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fac-Tris(*tert*-butyl isocyanide)tricarbonylmolybdenum(0)

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Key indicators

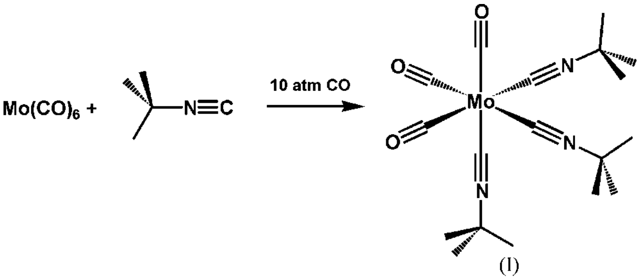
Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.007 Å
R factor = 0.052
wR factor = 0.117
Data-to-parameter ratio = 22.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Mo(C_5H_9N)_3(CO)_3]$, was produced from $Mo(CO)_6$ and *tert*-butyl isocyanide in the presence of 10 atm of carbon monoxide (1 atm = 101325 Pa). The octahedral complex shows a facial arrangement of the ligands, the Mo—C distances of the isocyanide ligands being about 0.15 Å longer than the corresponding bond lengths of the carbonyl ligands. The crystal structure is influenced by one short C—H···O contact, resulting in infinite chains which are interconnected by additional weak C—H···O interactions.

Comment

Recently, we reported the facile synthesis of *cis*- and *trans*-$[Ru(CN\text{-}^t Bu)_4(CN)_2]$ from $Ru_3(CO)_{12}$ and *tert*-butyl isocyanide by the reductive cleavage of isocyanide ligands and the concomitant oxidation of the Ru atoms (Imhof & Dönnecke, 2003). Our interest in those mixed cyanide–isocyanide coordination compounds with a defined stereochemistry of the cyano ligands results from the possibility of producing cyanide-bridged coordination polymers with a predefined supramolecular arrangement of the metal centres in the polymeric chain.



(I)

In the course of our investigations of the reactivity of other metal carbonyls, we introduced $Mo(CO)_6$ to the reaction conditions that led to the isolation of mixed cyanide–isocyanide complexes in the case of $Ru_3(CO)_{12}$. Nevertheless, the reaction of $Mo(CO)_6$ did not result in the reductive cleavage of isocyanide ligands but in the substitution of three carbonyl ligands by isocyanide ligands, producing the title compound, (I), in high yield. Obviously the much higher inherent stability of $Mo(CO)_6$ compared with $Ru(CO)_5$ favoured the substitution reaction over the redox reaction observed for ruthenium. The spectroscopic properties of the compound have already unequivocally revealed the *fac*-arrangement of the ligands (King & Saran, 1974). Strangely enough, only one structurally characterized derivative of the title compound has been published to date, using the highly electron-withdrawing 2,2,2-trifluorethyl isocyanide as the ligand (Lentz & Willemsen, 2000). In addition, the crystal structure of the *mer*-derivative

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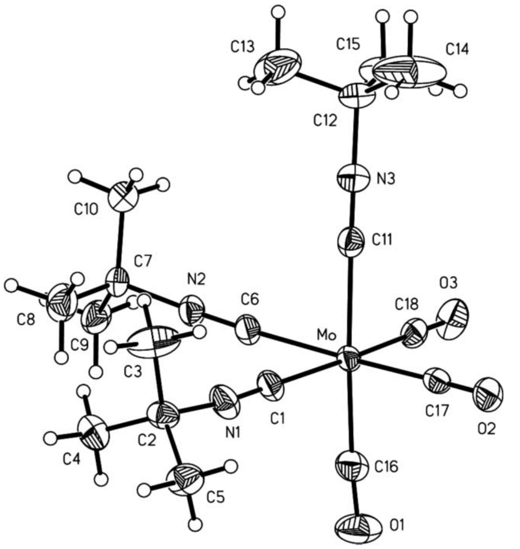

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 40% probability level.

