

Experimental

The title compound was synthesized from Cd(NO₃)₂·4H₂O, 4,4'-bipyridine and 2-nitroaniline in ethanol by a molecular self-assembly reaction. X-ray quality single crystals were obtained by slow evaporation of the solvent.

Crystal data

[Cd(NO₃)₂(C₁₀H₈N₂)₂]₂·
2C₆H₆N₂O₂
M_r = 825.04
Monoclinic
C2/c
a = 21.850 (2) Å
b = 11.7687 (7) Å
c = 13.3256 (8) Å
β = 100.544 (2)°
V = 3368.8 (3) Å³
Z = 4
D_x = 1.627 Mg m⁻³
D_m not measured

Mo Kα radiation

λ = 0.7107 Å

Cell parameters from 1096 reflections

θ = 1.34–27.09°

μ = 0.724 mm⁻¹

T = 298.2 K

Prism

0.3 × 0.2 × 0.1 mm

Yellow

Data collection

Bruker SMART CCD
diffractometer
ω scans
Absorption correction:
multi-scan (SADABS;
Sheldrick, 1996)
T_{min} = 0.800, T_{max} = 0.930
9000 measured reflections
3519 independent reflections

2733 reflections with

I > 2.5σ(I)

R_{int} = 0.024θ_{max} = 27.09°

h = 0 → 27

k = -14 → 14

l = -17 → 15

Intensity decay: none

Refinement

Refinement on F²
R(F) = 0.051
wR(F²) = 0.083
S = 1.09
2733 reflections
242 parameters
H atoms not refined
w = 1/[σ²(F_o) +
0.00055|F_o|²]

(Δ/σ)_{max} < 0.001Δρ_{max} = 0.48 e Å⁻³Δρ_{min} = -0.41 e Å⁻³

Extinction correction: none

Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cd—O2	2.352 (3)	N1—C1	1.342 (4)
Cd—O2 ⁱ	2.352 (3)	N2—C6	1.339 (4)
Cd—N1 ⁱⁱ	2.341 (4)	N3—C7	1.331 (4)
Cd—N2	2.348 (4)	N5—C17	1.336 (7)
Cd—N3	2.349 (2)	N6—C12	1.442 (7)
Cd—N3 ⁱ	2.349 (2)	C1—C2	1.381 (4)
O1—N4	1.152 (5)	C2—C3	1.391 (4)
O2—N4	1.249 (4)	C3—C4	1.485 (5)
O3—N4	1.218 (4)	C4—C5	1.383 (4)
O4—N6	1.244 (7)	C5—C6	1.381 (4)
O5—N6	1.223 (6)		
O2—Cd—O2 ⁱ	178.9 (1)	N1 ⁱⁱ —Cd—N2	180.0
O2—Cd—N3	97.3 (1)	N1 ⁱⁱ —Cd—N3	94.71 (6)
O2 ⁱ —Cd—N1 ⁱⁱ	90.55 (7)	N2—Cd—N3	85.29 (6)
O2 ⁱ —Cd—N3	82.6 (1)	Cd—O2—N4	128.1 (2)

Symmetry codes: (i) 2 - x, y, ½ - z; (ii) x, y - 1, z.

All H atoms were calculated and included in the structural model, but were fixed and not refined.

Data collection: SMART (Siemens, 1994). Cell refinement: SAINT (Siemens, 1994). Data reduction: SAINT. Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993). Program(s) used to refine structure: TEXSAN (Molecular Structure Corporation, 1995). Software used to prepare material for publication: TEXSAN.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1076). Services for accessing these data are described at the back of the journal.

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[1,1'-Bis(diphenylphosphino)ferrocene]trichloro(phenylimido)rhenium(V) dichloromethane solvate

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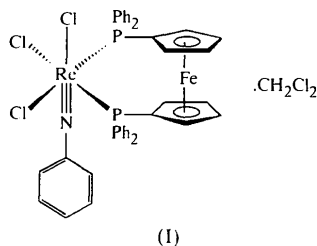
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Abstract

In the title compound, [Re(C₆H₅N)Cl₃(C₃₄H₂₈FeP₂)]·CH₂Cl₂, the coordination sphere of the Re atom can be described as a distorted octahedron. The two cyclopentadienyl ligands in the 1,1'-bis(diphenylphosphino)ferrocene moiety adopt a *gauche* conformation.

Comment

Various redox-active ligands have been reported to control the reactivities of transition metal complexes (Gan & Hor, 1995). 1,1'-Bis(diphenylphosphino)ferrocene (dppf) is a well known redox-active ligand and its complexes are expected to exhibit a ferrocene-centred oxidation process, together with the complimentary redox process at other metal centres in the molecule. In the course of our work on rhenium-imido compounds, aimed at investigating their reactivities and tuning their redox potentials, we prepared the title compound, (I).



