

(Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* (January 1994 version).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Bailey, M. F. & Dahl, L. F. (1965). *Inorg. Chem.* **4**, 1314–1319.  
 Bak, B., Hansen, L. & Rastrup-Andersen, J. (1954). *J. Chem. Phys.* **22**, 2013–2017.  
 Bugg, C. & Sass, R. L. (1965). *Acta Cryst.* **18**, 591–594.  
 Davies, S. G. & Shipman, M. R. (1989). *J. Chem. Soc. Chem. Commun.* pp. 995–996.  
 Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Kim, H. S., Jeffrey, G. A. & Rosenstein, R. D. (1971). *Acta Cryst.* **B27**, 307–314.  
 Meuterties, E. L., Bleeke, J. P., Wucherer, E. J. & Albright, T. A. (1982). *Chem. Rev.* **82**, 499–525.  
 Riley, P. E. & Davis, R. E. (1976). *Inorg. Chem.* **15**, 2735–2740.

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## Nonacarbonyl-1 $\kappa^4$ C,2 $\kappa^5$ C-pivalonitrile-1 $\kappa$ N-manganeserhenium(Mn—Re): Unsymmetrical Distortions of Equatorial Carbonyl Ligands

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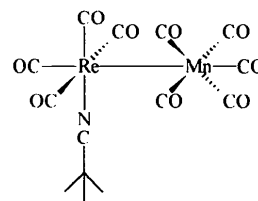
### Abstract

The title compound, [(CO)<sub>5</sub>MnRe(CO)<sub>4</sub>(C<sub>5</sub>H<sub>9</sub>N)], is a monosubstituted manganese-rhenium decacarbonyl and has the common staggered-ligand arrangement at both metal centres. The unexpected strong bending of two of

the four equatorial manganese CO groups is probably caused by intermolecular packing forces. The Mn—Re bond length is 2.969 (2) Å.

### Comment

Our investigations into the photochemical reactions of (CO)<sub>5</sub>MnRe(CO)<sub>4</sub>(PHR<sub>2</sub>) (R = alkyl, aryl) led to the synthesis of the first nitrile-substituted heteronuclear cluster compound (CO)<sub>5</sub>MnRe(CO)<sub>4</sub>NC<sup>t</sup>Bu [<sup>t</sup>Bu = C(CH<sub>3</sub>)<sub>3</sub>]. The reaction of MnRe(CO)<sub>10</sub> with (CH<sub>3</sub>)<sub>3</sub>NO in the presence of <sup>t</sup>BuCN in thf solution gives good yields of the title compound, (I). Air-stable monosubstituted complexes of the homonuclear carbonyls Mn<sub>2</sub>(CO)<sub>10</sub> and Re<sub>2</sub>(CO)<sub>10</sub> may be formed with acetonitrile (Koelle, 1978), whereas the heteronuclear complex needs more sterically demanding ligands for stabilization. As the title compound is the first nitrile-substituted manganese-rhenium carbonyl complex, we undertook a single-crystal structure determination.



(I)

The carbonyl *versus* nitrile ligand substitution took place at the Re atom (Fawcett, Poe & Twigg, 1973) in the equatorial position (Koelle, 1978), as expected (Fig. 1). The resulting molecular structure is closely related to that of the isonitrile compound (CO)<sub>5</sub>MnRe(CO)<sub>4</sub>CN<sup>t</sup>Bu (Leins, Billing, Levendis, du Toit & Coville, 1992) with an almost identical Mn—Re bond length: nitrile 2.969 (2), isonitrile 2.963 (3) Å. With respect to the carbonyl and nitrile/isonitrile groups, both compounds have the same staggered-ligand arrangement and to a great extent have comparable geometries. Carbonyl groups 2 and 4 at the Mn atom, which point to the nitrile side of the molecule, bend considerably towards the Re atom [by 8.3 (3) and 7.9 (3)°, respectively], their positions being significantly different from those of the carbonyl groups 1 and 3. As is known from the work of Jackson, Eisenstein, Martin, Albeniz & Crabtree (1991), the bending of the equatorial carbonyl ligands of a (CO)<sub>5</sub>MR molecule towards R depends on the electropositive character of the R group. Leins *et al.* (1992) noted for their isonitrile complex that it is not clear whether the observed Re—Mn—CO angles (82.7–86.4°) are a result of the electronic or the steric effects. It is reasonable to assume that substitution of the isonitrile *versus* a nitrile ligand, L, will not substantially influence the electronic properties of the Re(CO)<sub>4</sub>L group and so the bending of the equatorial carbonyl ligands

