

C3	0.8968 (5)	0.8568 (4)	-0.0274 (4)	0.0715 (13)
C4	0.8479 (4)	0.7830 (3)	0.0185 (5)	0.0747 (14)
C5	0.9482 (4)	0.7661 (3)	0.1504 (5)	0.0648 (12)
C6	0.8616 (13)	0.9594 (12)	0.2881 (10)	0.188 (7)
C7	0.8493 (10)	1.0156 (6)	0.1968 (12)	0.149 (4)
C8	0.7270 (8)	0.9981 (5)	0.0837 (7)	0.096 (2)
C9	0.6599 (6)	0.9236 (6)	0.1079 (8)	0.113 (2)
C10	0.7464 (12)	0.8997 (7)	0.2423 (12)	0.146 (4)
C11	1.3132 (3)	0.9501 (2)	0.3513 (3)	0.0445 (8)
C12	1.4196 (5)	0.9704 (4)	0.3038 (4)	0.0744 (14)
C13	1.4554 (7)	1.0610 (5)	0.3250 (6)	0.127 (3)
C14	1.3731 (8)	1.0989 (4)	0.3807 (7)	0.123 (3)
C15	1.2852 (5)	1.0329 (3)	0.3990 (4)	0.0720 (13)
C16	1.3637 (7)	0.7520 (4)	0.3495 (9)	0.146 (4)
C17	1.1861 (9)	0.8235 (7)	0.4892 (5)	0.163 (4)

Table 2. Selected geometric parameters (Å, °)

Fe1—C9	2.007 (5)	Fe2—C13	2.029 (6)
Fe1—C6	2.013 (8)	Fe2—C15	2.032 (4)
Fe1—C7	2.016 (7)	Fe2—C14	2.038 (5)
Fe1—C10	2.025 (6)	Fe2—C12	2.038 (4)
Fe1—C8	2.026 (5)	Fe2—C11	2.052 (3)
Fe1—C5	2.028 (4)	Si1—C17	1.838 (6)
Fe1—C4	2.028 (4)	Si1—C11	1.843 (4)
Fe1—C3	2.029 (4)	Si1—C1	1.858 (3)
Fe1—C2	2.040 (4)	Si1—C16	1.867 (6)
Fe1—C1	2.051 (4)		
C17—Si1—C11	111.5 (3)	C5—C1—Si1	128.6 (3)
C17—Si1—C1	111.4 (2)	Si1—C1—Fe1	129.1 (2)
C11—Si1—C1	107.8 (2)	C12—C11—Si1	126.1 (3)
C17—Si1—C16	109.3 (5)	C15—C11—Si1	129.1 (3)
C11—Si1—C16	108.2 (3)	C12—C11—Fe2	69.2 (2)
C1—Si1—C16	108.6 (2)	C15—C11—Fe2	68.9 (2)
C2—C1—Si1	125.4 (3)	Si1—C11—Fe2	126.7 (2)

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: *XCAD4* (Siemens, 1993). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: FG1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Tricarbonyl( $\eta^6$ -pyridine)chromium(0)

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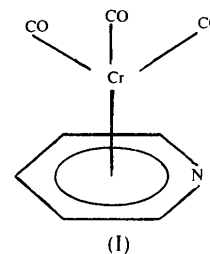
(Received 23 February 1994; accepted 13 June 1994)

## Abstract

The molecular structure of tricarbonyl( $\eta^6$ -pyridine)chromium(0),  $[\text{Cr}(\text{CO})_3(\text{C}_5\text{H}_5\text{N})]$ , is presented here. The Cr atom is bound to the pyridine ring *via* the  $\pi$ -electron system and is situated directly below the heteroarene ring centre. The pyridine ring is slightly distorted compared to free pyridine and the distance from the Cr atom to the plane of the pyridine ring is 1.698 (2) Å. The tricarbonyl moiety adopts an eclipsed conformation with respect to the pyridine ring atoms.

## Comment

The title compound, (I), consists of an unsubstituted pyridine ring with a tricarbonylchromium unit bonded to the  $\pi$ -electron system of the heterocycle.



This compound is analogous to the  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$  compound in which the  $\pi$ -bonded benzene ring exhibits no significant distortion from the sixfold  $D_{6h}$  symmetry of free benzene (Bailey & Dahl, 1965). No such symmetry exists for pyridine, however, as is evident from the results calculated from microwave measurements by Bak, Hansen & Rastrup-Andersen (1954), which indicate that the internal angles in the heteroaromatic ring vary from  $116.7(1)^\circ$  at the N atom to

124.0(1)° at the C atom α to the N atom. In the crystal the equivalent angles are 115.7(4) and 123.8(3)° (mean of two), respectively. The internal angle at C13 is 119.9(4)°, while the equivalent angles in free pyridine and bis(2,6-dimethylpyridine)chromium (Riley & Davis, 1976) are 118.1 and 115.8(9)°, respectively. Thus, the coordination of the π-system to the tricarbonylchromium unit causes a slight distortion of the pyridine ring system. The mean N—C distance in the crystal is 1.370(7) Å, compared with 1.340(5) Å in free pyridine. The equivalent distances in D-glucitol-pyridine (Kim, Jeffrey & Rosenstein, 1971) and pyridinium dicyanomethylide (Bugg & Sass, 1965) are 1.330(6) and 1.37(1) Å, respectively. The pyridine ring is essentially planar. The Cr atom sits at a distance of 1.698(2) Å from this mean plane, directly below the centre of the ring. This is significantly longer than the Cr to ring-plane distance of 1.620(1) Å in bis(2,6-dimethylpyridine)chromium.

