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Tetraethylammonium dicarbonyl(dicyanomethylene)[tris(3,5-dimethyl-1-pyrazolyl)hydroborato]molybdenum(0)

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Crystals of $[(C_2H_5)_4N][(Tp^{Me2})(CO)_2Mo{=}C(CN)_2]$ [Tp^{Me2} is (3,5-dimethyl-1-pyrazolyl)hydroborato], (1), the first example of an air-stable carbene complex bearing a metal-centred negative charge, contain discrete anions and cations separated by typical van der Waals distances. The coordination of the anion in (1) is octahedral about Mo, with the Tp^{Me2} ligand occupying three adjacent coordination sites and the two carbonyl ligands and the dicyanocarbene ligand occupying the remaining three sites. The anion contains an approximate mirror plane, which passes through the plane of the dicyanocarbene ligand, the Mo atom and one of the Tp^{Me2} rings.

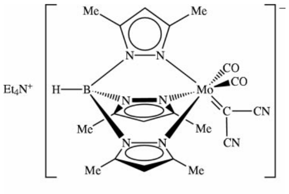
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
R factor = 0.038
wR factor = 0.091
Data-to-parameter ratio = 17.8

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

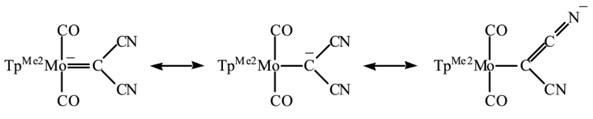
Comment

There have been few literature reports of carbene complexes with a metal-centred negative charge and most of those for which convincing evidence is available have been detected in solution only (Wang & Angelici, 1988; Adams *et al.*, 1995; Enriquez *et al.*, 2001). Prior to the present work, only four such complexes had been isolated in the solid state and all are air-sensitive (Lee & Cooper, 1990; Schrock *et al.*, 1996; Legzdins & Sayers, 1997). Recently, we have developed a synthetic route to the first entirely air-stable complexes of this type, of which the title complex, $[(C_2H_5)_4N][Tp^{Me2}(CO)_2Mo{=}C(CN)_2]$, (1), is a representative example (Lalor & O'Neill, 2003).



(1)

Crystals of (1) contain discrete anions (see Fig. 1) and cations separated by typical van der Waals distances. The structural details of the $[(C_2H_5)_4N]^+$ cation and the Tp^{Me2} ligand are unexceptional.



(1*a*) (1*b*) (1*c*)

The coordination of the anion (1*a*) in (1) is octahedral about Mo1, with the Tp^{Me2} ligand occupying three adjacent

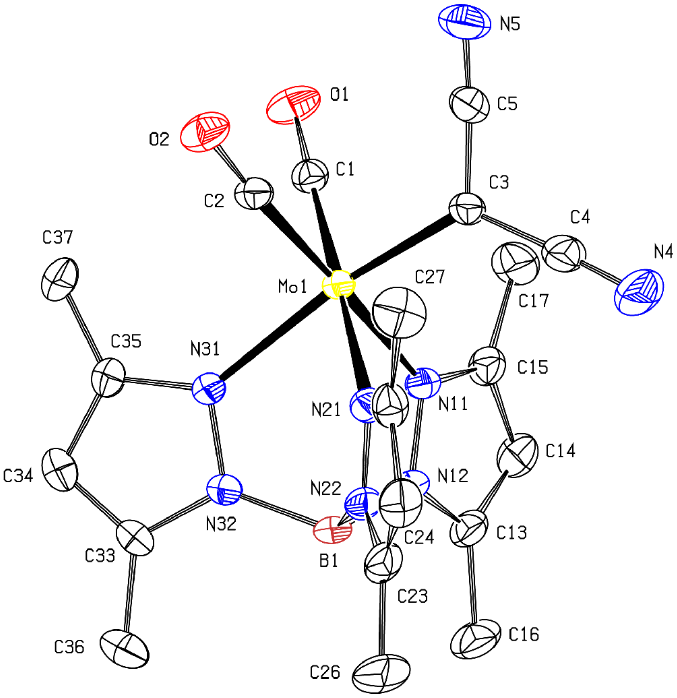


Figure 1
A view of the anion in (1), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

coordination sites and the two carbonyl ligands and the dicyanocarbene ligand occupying the remaining three sites. The anion contains an approximate mirror plane, which passes through the plane of the dicyanocarbene ligand, the Mo1 atom and the pyrazolyl ring atoms N31, N32 and C33–C35. The orientation of the carbene ligand within the mirror plane agrees with the predictions of MO calculations on related systems (Schilling *et al.*, 1979; Kostic & Fenske, 1982),

