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Mo^{IV} Chloromethylidyne Complexes: Structure of Dicarbonyl(chloromethylidyne)-[hydrotris(3,4,5-trimethyl-1-pyrazolyl)borato]molybdenum(IV)

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Abstract. $[Mo(CCl)\{B(C_6H_9N_2)_3H\}(CO)_2]$, M_r = 538·7, orthorhombic, $Pbn2_1$, $a = 9{\cdot}179\,(2)$, $b = 15{\cdot}899\,(3)$, $c = 17{\cdot}778\,(2)$ Å, $V = 2595\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}38$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 6{\cdot}2$ cm^{-1}, $F(000) = 1104$, $T = 291$ K, $R = 0{\cdot}028$ for 2101 reflections with $I > 3\sigma(I)$. The Mo atom has octahedral coordination, with principal dimensions Mo—C(chloromethylidyne) 1·798 (5), C—Cl 1·680 (6), Mo—C(carbonyl) 1·982 (6), 1·974 (6), Mo—N(*trans* to chloromethylidyne ligand) 2·268 (4), Mo—N(*trans* to CO) 2·224 (5), 2·234 (4) Å, Mo—C—Cl 165·7 (4)°.

Introduction. We have described earlier (Desmond, Lalor, Ferguson & Parvez, 1983) a synthetic route to complexes containing the previously unknown and synthetically useful halomethylidyne (halocarbyne) ligands. Our crystal structure analysis of a representative example, dicarbonyl(chloromethylidyne)[tetrakis(1-pyrazolyl)borato]molybdenum(IV), $[Mo(CCl)\{B(C_3H_3N_2)_4\}(CO)_2]$ ($C_3H_3N_2 \equiv$ 1-pyrazolyl), (I), revealed an Mo—C(methylidyne) bond length [mean 1·894 (10) Å for three crystallographically independent molecules] which was anomalously long when compared with related complexes containing formal Group 6*b* metal-to-carbon triple bonds, *e.g.* 1·801 (4) Å in $[Mo(CSC_6H_4NO_2\text{-}p)\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_2]$ ($3,5\text{-}Me_2C_3HN_2 \equiv$ 3,5-dimethyl-1-pyrazolyl), (II) (Desmond, Lalor, Ferguson & Parvez, 1984) and 1·807 Å in $[WCSC_6H_5)(\eta\text{-}C_5H_5)(CO)_2]$ (III) (Greaves, Angelici, Helland, Klima & Jacobson, 1979). The title complex (IV) was prepared and structurally characterized to obtain further information on the metal–carbon separation characteristic of complexed halomethylidyne ligands.

Experimental. Complex (IV) was prepared in 63% yield by oxidizing $[Et_4N][Mo\{HB(3,4,5\text{-}Me_3C_3N_2)_3\}(CO)_3]$ ($3,4,5\text{-}Me_3C_3N_2 \equiv$ 3,4,5-trimethyl-1-pyrazolyl) with $(p\text{-}Me_2NC_6H_4N_2)BF_4$ in CH_2Cl_2 (Desmond, Lalor, Ferguson & Parvez, 1983). Slow cooling of a concentrated solution of (IV) in hot acetonitrile gave yellow crystals suitable for crystallographic analysis.

Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $10 < \theta < 15°$. Crystal dimensions 0·30 × 0·35 × 0·40 mm; intensities of reflections with $2 < 2\theta < 54°$ measured; h 0–11, k 0–20, l 0–22; ω–2θ scans; ω scan width $(0{\cdot}60 + 0{\cdot}35\tan\theta)°$, graphite-monochromatized Mo $K\alpha$ radiation. Intensities of three reflections were measured every 2 h and showed no evidence of crystal decay. 2913 unique reflections were measured and 2096 with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement. Data were corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0·856, 0·802; Gaussian integration, grid 8 × 10 × 10). The systematic absences ($h0l$, $h + l = 2n + 1$; $0kl$, $k = 2n + 1$) allow the space group to be either $Pbn2_1$ (non-standard setting of $Pna2_1$, No. 33) or $Pbnm$ (non-standard setting of $Pnma$, No. 62). The structure was solved and refined in $Pbn2_1$ (equivalent positions x, y, z; $-x, -y, 0{\cdot}5 + z$; $0{\cdot}5 + x, 0{\cdot}5 - y, 0{\cdot}5 + z$; $0{\cdot}5 - x, 0{\cdot}5 + y, z$). The coordinates of the Mo atom were derived from the three-dimensional Patterson function. The Mo z coordinate was set at 0·25 to define the origin and with the Mo x coordinate also close to 0·25, the first heavy-atom-phased electron-density distribution was complicated somewhat by it having pseudo *mm* symmetry. By careful peak selection and subsequent rounds of structure-factor and difference-Fourier calculations, all non-H atoms were located unambiguously. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of the H atoms; in the final