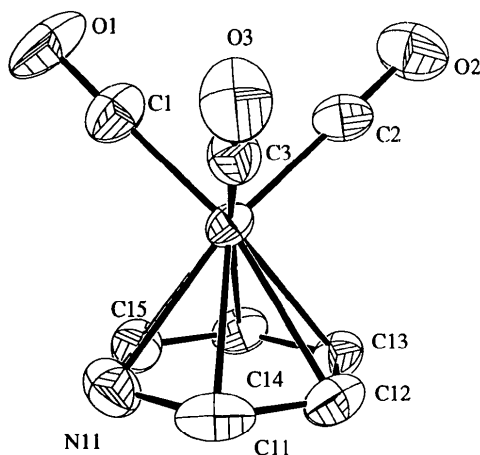


Fig. 1. A view of the molecule with atomic numbering scheme. The atoms are shown with displacement ellipsoids drawn at the 30% probability level.

The mean Cr to ring-atom distance in the title compound is 2.189(4) Å, compared with 2.136(15) Å in bis(2,6-dimethylpyridine)chromium. The conformation of the tricarbonyl unit is such that the carbonyl ligands eclipse atoms C11, C13 and C15. This is a relatively uncommon conformation; most [M(CO)<sub>3</sub>(η<sup>6</sup>-arene)] compounds (M = Cr or Mo) adopt a staggered conformation (Muettterties, Bleeke, Wucherer & Albright, 1982).

## Experimental

The [Cr(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>5</sub>H<sub>5</sub>N)] compound was synthesized by the method described by Davies & Shipton (1989). Suitable crystals were grown from diethyl ether/n-hexane solution.

### Crystal data

[Cr(CO)<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>N)]  
M<sub>r</sub> = 215.13

Mo Kα radiation  
λ = 0.7107 Å

Monoclinic  
P2<sub>1</sub>/c  
a = 10.752(5) Å  
b = 7.652(5) Å  
c = 11.110(2) Å  
β = 111.80(5)°  
V = 848.7(7) Å<sup>3</sup>  
Z = 4  
D<sub>x</sub> = 1.684 Mg m<sup>-3</sup>

### Data collection

Enraf-Nonius CAD-4  
diffractometer  
θ/2θ scans  
Absorption correction:  
none  
1589 measured reflections  
791 independent reflections  
751 observed reflections  
[I > 3.0σ(I)]

### Refinement

Refinement on F  
R = 0.044  
wR = 0.061  
S = 2.17  
751 reflections  
118 parameters  
H atoms refined as riding  
(C—H = 1.08 Å)  
w = 1/[σ<sup>2</sup>(F) + 0.0008F<sup>2</sup>]

Cell parameters from 25  
reflections  
θ = 1.00–22.00°  
μ = 1.28 mm<sup>-1</sup>  
T = 293 K  
Rectangular plate  
0.90 × 0.80 × 0.60 mm  
Yellow

R<sub>int</sub> = 0.046  
θ<sub>max</sub> = 19.90°  
h = -10 → 9  
k = 0 → 7  
l = 0 → 10  
3 standard reflections  
monitored every 100  
reflections  
intensity variation: 2.0%

(Δ/σ)<sub>max</sub> < 0.001  
Δρ<sub>max</sub> = 0.38 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.28 e Å<sup>-3</sup>  
Atomic scattering factors  
from *International Tables  
for X-ray Crystallography*  
(1974, Vol. IV, Table  
2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

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

	x	y	z	U <sub>eq</sub>
Cr1	0.24257(5)	0.02605(9)	0.18428(5)	0.0427(6)
C1	0.3175(4)	-0.0975(7)	0.3383(5)	0.070(3)
O1	0.3647(3)	-0.1745(6)	0.4330(3)	0.111(3)
C2	0.1775(4)	-0.1785(6)	0.1000(4)	0.058(3)
O2	0.1344(3)	-0.3074(5)	0.0447(3)	0.089(3)
C3	0.0883(5)	0.0442(5)	0.2178(4)	0.052(3)
O3	-0.0076(4)	0.0527(5)	0.2408(3)	0.076(2)
N11	0.3461(4)	0.2752(5)	0.2494(4)	0.072(3)
C11	0.2300(5)	0.3047(6)	0.1449(6)	0.074(4)
C12	0.1985(4)	0.2192(6)	0.0255(4)	0.064(3)
C13	0.2871(4)	0.1000(6)	0.0121(4)	0.063(3)
C14	0.4082(5)	0.0677(6)	0.1161(4)	0.061(3)
C15	0.4319(4)	0.1561(6)	0.2304(4)	0.066(3)

Table 2. Selected geometric parameters (Å)

Cr1—C1	1.857(5)	C1—O1	1.146(6)
Cr1—C2	1.825(5)	C2—O2	1.164(6)
Cr1—C3	1.835(5)	C3—O3	1.153(6)
Cr1—N11	2.190(4)	N11—C11	1.371(7)
Cr1—C11	2.171(5)	N11—C15	1.368(7)
Cr1—C12	2.213(4)	C11—C12	1.404(8)
Cr1—C13	2.211(4)	C12—C13	1.366(7)
Cr1—C14	2.202(4)	C13—C14	1.405(6)
Cr1—C15	2.149(4)	C14—C15	1.376(7)

The H atoms were located on a difference map and then given normalized bond lengths of 1.08 Å and allowed to ride on their parent atoms. Data collection and cell refinement: Enraf-Nonius CAD-4 software. Data reduction: NRCVAX DATRD2

(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.

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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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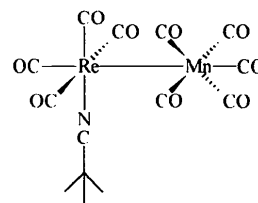
### Abstract

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'Bu [*t*'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 *t*'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'*t*'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