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fac-Tricarbonyl(4,4′-dimethyl-2,2′-bipyridine)triphenyltin(II)rhenium(I)

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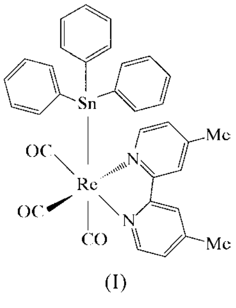
The title organometallic compound, *fac*-tricarbonyl-$2\kappa^3C$-(4,4′-dimethyl-2,2′-bipyridine)-$2\kappa^2N,N'$-triphenyl-$1\kappa^3C^1$-tin(II)-rhenium(I)(*Sn*—*Re*), $[ReSn(C_6H_5)_3(C_{12}H_{12}N_2)(CO)_3]$, contains three unique π–π stacking interactions. The result is an infinite chain of uninterrupted alternating intra- and intermolecular offset π–π stacking interactions throughout the crystal lattice. This extended π–π stacking arrangement, and an additional isolated intramolecular π–π interaction between the remaining 4,4′-dimethyl-2,2′-bipyridine ring and a second phenyl group, impose geometric constraints on the Re and Sn atoms, yielding distorted octahedral and tetrahedral coordinations, respectively, for the metal centers.

Comment

The title compound, *fac*-$(CO)_3$(dmbpy)Re(I)Ph_3Sn(I) (dmbpy is 4,4′-dimethyl-2,2′-bipyridine), (I), was prepared and its structure determined as part of a general effort to characterize rhenium polypyridine complexes, or their derivatives, which might be involved in CO_2 reduction (Gibson *et al.*, 2003).



(I)

The molecules of (I) pack in a columnar network *via* an extended arrangement of parallel displaced π–π stacking interactions (Fig. 1). The atomic labelling scheme shown in Fig. 2 identifies the four aromatic rings involved in the detailed structural analysis. The first slipped stack is formed between the phenyl group containing atoms C16–C21 (Ph1) and the six-membered N2/C9–C13 ring (dmbpy1). The second intramolecular interaction occurs between the phenyl ring defined by atoms C22–C27 (Ph2) and the N1/C4–C8 ring (dmbpy2).

The chelating dmbpy ligand contains a pinched N1—Re—N2 bond angle, which requires the Re atom to adopt a distorted octahedral geometry. The Sn—Re—C3 bond angle is non-linear and the Re—C3 bond is slightly longer than the Re—C1 and Re—C2 bonds. Significant differences are observed in bond angles involving the *ipso* phenyl C atoms, the Sn atom and the Re atom, with the C28—Sn—Re bond angle being more than 10° greater than the other two. This is the consequence of inter- and intramolecular π–π stacking, involving two phenyl groups and both pyridine rings of the dmbpy ligand in each molecule.

It has been noted previously (Magistrato *et al.*, 2001) that such aromatic π–π stacking interactions are rare within ligands of transition metal compounds, and their role in

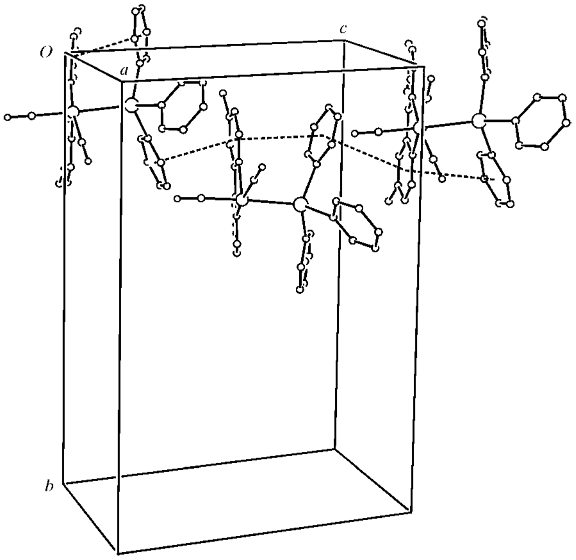


Figure 1
A packing diagram for (I), illustrating the intra- and intermolecular offset π–π stacking interactions between neighboring phenyl and dimethylpyridine rings.

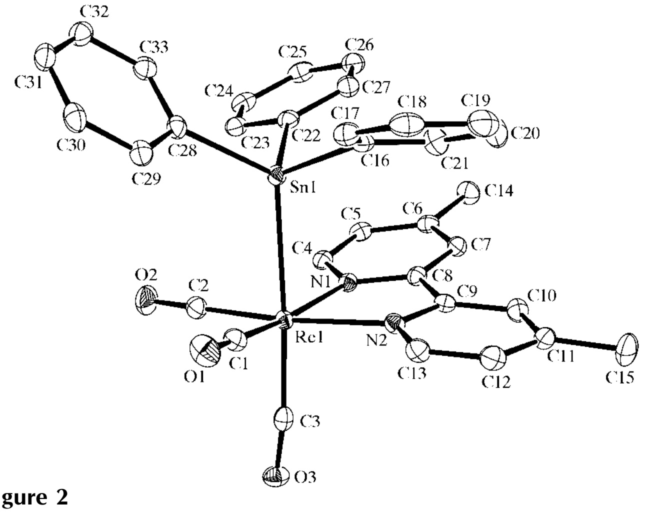


Figure 2
A view of the molecule of (I), showing the atom-numbering scheme and 40% probability displacement ellipsoids. H atoms are not shown.