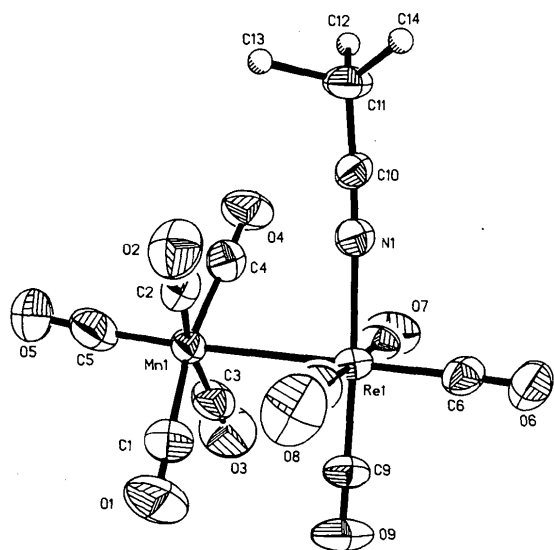


Fig. 1. Molecular structure of the title compound showing 50% probability for displacement ellipsoids. H atoms have been omitted.

on Mn should not differ for the two compounds. This is true for the CO groups 1 and 3, which have Re—Mn—CO angles of 86.4 (4) and 87.7 (4)°, respectively; the related angles of the isonitrile compound average 85.6 (7) and 86.4 (7)°, respectively. Inspection of the crystal packing revealed that for the strongly bent carbonyl groups 2 and 4 [Re—Mn—CO angles 81.7 (3) and 82.1 (3)°, respectively] there exist short intermolecular O2···O4( $x + \frac{1}{2}, \frac{1}{2} - y, -z$ ) contacts of 3.018 (13) Å, a distance which is close to the sum of the van der Waals radii. A 'normal' angle of 87.0° for carbonyl groups 2 and 4 would result in O···O contacts being too short [2.80 (1) Å] for these groups. The intramolecular distances from these carbonyls to the nitrile group are N1···O4 3.18 (1) and N1···O2 3.25 (1) Å. Other short non-bonding intermolecular distances are 3.07 (1) Å for O6···O8( $x - \frac{1}{2}, y, \frac{1}{2} - z$ ) and 3.17 (1) Å for O4···O9( $x, \frac{1}{2} - y, z - \frac{1}{2}$ ). The strong asymmetric bending of carbonyl groups 2 and 4 in the title compound is a result of intermolecular repulsion, rather than electronic effects.

The 'Bu group is disordered; the positions of the methyl C atoms have large e.s.d.'s and show large displacement parameters. It was not possible to treat this disorder successfully.

## Experimental

### Crystal data

[MnRe(CO)<sub>9</sub>(C<sub>5</sub>H<sub>9</sub>N)]

$M_r = 576.36$

Orthorhombic

*Pbca*

$a = 12.226$  (3) Å

$b = 16.873$  (3) Å

$c = 18.401$  (4) Å

$V = 3795.9$  (14) Å<sup>3</sup>

$Z = 8$

$D_x = 2.017$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 8-23^\circ$

$\mu = 7.081$  mm<sup>-1</sup>

$T = 293$  (2) K

Prism

$0.75 \times 0.42 \times 0.37$  mm

Yellowish

### Data collection

Siemens R3m/V diffractometer

$\omega-2\theta$  scans

Absorption correction:

empirical ( $\psi$  scans)

$T_{\min} = 0.552, T_{\max} = 0.910$

4337 measured reflections

4337 independent reflections

2893 observed reflections

$[I > 2\sigma(I)]$

$\theta_{\max} = 27.56^\circ$

$h = 0 \rightarrow 15$

$k = 0 \rightarrow 21$

$l = 0 \rightarrow 23$

25 standard reflections

monitored every 400 reflections

intensity variation:

$-0.7 \rightarrow +0.2\%$

### Refinement

Refinement on  $F^2$

$R(F) = 0.0505$

$wR(F^2) = 0.1223$

$S = 1.071$

4332 reflections

221 parameters

$\Delta\rho_{\max} = 2.047$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -3.465$  e Å<sup>-3</sup>

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient: 0.002

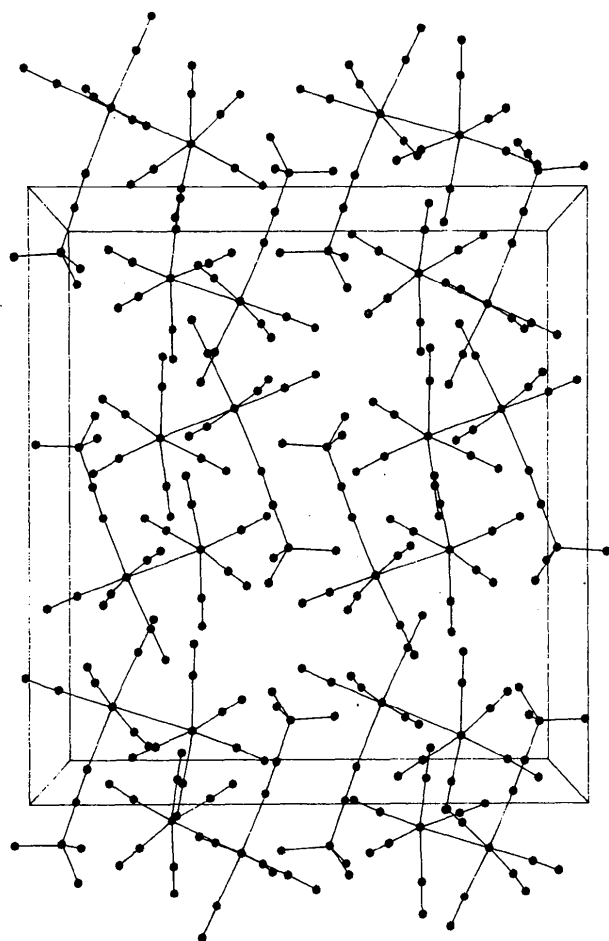


Fig. 2. View of the crystal packing along [100] ( $b$  horizontal,  $c$  vertical).

