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: *XCAD*4 (Siemens, 1993). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

This research was supported by NSERC Canada and the University of Toronto.

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.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Foucher, D. A., Tang, B. Z. & Manners, I. (1992). *J. Am. Chem. Soc.* **114**, 6246–6248.

Manners, I. (1994). *Adv. Mater.* **6**, 68–71.

Rulkens, R., Lough, A. J. & Manners, I. (1994). *J. Am. Chem. Soc.* **116**, 797–798.

Sheats, J. E., Carraher, C. E. & Pittman, C. U. (1985). In *Metal Containing Polymer Systems*. New York: Plenum.

Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1994). *SHELXL93. Program for the Refinement of Crsytal Structures*. Univ. of Göttingen, Germany.

Siemens (1993). *XCAD4. Program to Extract Intensity Data from the Enraf–Nonius CAD-4*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1994). **C50**, 1669–1671

Tricarbonyl(η^6-pyridine)chromium(0)

Sylvia M. Draper and Janice J. Byrne

Department of Chemistry, Trinity College, Dublin 2, Ireland

Ciara J. Breheny and Conor Long

School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

John N. Low

Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland

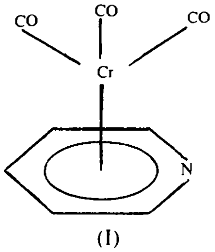
(*Received* 23 *February* 1994; *accepted* 13 *June* 1994)

Abstract

The molecular structure of tricarbonyl(η^6-pyridine)chromium(0), $[Cr(CO)_3(C_5H_5N)]$, is presented here. The Cr atom is bound to the pyridine ring *via* the π-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 π-electron system of the heterocycle.



(I)

This compound is analogous to the $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ compound in which the π-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)° 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.

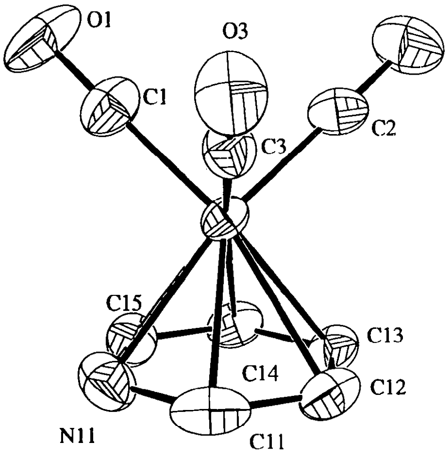


Fig. 1. A view of the molecule with atomic numbering scheme. The atoms are shown with displacement ellipsoids drawn at the 30% probability level.

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 [$M(CO)_3(\eta^6$-arene)] compounds (M = Cr or Mo) adopt a staggered conformation (Muetterties, Bleeke, Wucherer & Albright, 1982).

Experimental

The [$Cr(CO)_3(\eta^6-C_5H_5N)$] compound was synthesized by the method described by Davies & Shipton (1989). Suitable crystals were grown from diethyl ether/n-hexane solution.

Crystal data

[$Cr(CO)_3(C_5H_5N)$]
M_r = 215.13
Monoclinic
$P2_1/c$
a = 10.752 (5) Å
b = 7.652 (5) Å
c = 11.110 (2) Å
β = 111.80 (5)°
V = 848.7 (7) Å^3
Z = 4
D_x = 1.684 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 1.00–22.00°
μ = 1.28 mm^{-1}
T = 293 K
Rectangular plate
0.90 × 0.80 × 0.60 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1589 measured reflections
791 independent reflections
751 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int}$ = 0.046
$\theta_{\rm max}$ = 19.90°
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 100 reflections intensity variation: 2.0%

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)
$w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.38 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.28 e Å^{-3}
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^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
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: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* (January 1994 version).

The authors would like to thank Professor George Ferguson for his advice.

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). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kim, H. S., Jeffrey, G. A. & Rosenstein, R. D. (1971). *Acta Cryst.* B**27**, 307–314.

Meutterties, 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.

Acta Cryst. (1994). C**50**, 1671–1673

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

Hans-Günther Beckers, Ulrich Flörke*
and Hans-Jürgen Haupt

*Anorganische und Analytische Chemie,
Universität-GH Paderborn, Warburgerstrasse 100,
D-33098 Paderborn, Germany*

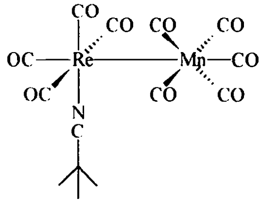
(*Received* 21 *February* 1994; *accepted* 28 *March* 1994)

Abstract

The title compound, $[(CO)_5MnRe(CO)_4(C_5H_9N)]$, 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 $(CO)_5MnRe(CO)_4(PHR_2)$ (R = alkyl, aryl) led to the synthesis of the first nitrile-substituted heteronuclear cluster compound $(CO)_5MnRe(CO)_4NC^tBu$ [^tBu = $C(CH_3)_3$]. The reaction of $MnRe(CO)_{10}$ with $(CH_3)_3NO$ in the presence of ^tBuCN in thf solution gives good yields of the title compound, (I). Air-stable monosubstituted complexes of the homonuclear carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ 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 $(CO)_5MnRe(CO)_4CN^tBu$ (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 $(CO)_5MR$ 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 $Re(CO)_4L$ group and so the bending of the equatorial carbonyl ligands

Acta Crystallographica Section C
ISSN 0108-2701 ©1994