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Acetonitriletricarbonyl(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)rhenium(I) hexafluorophosphate

Shih-Sheng Sun,[a] Peter Y. Zavalij[b]* and Alistair J. Lees[a]

[a]Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA, and [b]Institute for Materials Research and Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA

Correspondence e-mail:
zavalij@binghamton.edu

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.042
wR factor = 0.100
Data-to-parameter ratio = 23.0

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

The novel title compound, $[Re(C_{26}H_{20}N_2)(C_2H_3N)(CO)_3](PF_6)$, has been synthesized and found to crystallize in the monoclinic system with space group $P2_1/n$. The molecular ionic structure consists of an Re^I complex cation and a PF_6^- anion, where the Re atom is octahedrally coordinated by chelating dimethyldiphenylphenanthroline, three carbonyl groups and acetonitrile.

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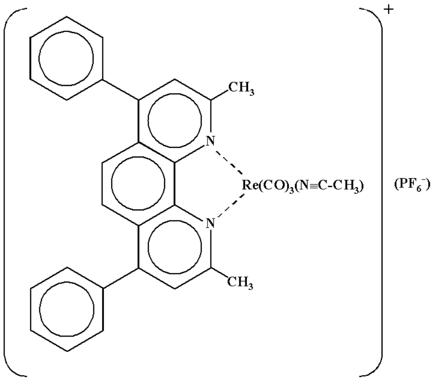
Comment

It is well known (Sun & Lees, 2000) that rhenium(I) readily forms tricarbonyl molecular complexes of the general formula $(L)Re(CO)_3X$, where L is chelating bipyridyl ligand, and X is Cl or Br. Substitution of the halogen with a neutral molecule such as CH_3CN leads to formation of a complex cation and an additional anion is needed for charge compensation.

A new molecular ionic compound has been prepared by reacting $BrRe(CO)_3(DMDPP)$ and $AgPF_6$ in refluxing CH_3CN (DMDPP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, $C_{26}H_{20}N_2$). The crystal structure of this molecular ionic compound, acetonitriletricarbonyl(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)rhenium(I) hexafluorophosphate, (I), has been determined. The Re atom is octahedrally coordinated and the base of the octahedron is formed by two N atoms (N2 and N3) of the chelating DMDPP ligand and C atoms (C1 and C2) of two carbonyl groups, whereas the third carbonyl ligand (C3) and acetonitrile (N1) form apices (Fig. 1). This octahedron is slightly distorted (see N—Re—C angles in Table 1) due to the chelating DMDPP ligand. However, C3, N1 and Re are practically collinear [N1—Re—C3 is 179.1 (2)°].



(I)

Each individual ring in the DMDPP ligand lies in a plane with deviations of less than 0.01 Å. This deviation is tripled

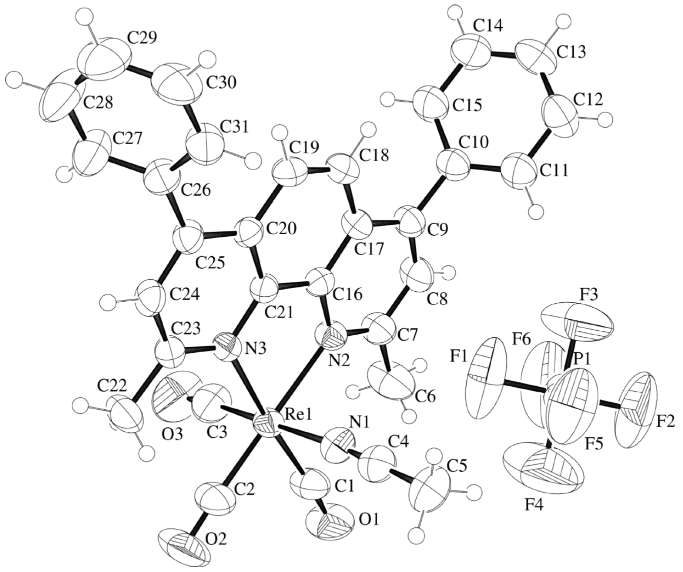


Figure 1
View of (I) with displacement ellipsoids at the 50% probability level.

when the three rings of phenanthroline are taken together, but even then this does not exeed 0.03 Å. The two phenyl groups, C10—C15 and C26—C31, are tilted from the phenanthroline plane by 64.7 (2) and 56.1 (2)°, respectively. The ligand has only a twofold axis as the local symmetry element because of this tilt.

The Re cations and PF_6^- anions are held together by weak C—H···F hydrogen bonds, as listed in Table 2.

