Refinement

Refinement on *F*
R = 0.039
wR = 0.036
S = 1.17
1299 reflections
175 parameters
H atoms riding (C—H = 0.95 Å) and H2 coordinates refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.0003$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute configuration: confirmed by refinement of the alternate enantiomer which produced *R* = 0.045, *wR* = 0.045 and *S* = 1.43

Table 1. *Selected geometric parameters (Å, °) and hydrogen-bonding geometry (Å, °)*

Fe1—*Cg*1	1.631 (2)	S1—C11	1.855 (5)
Fe1—*Cg*2	1.656 (3)	O2—C15	1.407 (7)
S1—O1	1.504 (4)	C1—C5	1.430 (7)
S1—C1	1.766 (4)	C2—C15	1.493 (7)
*Cg*1—Fe1—*Cg*2	178.79 (13)	S1—C1—C5	126.7 (4)
O1—S1—C1	107.6 (2)	C1—C2—C15	128.5 (4)
O1—S1—C11	105.9 (2)	C3—C2—C15	125.0 (5)
C1—S1—C11	101.2 (3)	O2—C15—C2	108.8 (5)
S1—C1—C2	123.8 (3)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.99 (6)	1.73 (6)	2.711 (5)	172 (6)

Symmetry code: (i) *x*, *y*, 1 + *z*.

The Fe- and S-atom positions were provided by *SHELXS*86 (Sheldrick, 1985) and the remaining atomic sites were located with *DIRDIF* (Beurskens, 1984).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH* and *PLATON* (Spek, 1990).

DHH thanks Research Corporation and National Science Foundation, EPSCoR program for financial support of this project.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1237). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 447–449

Tricarbonyl[3-(η^5-cyclopentadienylcarbonylamino)propionic acid]rhenium

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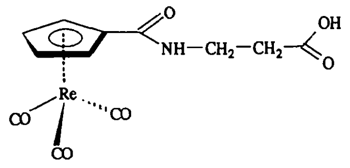
Abstract

The crystal structure of $[\mathrm{Re}\{\eta^5\text{-}\mathrm{C_5H_4CONH(CH_2)_2COOH}\}(\mathrm{CO})_3]$ is reported. This complex adopts a three-legged piano-stool geometry in the solid phase. The average bonding parameters are Re—C(η^5) 2.29 (1) and Re—CO 1.88 (1) Å. The dihedral angle between the planes formed by the CONH group and the cyclopentadienyl ring is 6.15°.

Comment

The selective acylation of amines with *N*-succinimidyl (Ns) esters is widely used in liquid-phase peptide synthesis (Anderson, Zimmerman & Callahan, 1964;

Bodanszky, 1984) and in protein-labelling experiments with reporter groups (Bolton & Hunter, 1973; Means & Feeney, 1990; Salmain, Gunn, Gorfti, Top & Jaouen, 1994; Gorfti *et al.*, 1996). The title compound, (I), was obtained by acylation of β-alanine with the ester [Re(η^5-C_5H_4COONs)(CO)$_3$].



(I)

The structural analysis of the reaction product was carried out in order to assess the formation of the amide bond between the metallo-organic moiety and the amino acid. It crystallized in space group $P2_1/a$, with four molecules per unit cell. The atomic labelling scheme and a projection onto the cyclopentadienyl (Cp) ring plane of the complex are shown as *ORTEP*II (Johnson, 1976) plots in Figs. 1 and 2, respectively. The complex possesses a three-legged piano-stool geometry. The mean Re—C(η^5) and Re—CO distances are 2.29 (1) and 1.88 (1) Å, respectively, and are equal to those reported by Meyer, Arif & Gladysz (1995). The average C—C bond length in the Cp ring is 1.40 (1) Å [range 1.39 (1)–1.43 (1) Å, standard deviation 0.02 Å] and the average C—C—C angle is 108° [range 107.1 (8)–109.4 (8)°, standard deviation 0.93°].

The coupling of β-alanine is demonstrated by the covalent N—C9 bond of 1.34 (1) Å. The dihedral angle between the mean planes formed by the CONH group and the Cp ring is 6.15°, corresponding to a slight bending of the N atom towards the metal, whereas the O4 atom is slightly above the Cp average plane (Fig. 1).

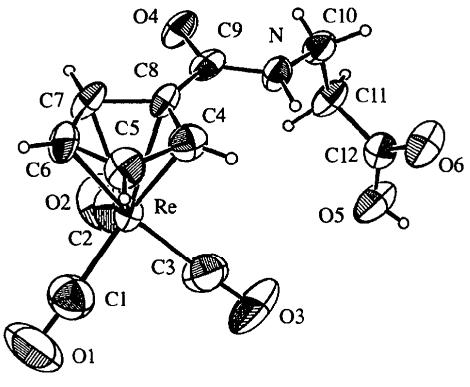


Fig. 1. The molecular configuration and atom-numbering scheme for [Re{η^5-$C_5H_4CONH(CH_2)_2COOH$}(CO)$_3$]. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

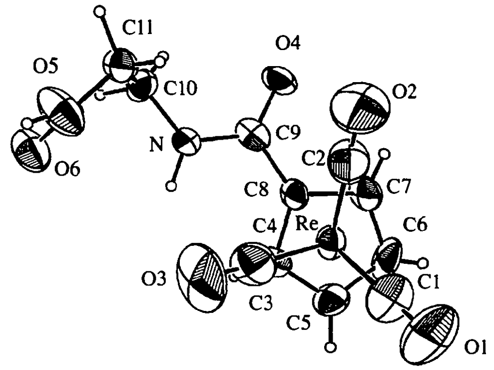


Fig. 2. A projection on the cyclopentadienyl ring of [Re{η^5-$C_5H_4CONH(CH_2)_2COOH$}(CO)$_3$].