H-atoms fixed at calculated positions

$$w = 1/[\sigma^2(F_o^2) + (0.0806P)^2 + 12.7786P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Jackson, S. A., Eisenstein, O., Martin, J. D., Albeniz, A. C. & Crabtree, R. H. (1991). *Organometallics*, **10**, 3062–3069.  
 Koelle, K. (1978). *J. Organomet. Chem.* **155**, 53–62.  
 Leins, A. E., Billing, D. G., Levendis, D. C., du Toit, J. & Coville, N. J. (1992). *Inorg. Chem.* **31**, 4756–4761.  
 Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen. Germany.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Re1	0.20300 (3)	0.13691 (2)	0.14701 (2)	0.0391 (2)
Mn1	0.32317 (12)	0.28031 (8)	0.09839 (8)	0.0401 (3)
C1	0.3896 (10)	0.2792 (7)	0.1895 (7)	0.065 (3)
O1	0.4290 (8)	0.2795 (7)	0.2433 (5)	0.101 (3)
C2	0.4195 (9)	0.2052 (7)	0.0649 (6)	0.056 (3)
O2	0.4783 (7)	0.1589 (6)	0.0427 (6)	0.083 (3)
C3	0.2124 (11)	0.3396 (8)	0.1376 (7)	0.066 (3)
O3	0.1415 (10)	0.3769 (7)	0.1618 (7)	0.103 (4)
C4	0.2414 (10)	0.2645 (6)	0.0157 (6)	0.053 (3)
O4	0.1940 (7)	0.2545 (6)	-0.0358 (5)	0.075 (3)
C5	0.3982 (12)	0.3613 (7)	0.0647 (7)	0.072 (3)
O5	0.4485 (9)	0.4142 (6)	0.0387 (5)	0.093 (3)
C6	0.1304 (9)	0.0427 (6)	0.1788 (6)	0.051 (2)
O6	0.0903 (8)	-0.0141 (5)	0.2001 (4)	0.076 (2)
C7	0.0623 (9)	0.1846 (6)	0.1132 (6)	0.051 (2)
O7	-0.0171 (7)	0.2137 (6)	0.0960 (5)	0.081 (3)
C8	0.3473 (9)	0.0958 (7)	0.1804 (6)	0.057 (3)
O8	0.4271 (8)	0.0759 (7)	0.2031 (6)	0.101 (3)
C9	0.1808 (9)	0.1859 (7)	0.2395 (5)	0.053 (3)
O9	0.1686 (8)	0.2150 (6)	0.2953 (4)	0.084 (3)
N1	0.2313 (7)	0.0878 (5)	0.0407 (4)	0.045 (2)
C10	0.2448 (8)	0.0657 (6)	-0.0159 (5)	0.042 (2)
C11	0.2706 (10)	0.0374 (7)	-0.0888 (5)	0.057 (3)
C12	0.1940 (19)	0.0740 (18)	-0.1459 (13)	0.154 (10)
C13	0.3939 (25)	0.0663 (17)	-0.1069 (15)	0.184 (10)
C14	0.2979 (25)	-0.0522 (23)	-0.0939 (19)	0.221 (15)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Re1—N1	2.152 (8)	Mn1—C2	1.836 (12)
Re1—Mn1	2.969 (2)	Mn1—C1	1.862 (12)
Re1—C6	1.913 (11)	C1—O1	1.102 (13)
Re1—C7	1.999 (11)	C2—O2	1.137 (13)
Re1—C8	1.992 (11)	C3—O3	1.16 (2)
Re1—C9	1.912 (10)	C4—O4	1.124 (13)
Mn1—C3	1.832 (13)	N1—C10	1.119 (11)
Mn1—C4	1.840 (13)	C10—C11	1.458 (13)
C9—Re1—N1	176.9 (4)	C1—Mn1—Re1	86.4 (4)
C6—Re1—N1	91.9 (4)	O1—C1—Mn1	179.2 (12)
C8—Re1—N1	90.2 (4)	O2—C2—Mn1	178.6 (11)
C7—Re1—N1	90.6 (3)	O3—C3—Mn1	179.3 (12)
N1—Re1—Mn1	87.7 (2)	O4—C4—Mn1	178.2 (11)
C3—Mn1—Re1	87.7 (4)	C10—N1—Re1	176.7 (8)
C4—Mn1—Re1	82.1 (3)	N1—C10—C11	176.0 (12)
C2—Mn1—Re1	81.7 (3)		

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: AB1171). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Fawcett, J. P., Poe, A. J. & Twigg, M. V. (1973). *J. Organomet. Chem.* **61**, 315–321.

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## 4-(Ferrocenylmethyl)-2,2,6,6-tetramethyl-3,5-heptanedione, a Non-Enolized 1,3-Diketone

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## Abstract

The analysis of the title compound,  $(\eta^5\text{-cyclopentadienyl})\{\eta^5\text{-}[2,2\text{-bis}(2,2\text{-dimethylpropanoyl)ethyl]cyclopentadienyl}\text{iron}$ ,  $[(\text{C}_5\text{H}_5)\text{Fe}\{(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}(\text{COCMe}_3)_2\}]$ , shows that it exists in the solid state in the diketo form; there is no evidence at all for any keto-enol tautomeric contribution to the ground-state structure.

## Comment

Both in solution and in the vapour phase (Lowrey, George, D'Antonio & Karle, 1971), 1,3-diketones  $R^1\text{COCH}_2\text{COR}^2$  generally exist as equilibrium mixtures of keto and enol tautomers where the enol tautomer contains a six-membered hydrogen-bonded ring. In the solid state, however, only a single form is generally observed. This is most frequently the enol form in which the hydrogen-bonded ring is virtually planar with the two C—O bonds necessarily *cis* (Tønnesen, Karlsen & Mostad, 1982; Tønnesen, Karlsen, Mostad, Pedersen, Rasmussen & Lawesson, 1983; Mostad, Pedersen, Rasmussen & Lawesson, 1983; Etter, Jahn & Urbanczyk-Lipkowska, 1987; Baxter, Blake, Heath & Stephenson, 1990). The enol H atom has been located