculated m/z = 1407.3 for [M-PF$_6^-$]$^+$). Analysis calculated for $C_{54}H_{60}N_6O_6Re_2P_2F_{12}$: C 41.81, H 3.90, N 5.42%; found: C 41.87, H 3.79, N, 5.52%.

Crystal data

$[Re(C_{12}H_{12}N_2)(C_{18}H_{24}N_2)_2(CO)_6](PF_6)_2\cdot 2CH_2Cl_2$	D_x = 1.791 Mg m^{-3}
M_r = 1721.28	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6778 reflections
a = 12.0280 (7) Å	θ = 5.1–62.8°
b = 10.2060 (6) Å	μ = 4.09 mm^{-1}
c = 26.1366 (14) Å	T = 110 K
β = 95.695 (2)°	Prism, light yellow
V = 3192.6 (3) Å^3	0.35 × 0.24 × 0.18 mm
Z = 2	

Data collection

Bruker SMART Apex CCD diffractometer	7907 independent reflections
ω scans	7044 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.033
T_{min} = 0.342, T_{max} = 0.479	θ_{max} = 28.3°
32788 measured reflections	$h = -16 \rightarrow 15$
	$k = -13 \rightarrow 13$
	$l = -34 \rightarrow 34$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 12.0416P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	$(\Delta/\sigma)_{max}$ = 0.003
$wR(F^2)$ = 0.099	$\Delta\rho_{max}$ = 2.62 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −1.61 e Å^{-3}
7907 reflections	
403 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Re1—C2	1.922 (4)	Re1—N3	2.167 (3)
Re1—C1	1.932 (4)	Re1—N1	2.220 (4)
Re1—C3	1.939 (4)	C9—C9^i	1.495 (10)
Re1—N2	2.164 (3)		
C3—Re1—N2	172.47 (15)	C1—Re1—N1	179.27 (16)
C2—Re1—N3	170.71 (16)		
N2—C14—C15—N3	−0.4 (5)	C18—C17—C24—C27	179.7 (5)
C11—C12—C20—C21	2.5 (6)		

Symmetry code: (i) $-x$, $-y$, $2 - z$.

All H atoms were included in calculated positions, with C—H distances of 0.93–0.97 Å. They were included in the refinement in riding-motion approximation with $U_{iso} = 1.2U_{eq}$ ($U_{iso} = 1.5U_{eq}$ for methyl) of the carrier atom. The maximum electron-density peak is located in the vicinity of the Re1 atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

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