The coordination sphere of the Re atom can be described as a distorted octahedron. The equatorial plane, defined by C11, C12, P1 and P2, is roughly planar, with an average atomic displacement of 0.1008 Å. The Re atom lies below the equatorial plane by 0.1734 (8) Å. The imido phenyl ring (C1–C6) is twisted out of the equatorial plane with a dihedral angle of 78.5 (2)°. The Re–Cl bond distance [2.3961 (15) Å] *trans* to the imido ligand is shorter than those [2.4193 (15) and 2.4392 (15) Å] *trans* to the phosphine ligands.

The two cyclopentadienyl (Cp) rings are not perfectly parallel but twisted from each other with a dihedral angle of 3.9 (4)°. The P1–C7–C12–P2 torsion angle is 25.2 (3)°, indicating that the two Cp rings adopt a *gauche* (or staggered) conformation. For comparison, the ideal torsion angle for the *gauche* conformation is 36°. The Fe–Ct (Ct is a Cp ring centroid) distances are 1.646 (for Ct2, the C12–C16 centroid) and 1.651 Å (for Ct1, the C7–C11 centroid), and the Ct1–Fe–Ct2 angle is 176.92°. The P1···Fe···P2 bite angle is 66.83 (4)° and the P1···P2 distance is 3.822 (2) Å. These bonding parameters within the ferrocene moiety are consistent with those found in octahedral rhenium complexes in which a dppf fragment acts as a ligand (Gan & Hor, 1995).

Of particular interest are the bonding parameters of the Re–N–C bond. The Re–N–C bond angle of 170.7 (4)° is fairly typical of the phenylimido (NPh) ligand in a high oxidation-state complex, in which the metal is relatively electron deficient and some π bonding between the imido N atom and the metal is likely (Wigley, 1994). This angle indicates that the phenylimido group is linear and that the Re–N bond has triple-bond character with an *sp*-hybridized

nitrogen. The Re–N bond distance of 1.717 (5) Å is also consistent with those found in arylimido–rhenium compounds (Nugent, 1988). The formal oxidation state of the Re atom is +5, indicating that it is unchanged in the reaction. The Re atom is an 18-electron centre, assuming that the NPh ligand is a six-electron donor. The Re···Fe distance is 4.451 (1) Å, which clearly rules out direct bonding between the two metals.

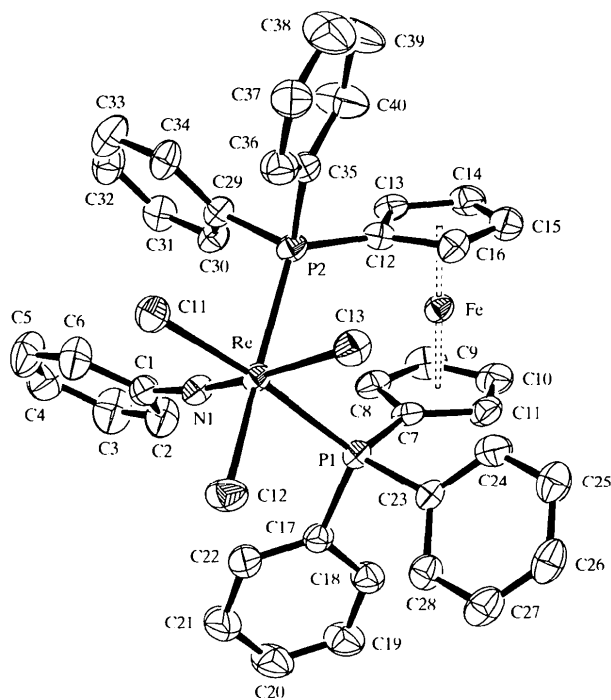


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

A mixture of *mer,trans*-[ReCl₃(NPh)(PPh₃)₂] (0.29 g, 0.32 mmol) (Goeden & Haymore, 1983) and dppf (0.183 g, 0.33 mmol) (de Lang *et al.*, 1995) in benzene (60 ml) was refluxed for 1 h. The resulting green precipitates were filtered off and washed with benzene (2 × 30 ml), diethyl ether (2 × 30 ml) and pentane (1 × 30 ml) to give the title compound. Recrystallization from dichloromethane–hexane gave a dichloromethane-solvated product. ¹H NMR (CDCl₃): δ 6.665–8.015 (25H, *m*, Ph), 5.270 (2H, *s, br*, Cp), 4.676 (2H, *s, br*, Cp), 4.639 (2H, *s, br*, Cp), 4.583 p.p.m. (2H, *s, br*, Cp). ¹³C{¹H} NMR (CDCl₃): δ 155.133 (*s*, Ph), 136.017 (*t*, *J* = 4.15 Hz, Ph), 135.692 (*s*, Ph), 134.790 (*d*, *J* = 4.65 Hz, Ph), 134.359 (*s*, Ph), 133.897 (*s*, Ph), 130.900 (*d*, *J* = 13.58 Hz, Ph), 129.560 (*s*, Ph), 129.016 (*s*, Ph), 128.450 (*d*, *J* = 5.16 Hz, Ph), 127.968 (*t*, *J* = 5.16 Hz, Ph), 122.497 (*s*, Ph), 84.620 (*s*, Cp), 84.154 (*s*, Cp), 76.835 (*s*, Cp), 75.485 (*s*, Cp), 73.715 (*s*, Cp), 73.195 p.p.m. (*s*, Cp). ³¹P{¹H} NMR (CDCl₃): –17.190 p.p.m. (*s*).