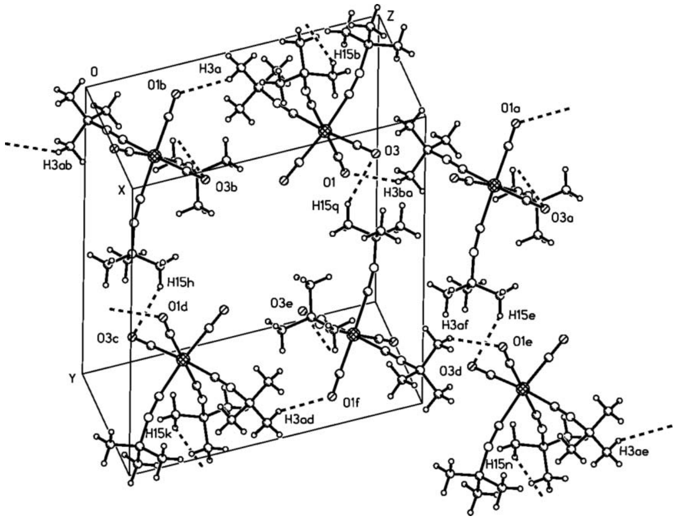

Figure 2
Packing diagram of (I). Dashed lines indicate hydrogen bonds.

of $Mo(CO)_3(CN-C_6F_5)_3$ has been described (Lentz *et al.*, 1998), as well as several other tungsten derivatives, in which the *fac* arrangement is caused by the use of a tripodal iyocyanide ligand (Hahn & Tamm, 1991, 1992, 1994).

Fig. 1 shows the molecular structure of (I), which crystallizes in the monoclinic space group $P2_1/n$. In contrast to *fac*-$[Mo(CO)_3(CN-CH_2-CF_3)_3]$, which showed crystallographic C_s symmetry (Lentz & Willemsen, 2000), the title compound lacks any crystallographic symmetry. Most probably this results from the bulky *tert*-butyl substituents which cause the C—N—C angles of the isocyanide ligands to deviate from linearity by approximately 10°. As has been observed for *fac*-$[Mo(CO)_3(CN-CH_2-CF_3)_3]$, the Mo—C bond distances of the isocyanide ligands in *fac*-$[Mo(CO)_3(CN\text{-}^t\text{Bu})_3]$ are longer than the corresponding bond lengths to the CO ligands. Whereas this difference has been measured as approximately 0.1 Å in the former case, we observed approximately 0.15 Å longer Mo—C(isocyanide) bonds, corresponding to the weaker π-acceptor properties of the *tert*-butyl-substituted isocyanide ligand (Lentz, 1994).

The supramolecular structure of the title compound is depicted in Fig. 2. There is one quite strong C—H⋯O interaction between O1 and an H atom of the methyl group C3 (2.604 Å; Desiraju & Steiner, 1999), producing infinite chains of molecules. These chains are interconnected by additional C—H⋯O contacts, which are much weaker, to produce the observed crystal structure. The shortest one, between O3 and the methyl substituent C15 (2.814 Å), is also shown in Fig. 2; the others have been omitted for the sake of clarity.

Experimental

In a stainless steel autoclave, a sample of $Mo(CO)_6$ (179 mg, 0.67 mmol) together with CN-^{t}Bu (0.6 ml, 5.31 mmol) in dry toluene (4 ml) was pressurized with 10 atm (1 atm = 101325 Pa) of carbon monoxide and heated to 413 K for 16 h. After the autoclave had cooled down, the solution was transferred to a Schlenk tube and all volatile material removed *in vacuo*. The resulting green–yellow residue was recrystallized from a mixture of dichloromethane and light petroleum (b.p. 313–333 K) in a 1:2 (*v*/*v*) ratio at 253 K. Crystals of (I) suitable for X-ray structure determination were produced by the slow diffusion of light petroleum into a dichloromethane solution of the title compound. IR (KBr, 298 K) (cm^{-1}): 2986 (*m*), 2153 (*m*), 2113 (*m*), 1930 (*sh*), 1921 (*vs*), 1865 (*vs*), 1850 (*vs*), 1457 (*m*), 1397 (*w*), 1370 (*m*); MS (DEI), *m*/*z* (%): 432 (89, [MH$^+$]), 404 {9, $[Mo(CO)_2(CN\text{-}^t\text{Bu})_3H^+]$}, 374 {35, $[Mo(CO)_3(CN)(CN\text{-}^t\text{Bu})_2H^+]$}, 347 {16, $[Mo(CO)_2(CN)(CN\text{-}^t\text{Bu})_2H^+]$}, 317 {23, $[Mo(CO)_3(CN)_2(CN\text{-}^t\text{Bu})H^+]$}, 289 {17, $[Mo(CO)_2(CN)_2(CN^t\text{Bu})H^+]$}, 260 {63, $[Mo(CO)_3(CN)_3H^+]$}, 232 {21, $[Mo(CO)_2(CN)_3H^+]$}, 204 {53, $[Mo(CO)(CN)_3H^+]$}, 176 {30, $[Mo(CN)_3H^+]$}; ^{1}H NMR (298 K, CD_2Cl_2, δ, p.p.m.): 1.3–1.5 (CH_3); ^{13}C NMR (298 K, CD_2Cl_2, δ, p.p.m.): 31.0 (CH_3), 57.2 (C), 158.3 (CN), 215.0 (CO).