The substituted C8 atom is positioned directly above the middle of the C2—Re—C3 angle, giving it a 'maximally staggered' position (Fig. 2). The C6 and C7 atoms are slightly staggered and the C4 atom is directly over C3. This is reflected in the pattern of the Re—C(η^5) bond distances, with two long (involving C5 and C6), two medium (involving C4 and C7) and one short (involving C8). The Re—C8 distance of 2.276 (8) Å is significantly shorter than the remaining Re—C(η^5) bonds.

Experimental

To an aqueous solution of β-alanine (15 mg, 0.17 mmol) at pH 9.5 was added one equivalent of (η^5-*N*-succinimidylcarboxycyclopentadienyl)tricarbonylrhenium in the same volume of THF. The mixture was stirred at room temperature for 18 h. After acidification with aqueous HCl, the aqueous layer was extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and the solvent evaporated off under vacuum. The raw white powder was washed several times with chloroform. Single crystals suitable for X-ray diffraction analysis were obtained by successive slow evaporation at room temperature of acetone/diethyl ether solutions.

Crystal data

[Re($C_9H_{10}NO_3$)(CO)$_3$]
M_r = 450.42
Monoclinic
$P2_1/a$
a = 8.058 (1) Å
b = 14.546 (3) Å
c = 12.247 (2) Å
β = 95.57 (1)°
V = 1428.8 (4) Å^3
Z = 4
D_x = 2.094 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.5–18.0°
μ = 8.648 mm^{-1}
T = 293 K
Prism
0.35 × 0.30 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
$T_{\min} = 0.090$, $T_{\max} = 0.115$
3230 measured reflections
2888 independent reflections

1732 reflections with $I > 3\sigma(I)$
$R_{\text{int}} = 0.049$
$\theta_{\max} = 26.32°$
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 18$
$l = -15 \rightarrow 15$
3 standard reflections frequency: 60 min intensity decay: 3.2%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.033$
$S = 0.972$
1732 reflections
212 parameters
H-atom coordinates refined
$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$
$(\Delta/\sigma)_{\max} = 0.03$

$\Delta\rho_{\max} = 0.724$ e Å^{-3}
$\Delta\rho_{\min} = 0.000$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 4.584×10^{-9}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Re—C1	1.89 (1)	O5—C12	1.30 (1)
Re—C2	1.88 (1)	O6—C12	1.21 (1)
Re—C3	1.88 (1)	N—C9	1.34 (1)
Re—C4	2.290 (9)	N—C10	1.45 (1)
Re—C5	2.313 (9)	C4—C5	1.39 (1)
Re—C6	2.297 (8)	C4—C8	1.42 (1)
Re—C7	2.291 (8)	C5—C6	1.39 (1)
Re—C8	2.276 (8)	C6—C7	1.39 (1)
Re—Cnt	1.958	C7—C8	1.43 (1)
O1—C1	1.16 (1)	C8—C9	1.48 (1)
O2—C2	1.17 (1)	C10—C11	1.52 (1)
O3—C3	1.16 (1)	C11—C12	1.51 (1)
O4—C9	1.24 (1)		
C1—Re—C2	91.0 (5)	Re—C3—O3	177.0 (1)
C1—Re—C3	87.8 (5)	C9—N—C10	122.3 (7)
C1—Re—C8	157.6 (4)	O4—C9—N	121.6 (8)
C2—Re—C3	88.0 (5)	O4—C9—C8	120.5 (7)
C2—Re—C8	101.2 (4)	N—C9—C8	117.8 (7)
C3—Re—C8	111.1 (4)	N—C10—C11	111.9 (7)
C4—Re—C5	35.1 (3)	C10—C11—C12	112.5 (7)
C4—Re—C8	36.1 (3)	O5—C12—O6	123.5 (8)
C5—Re—C6	35.2 (3)	O5—C12—C11	113.1 (7)
C6—Re—C7	35.3 (3)	O6—C12—C11	123.4 (7)
C7—Re—C8	36.4 (3)	Cnt—Re—C1	126.5
Re—C1—O1	176 (1)	Cnt—Re—C2	124.4
Re—C2—O2	176.5 (9)	Cnt—Re—C3	127.1

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1982). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DU1167). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 449–451

Epimer B of Tetraphenylarsonium (Mercaptoacetylalanylglycylglycinato-*N*,*N*′,*N*″,*S*)oxotechnetate(V) (^{99}Tc) Chloroform Solvate

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Abstract

In the title compound, $(C_{24}H_{20}As)[TcO(C_9H_{11}N_3O_5S)]\cdot CHCl_3$, technetium is coordinated to three amide N atoms and one S atom which form a square pyramid,