Crystal data

[Re(C₆H₅N)Cl₃·
(C₃₄H₂₈FeP₂)]·CH₂Cl₂*M_r* = 1022.94

Monoclinic

*P*2₁/*n**a* = 11.093 (2) Å*b* = 21.665 (4) Å*c* = 16.823 (5) Å

β = 104.404 (18)°

V = 3916.1 (16) Å³*Z* = 4*D_x* = 1.735 Mg m⁻³*D_m* not measured

Data collection

Siemens P4 diffractometer

ω scans

Absorption correction:

ψ scan (North *et al.*,
1968)*T_{min}* = 0.632, *T_{max}* = 0.731

7673 measured reflections

7284 independent reflections

5538 reflections with

F > 4σ(*F*)

Refinement

Refinement on *F*²*R*(*F*) = 0.038*wR*(*F*²) = 0.077*S* = 1.030

7284 reflections

461 parameters

H atoms constrained

w = 1/[σ²(*F_o*²) + (0.0263*P*)²
+ 5.2393*P*]where *P* = (*F_o*² + 2*F_c*²)/3Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 38
reflections

θ = 1.99–25.5°

μ = 3.913 mm⁻¹*T* = 294 (2) K

Plate

0.60 × 0.10 × 0.08 mm

Green

R_{int} = 0.033θ_{max} = 25.50°*h* = 0 → 13*k* = -26 → 0*l* = -20 → 19

3 standard reflections

every 97 reflections

intensity decay: none

(Δ/σ)_{max} = 0.001Δρ_{max} = 0.789 e Å⁻³Δρ_{min} = -0.762 e Å⁻³

Extinction correction:

SHELXTL (Bruker, 1997)

Extinction coefficient:

0.00025 (4)

Scattering factors from

*International Tables for
Crystallography* (Vol. C)This paper was supported by the 63 Research Fund
of Sung Kyun Kwan University (1997).Supplementary data for this paper are available from the IUCr
electronic archives (Reference: DA1088). Services for accessing these
data are described at the back of the journal.

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Carbonyl-μ-dimethylacetylene dicarboxylate and carbonyl-μ-methyltetraolate manganesecobalt complexes

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Abstract

The title complexes, heptacarbonyl-1κ⁴C,2κ³C-μ-(dimethyl but-2-ynedioato)-1:2κ²C²,1:2κ²C³-cobalt-manganese(*Mn—Co*), [MnCo(C₆H₆O₄)(CO)₇], (5), and heptacarbonyl-1κ⁴C,2κ³C-μ-(methyl but-2-ynoato)-1:2κ²C²,1:2κ²C³-cobaltmanganese(*Mn—Co*), [MnCo(C₅H₆O₂)(CO)₇], (6), were synthesized from MnCo(CO)₉ and the corresponding alkyne. The Mn—Co bond length is 2.5527 (5) Å for (5) and 2.5468 (4) Å for (6). The alkyne C—C bond is perpendicular to the Mn—Co bond.

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Table 1. Selected geometric parameters (Å, °)

Re—N1	1.717 (5)	Fe—C13	2.040 (6)
Re—Cl3	2.3961 (15)	Fe—C9	2.057 (6)
Re—Cl2	2.4193 (16)	Fe—C11	2.060 (6)
Re—Cl1	2.4392 (15)	Fe—C15	2.063 (6)
Re—P2	2.4620 (15)	Fe—C10	2.068 (6)
Re—P1	2.4674 (15)	Fe—C14	2.068 (6)
Fe—C12	2.020 (6)	P1—C7	1.812 (5)
Fe—C7	2.024 (5)	P2—C12	1.801 (6)
Fe—C8	2.028 (6)	N1—C1	1.395 (7)
Fe—C16	2.028 (6)		
N1—Re—Cl3	173.19 (16)	Cl2—Re—P2	165.07 (5)
N1—Re—Cl2	100.53 (16)	Cl1—Re—P2	86.24 (5)
Cl3—Re—Cl2	85.90 (6)	N1—Re—P1	91.58 (16)
N1—Re—Cl1	92.37 (16)	Cl3—Re—P1	86.69 (5)
Cl3—Re—Cl1	90.29 (5)	Cl2—Re—P1	85.40 (5)
Cl2—Re—Cl1	85.90 (6)	Cl1—Re—P1	170.98 (5)
N1—Re—P2	92.47 (16)	P2—Re—P1	101.69 (5)
Cl3—Re—P2	81.45 (5)	Cl1—N1—Re	170.7 (4)

Data collection: XSCANS (Siemens, 1995). Cell refinement: XSCANS. Data reduction: *SHELXTL* (Bruker, 1997). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *SHELXTL*.