Crystal data

$[Mo(C_5H_9N)_3(CO)_3]$
M_r = 429.37
Monoclinic, $P2_1/n$
a = 9.5070 (3) Å
b = 15.6817 (7) Å
c = 15.3422 (6) Å
β = 103.149 (3)°
V = 2227.34 (15) Å^3
Z = 4

D_x = 1.280 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3828 reflections
θ = 1.9–27.4°
μ = 0.61 mm^{-1}
T = 183 (2) K
Cube, light yellow
0.03 × 0.03 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
8441 measured reflections
5027 independent reflections
3828 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.033
$\theta_{\rm max}$ = 27.4°
$h = -12 \rightarrow 12$
$k = -20 \rightarrow 18$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.117$
S = 1.10
5027 reflections
226 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 4.4505P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.59 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.06 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo—C16	1.992 (5)	O3—C18	1.155 (5)
Mo—C17	1.991 (4)	C1—N1	1.159 (5)
Mo—C18	1.994 (4)	C6—N2	1.146 (5)
Mo—C1	2.140 (4)	C11—N3	1.162 (5)
Mo—C11	2.148 (4)	N1—C2	1.454 (5)
Mo—C6	2.156 (4)	N2—C7	1.471 (5)
O1—C16	1.157 (5)	N3—C12	1.464 (5)
O2—C17	1.158 (5)		
C16—Mo—C17	87.39 (16)	C18—Mo—C6	91.97 (15)
C16—Mo—C18	88.80 (19)	C1—Mo—C6	83.09 (15)
C17—Mo—C18	92.91 (16)	C11—Mo—C6	85.38 (15)
C16—Mo—C1	90.45 (19)	N1—C1—Mo	175.3 (4)
C17—Mo—C1	92.12 (16)	N2—C6—Mo	173.4 (4)
C18—Mo—C1	174.88 (15)	N3—C11—Mo	175.8 (4)
C16—Mo—C11	177.20 (18)	C1—N1—C2	173.9 (5)
C17—Mo—C11	91.16 (15)	C6—N2—C7	171.0 (4)
C18—Mo—C11	88.87 (17)	C11—N3—C12	169.3 (4)
C1—Mo—C11	92.01 (17)	O1—C16—Mo	175.7 (4)
C16—Mo—C6	96.26 (16)	O2—C17—Mo	179.0 (4)
C17—Mo—C6	173.97 (17)	O3—C18—Mo	179.2 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C3—H3*A*⋯O1^{i}	0.98	2.60	3.345 (8)	133
C15—H15*B*⋯O3^{ii}	0.98	2.81	3.701 (9)	151
C9—H9*B*⋯O3^{iii}	0.98	2.82	3.611 (9)	139
C8—H8*A*⋯O1^{iv}	0.98	2.85	3.754 (10)	154

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y, -z+2$; (iv) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

All H atoms were placed in calculated positions (C—H = 0.98 Å) and were refined as riding with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C). The deepest hole in the final difference map is located 0.80 Å from Mo.

Data collection: *COLLECT*, Nonius 1998; cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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