The Mo=C (Mo1—C3) bond distance of 2.018 (3) Å lies towards the short end of the range 1.95–2.15 Å which is accepted for typical Mo=C double bonds (Curtis *et al.*, 1986). However, it is still considerably longer than the Mo=C distances of 1.96 and 1.94 Å found in the related Mo^0 complex $[Mo(=CHSiMe_3)(NO)(CH_2SiMe_3)(\eta\text{-}C_5H_5)]^-$ (Legzdins & Sayers, 1997), which crystallizes as a solvated cation-bridged dimer in which the two carbene ligands are not identical. We conclude that the metal–carbene bond in complex (1) has similar multiple-bond character to that in conventional Fischer carbene complexes of low-valent mid-transition metals, but that the metal–carbene bond is polarized in the opposite direction to normal, *i.e.* that *via* resonance forms (1*b*) and (1*c*), facilitated by the electron-withdrawing cyano substituents, the carbene ligand is electron-rich rather than electron-poor.

Unfavourable steric interactions of the carbene cyano groups with the adjacent pyrazolyl 3-Me groups make rotation of the dicyanocarbene ligand about the molybdenum–carbene (Mo1—C3) bond impossible, hence the inequivalence of the cyano groups observed in the ^{13}C NMR spectrum. Both the C3—C4 and C3—C5 bond lengths of the $C(CN)_2$ fragment, 1.394 (5) and 1.379 (4) Å, respectively, are markedly shortened compared with the norm for $Csp^2—Csp$ single bonds (1.431 Å; Orpen *et al.*, 1994). There can be little doubt that there is a significant π-component to these bonds, as would be anticipated if resonance form (1*c*), in which the negative charge is delocalized on to the cyano N atoms, makes an important contribution to the ground state.

Experimental

Compound (1) was prepared as described elsewhere (Lalor & O'Neill, 2003). Crystals were grown by vapour-phase diffusion of ether into a concentrated solution of (1) in dichloromethane.

Crystal data

$(C_8H_{20}N)[Mo(C_{15}H_{22}BN_6)(C_3N_2)(CO)_2]$
$M_r = 643.46$
Monoclinic, $C2/c$
$a = 40.153$ (3) Å
$b = 8.113$ (2) Å
$c = 20.161$ (3) Å
$\beta = 109.989$ (8)°
$V = 6172.0$ (18) Å^3
$Z = 8$

$D_x = 1.385$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.6$–15.2°
$\mu = 0.47$ mm^{-1}
$T = 294$ (1) K
Plate, green
0.40 × 0.28 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.891$, $T_{max} = 0.963$
6846 measured reflections
6761 independent reflections
4379 reflections with $I > 2\sigma(I)$

$R_{int} = 0.013$
$\theta_{max} = 27.0°$
$h = -50 \rightarrow 48$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 25$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.091$
$S = 0.96$
6761 reflections
380 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Mo1—C1	1.874 (3)	O1—C1	1.113 (3)
Mo1—C2	1.900 (3)	O2—C2	1.124 (4)
Mo1—C3	2.018 (3)	N4—C4	1.104 (5)
Mo1—N11	2.201 (3)	N5—C5	1.093 (4)
Mo1—N21	2.193 (2)	C3—C5	1.379 (4)
Mo1—N31	2.215 (2)	C3—C4	1.394 (5)

H atoms were visible in difference maps and were allowed for as riding atoms (C—H = 0.93–0.97 Å and B—H = 0.98 Å). The U_{iso} values for the methyl H atoms were set at 1.5 times the U_{eq} values of the C atom on which they were riding; for all other H atoms, the U_{iso} values were set at 1.2 times the U_{eq} value of the atom on which they were riding.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC Software*; data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989); program(s) used to solve structure: *NRCVAX*96 *via* Patterson heavy-atom method; program(s) used to refine structure: *SHELXL*97 (Sheldrick,

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1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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