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Table 1. *Fractional coordinates and mean isotropic thermal parameters*

$U_{eq} = 0{\cdot}33(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
Mo	0·24349 (4)	0·15708 (2)	0·25*	0·042 (1)
Cl	0·3209 (3)	0·0276 (1)	0·0994 (1)	0·099 (1)
O(1)	−0·0373 (6)	0·1535 (3)	0·1495 (3)	0·082 (3)
O(2)	0·3679 (6)	0·2892 (3)	0·1355 (3)	0·082 (3)
C(1)	0·0623 (7)	0·1565 (4)	0·1894 (3)	0·054 (3)
C(2)	0·3210 (7)	0·2424 (4)	0·1800 (3)	0·053 (3)
C(3)	0·2984 (7)	0·0829 (3)	0·1791 (3)	0·049 (3)
N(11)	0·1537 (4)	0·2582 (2)	0·3271 (2)	0·043 (2)
N(12)	0·1773 (4)	0·2524 (2)	0·4024 (2)	0·039 (2)
C(13)	0·1238 (6)	0·3201 (3)	0·4376 (3)	0·045 (3)
C(14)	0·0616 (6)	0·3718 (3)	0·3843 (3)	0·049 (3)
C(15)	0·0823 (6)	0·3318 (3)	0·3165 (3)	0·051 (3)
C(16)	0·1326 (8)	0·3334 (4)	0·5216 (4)	0·071 (4)
C(17)	−0·0131 (8)	0·4556 (3)	0·3956 (4)	0·080 (5)
C(18)	0·0343 (8)	0·3600 (4)	0·2399 (4)	0·082 (5)
N(21)	0·4332 (5)	0·1654 (3)	0·3274 (3)	0·049 (3)
N(22)	0·4118 (4)	0·1711 (2)	0·4035 (3)	0·056 (2)
C(23)	0·5426 (6)	0·1725 (3)	0·4388 (3)	0·050 (3)
C(24)	0·6475 (6)	0·1694 (3)	0·3850 (4)	0·058 (3)
C(25)	0·5769 (6)	0·1636 (3)	0·3169 (4)	0·059 (3)
C(26)	0·5561 (8)	0·1785 (4)	0·5221 (4)	0·080 (5)
C(27)	0·8125 (7)	0·1683 (5)	0·3984 (6)	0·095 (6)
C(28)	0·6411 (7)	0·1567 (5)	0·2388 (5)	0·095 (5)
N(31)	0·1594 (4)	0·0728 (2)	0·3407 (3)	0·046 (2)
N(32)	0·1736 (5)	0·0943 (2)	0·4142 (2)	0·042 (2)
C(33)	0·1128 (5)	0·0349 (3)	0·4586 (3)	0·050 (3)
C(34)	0·0561 (6)	−0·0260 (3)	0·4124 (4)	0·055 (3)
C(35)	0·0877 (5)	−0·0014 (3)	0·3397 (3)	0·052 (3)
C(36)	0·1095 (8)	0·0416 (4)	0·5415 (4)	0·079 (4)
C(37)	−0·0248 (9)	−0·1049 (4)	0·4359 (5)	0·086 (5)
C(38)	0·0510 (8)	−0.0451 (4)	0·2682 (4)	0·083 (5)
B	0·2580 (6)	0·1755 (3)	0·4359 (3)	0·042 (3)

*The z coordinate of Mo was fixed at 0·25 to define the origin.

rounds of calculations the H atoms were positioned on geometrical grounds (B—H 1·08, C—H 0·95 Å) and included (as riding atoms) in the structure-factor calculations. The final cycle of refinement included 370 variable parameters, $R = 0{\cdot}028$, $wR = 0{\cdot}031$, $w = 1/[\sigma^2(F_o) + 0{\cdot}003(F_o)^2]$. Max. shift/e.s.d. = 0·07; density in final difference map +0·56 to −0·33 e Å^{-3} adjacent to Mo atoms; no chemically significant features. Space group $Pbn2_1$ is polar and refinement with the direction of the polar axis reversed, converged with higher R values ($R = 0{\cdot}035$, $wR = 0{\cdot}040$). Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). All calculations used the *SHELX* program system (Sheldrick, 1976). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2 respectively.* Fig. 1, prepared using *ORTEP*II (Johnson, 1976), shows the molecule (IV) and our numbering scheme.