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organometallic compounds is largely unknown. However, systems containing bipyridine ligands coordinated to the metal are well suited for π–π interactions because of their low π-electron density (Janiak, 2000).

Both pyridine rings of the dmbpy ligand which are bound to the Re atom in each molecule of (I) are involved in intramolecular π–π stacking interactions with two of the phenyl ligands bound to the Sn atom. In the first interaction, the pyridine-centroid to phenyl-centroid distance is 3.67 Å. In the second interaction, the phenyl ring is slightly tilted away from the pyridine ring, and the pyridine centroid to phenyl centroid distance is 4.12 Å.

This second pyridine ring also participates in an intermolecular π–π stacking interaction with the phenyl group in a second molecule, which is involved in the longer range π–π interaction within that molecule. The intermolecular centroid-to-centroid distance is 4.22 Å. The angle formed by the two centroid–centroid vectors is 160°. The result is a well defined array that is controlled by the π–π interactions but does not have parallel arrangements of the aromatic groups because of the distorting effect of the third phenyl group bound to each Sn atom.

The bond angles around the Sn atom are also affected by the π–π stacking: the $C_{ipso}—Sn—C_{ipso}$ bond angles vary from 101.32 (7) to 110.33 (7)°. The largest angle is associated with the two phenyl rings involved in π–π stacking.

Experimental

Compound (I) was synthesized according to the published procedure of Luong *et al.* (1980). *fac*-Re(dmbpy)(CO)$_3$Br (0.52 g, 0.97 mmol) in tetrahydrofuran (THF, 25 ml) was stirred for 2 h with Na–Hg (0.2 g Na, 5 ml Hg). The mixture was allowed to settle, the supernatant was drawn off and added dropwise to Ph$_3$SnCl (0.44 g, 1.14 mmol) in THF (15 ml) in a foil-covered flask. The mixture was stirred for 2 h, the solvent was evaporated, and the residue was triturated with toluene. Toluene was removed from the extracts by evaporation, the residue was dissolved in THF, and hexane was added to precipitate the product. The product had spectroscopic properties analogous to those reported previously (Andréa *et al.*, 1988). Single crystals of (I) suitable for X-ray analysis were grown by slow diffusion from a solution in THF layered with hexane at 295 K.

Crystal data

$[ReSn(C_6H_5)_3(C_{12}H_{12}N_2)(CO)_3]$
$M_r = 804.46$
Monoclinic, $P2_1/n$
$a = 10.1077$ (5) Å
$b = 20.0087$ (11) Å
$c = 14.3020$ (8) Å
$\beta = 99.4830$ (10)°
$V = 2852.9$ (3) Å^3
$Z = 4$
$D_x = 1.873$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9678 reflections
$\theta = 2.3$–28.1°
$\mu = 5.15$ mm^{-1}
$T = 100$ (2) K
Block, orange
0.39 × 0.14 × 0.14 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.420$, $T_{max} = 0.490$
24 721 measured reflections
6622 independent reflections
6330 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 28.2°$
$h = -13 \rightarrow 13$
$k = -26 \rightarrow 25$
$l = -18 \rightarrow 18$

Table 1
Selected geometric parameters (Å, °).

Re1—C1	1.9207 (19)	Re1—Sn1	2.7717 (2)
Re1—C2	1.9160 (19)	Sn1—C16	2.1712 (19)
Re1—C3	1.940 (2)	Sn1—C22	2.1706 (19)
Re1—N1	2.1713 (15)	Sn1—C28	2.1661 (18)
Re1—N2	2.1743 (15)		
C1—Re1—N1	167.49 (7)	N1—Re1—N2	74.20 (6)
C2—Re1—N1	96.80 (7)	Sn1—Re1—C1	87.16 (6)
C3—Re1—N1	98.19 (7)	Sn1—Re1—C2	86.75 (6)
C1—Re1—N2	97.84 (7)	Sn1—Re1—C3	176.52 (5)
C2—Re1—N2	170.74 (7)	Sn1—Re1—N1	83.25 (4)
C3—Re1—N2	93.51 (7)	Sn1—Re1—N2	89.94 (4)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.039$
$S = 1.03$
6622 reflections
384 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 1.1474P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Coordinates for all H-atom positions were calculated. Methyl groups were allowed to ride (the torsion angle which defines the orientation was allowed to refine) on their parent C atoms and the positions of the phenyl H atoms were constrained so that C—H = 0.95 Å. The U_{iso} values for all H atoms were refined, except for those of the methyl groups, which were constrained to $1.5U_{eq}$(C). The maximum residual electron density was 0.82 Å from Re1 and the deepest hole was 1.15 Å from C5.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *SHELXTL* (Bruker, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1491). Services for accessing these data are described at the back of the journal.

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