Experimental

The compound $(DMDPP)Re(CO)_3(CH_3CN)(PF_6)$ was prepared by modifying the literature method of Caspar & Meyer (1983). To a 250 ml flask containing $(DMDPP)Re(CO)_3Br$ (500 mg, 0.7 mmol) and $AgPF_6$ (215 mg, 0.85 mmol) was added 100 ml anhydrous CH_3CN. The resulting mixture was refluxed under argon for 8 h. The solvent was filtered under argon to remove AgBr precipitate and the filtrate was evaporated to dryness under reduced pressure. The crude product was recrystallized from CH_3CN/ether to afford a bright-yellow solid in 92% yield. IR [ν(C≡O), CH_3CN, cm^{-1}]: 2038, 1937. ^1H NMR (DMSO-d_6): 8.23 (*s*, 2H, H5,6-phen), 8.05 (*s*, 2H, H3,8-phen), 7.70–7.63 (*m*, 10H, Ph), 3.33 (*s*, 6H, CH_3), 2.28 (*s*, 3H, CH_3CN). ^{13}C NMR (DMSO-d_6): 196.0, 191.4, 163.4, 151.2, 147.6, 135.2, 129.8, 129.6, 129.1, 128.9, 127.0, 124.6, 118.0, 30.4, 1.06. Single crystals were grown by layering an acetonitrile solution of the complex with ether.

Crystal data

$[Re(C_{26}H_{20}N_2)(C_2H_3N)(CO)_3](PF_6)$
$M_r = 816.7$
Monoclinic, $P2_1/n$
$a = 10.2648$ (5) Å
$b = 23.4667$ (11) Å
$c = 13.2040$ (6) Å
$\beta = 103.847$ (1)°
$V = 3088.2$ (3) Å^3
$Z = 4$

$D_x = 1.757$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7718 reflections
$\theta = 4.4$–54.6°
$\mu = 4.06$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.20 × 0.18 × 0.13 mm

Data collection

CCD Smart Apex diffractometer
ω scans
Absorption correction: ψ scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.46$, $T_{max} = 0.59$
26 336 measured reflections
9420 independent reflections

6049 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 30.6°$
$h = -13 \rightarrow 14$
$k = -25 \rightarrow 33$
$l = -11 \rightarrow 18$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.100$
$S = 0.93$
9420 reflections
409 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Re1—C3	1.899 (6)	C11—C12	1.395 (7)
Re1—C2	1.904 (5)	C12—C13	1.355 (8)
Re1—C1	1.916 (5)	C13—C14	1.368 (7)
Re1—N1	2.125 (4)	C14—C15	1.358 (7)
Re1—N2	2.211 (3)	N2—C16	1.387 (5)
Re1—N3	2.215 (3)	C16—C17	1.392 (5)
P1—F1	1.549 (4)	C16—C21	1.442 (5)
P1—F2	1.536 (4)	C17—C18	1.429 (6)
P1—F3	1.477 (5)	C18—C19	1.343 (6)
P1—F4	1.521 (5)	C19—C20	1.420 (6)
P1—F5	1.558 (4)	C20—C21	1.410 (5)
P1—F6	1.537 (5)	C20—C25	1.412 (6)
C1—O1	1.148 (6)	C21—N3	1.371 (5)
C2—O2	1.156 (6)	N3—C23	1.348 (5)
C3—O3	1.152 (6)	C22—C23	1.486 (6)
N1—C4	1.132 (6)	C23—C24	1.382 (5)
C4—C5	1.450 (7)	C24—C25	1.367 (6)
C6—C7	1.482 (6)	C25—C26	1.484 (6)
C7—N2	1.345 (5)	C26—C27	1.381 (7)
C7—C8	1.394 (6)	C26—C31	1.390 (6)
C8—C9	1.360 (6)	C27—C28	1.384 (7)
C9—C17	1.419 (6)	C28—C29	1.366 (9)
C9—C10	1.480 (6)	C29—C30	1.371 (8)
C10—C11	1.377 (6)	C30—C31	1.387 (6)
C10—C15	1.384 (7)		
C3—Re1—N1	179.1 (2)	F6—P1—F5	176.5 (3)
C2—Re1—N2	174.82 (19)	O1—C1—Re1	174.8 (5)
C1—Re1—N3	174.91 (18)	O2—C2—Re1	175.5 (5)
N2—Re1—N3	75.66 (12)	O3—C3—Re1	175.3 (5)
F3—P1—F4	178.8 (5)	C4—N1—Re1	173.8 (4)
F2—P1—F1	178.4 (3)	N1—C4—C5	179.2 (5)
C24—C25—C26—C27	−51.4 (7)	C8—C9—C10—C11	−65.9 (6)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*B*···F1^i	0.960 (6)	2.337 (5)	3.226 (8)	153.7 (3)
C11—H11···F3	0.932 (5)	2.447 (8)	3.377 (9)	176.2 (4)
C24—H24···F2^{ii}	0.929 (4)	2.474 (5)	3.280 (6)	145.1 (3)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x, y, 1 + z$.

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

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