Discussion. Our analysis confirms that complex (IV) has the anticipated octahedral geometry about molybdenum. There was no evidence (from electron-

Table 2. *Molecular dimensions* (Å *and* °) *for* HB(Me$_3$pz)$_3$Mo(CO)$_2$(CCl)

Mo—C(1)	1·982 (6)	N(21)—N(22)	1·369 (6)
Mo—C(2)	1·974 (6)	N(21)—C(25)	1·333 (6)
Mo—C(3)	1·798 (5)	N(22)—C(23)	1·354 (6)
Mo—N(11)	2·268 (4)	C(23)—C(24)	1·358 (9)
Mo—N(21)	2·224 (5)	C(23)—C(26)	1·490 (8)
Mo—N(31)	2·234 (4)	C(24)—C(25)	1·377 (9)
C(1)—O(1)	1·158 (7)	C(24)—C(27)	1·533 (8)
C(2)—O(2)	1·168 (7)	C(25)—C(28)	1·512 (9)
C(3)—Cl	1·680 (6)	N(31)—N(32)	1·357 (6)
B—N(12)	1·549 (6)	N(31)—C(35)	1·351 (6)
B—N(22)	1·527 (7)	N(32)—C(33)	1·351 (6)
B—N(32)	1·553 (7)	C(33)—C(34)	1·372 (8)
N(11)—N(12)	1·359 (5)	C(33)—C(36)	1·478 (8)
N(11)—C(19)	1·354 (6)	C(34)—C(35)	1·382 (8)
N(12)—C(13)	1·338 (6)	C(34)—C(37)	1·516 (7)
C(13)—C(14)	1·377 (8)	C(35)—C(38)	1·487 (8)
C(13)—C(16)	1·511 (7)		
C(14)—C(15)	1·376 (8)		
C(14)—C(17)	1·512 (6)		
C(15)—C(18)	1·500 (8)		

C(1)—Mo—C(2)	87·9 (3)	Mo—N(21)—N(22)	120·2 (3)
C(1)—Mo—C(3)	81·4 (3)	Mo—N(21)—C(25)	133·4 (4)
C(1)—Mo—N(11)	91·5 (2)	N(22)—N(21)—C(25)	106·4 (5)
C(1)—Mo—N(21)	173·8 (2)	N(21)—N(22)—C(23)	109·4 (4)
C(1)—Mo—N(31)	95·7 (2)	N(21)—N(22)—B	120·5 (4)
C(2)—Mo—C(3)	84·7 (3)	C(23)—N(22)—B	130·1 (5)
C(2)—Mo—N(11)	91·4 (2)	N(22)—C(23)—C(24)	107·6 (5)
C(2)—Mo—N(21)	93·9 (2)	N(22)—C(23)—C(26)	122·4 (5)
C(2)—Mo—N(31)	172·7 (2)	C(24)—C(23)—C(26)	130·0 (4)
C(3)—Mo—N(11)	172·1 (2)	C(23)—C(24)—C(25)	106·7 (4)
C(3)—Mo—N(21)	104·7 (2)	C(23)—C(24)—C(27)	126·3 (6)
C(3)—Mo—N(31)	102·1 (2)	C(25)—C(24)—C(27)	126·9 (6)
N(11)—Mo—N(21)	82·4 (2)	N(21)—C(25)—C(24)	110·0 (5)
N(11)—Mo—N(31)	82·1 (1)	N(21)—C(25)—C(28)	121·1 (6)
N(21)—Mo—N(31)	81·9 (2)	C(24)—C(25)—C(28)	129·0 (5)
Mo—C(1)—O(1)	174·7 (5)	Mo—N(31)—N(32)	120·7 (3)
Mo—C(2)—O(2)	176·0 (5)	Mo—N(31)—C(35)	133·0 (4)
Mo—C(3)—Cl	165·7 (4)	N(32)—N(31)—C(35)	106·2 (4)
Mo—N(11)—N(12)	119·3 (3)	N(31)—N(32)—C(33)	110·2 (4)
Mo—N(11)—C(15)	134·8 (4)	N(31)—N(32)—B	119·7 (4)
N(12)—N(11)—C(15)	105·8 (4)	C(33)—N(32)—B	130·0 (4)
N(11)—N(12)—C(13)	110·3 (4)	N(32)—C(33)—C(34)	107·6 (5)
N(11)—N(12)—B	120·6 (4)	N(32)—C(33)—C(36)	122·7 (5)
C(13)—N(12)—B	129·1 (4)	C(34)—C(33)—C(36)	129·7 (5)
N(12)—C(13)—C(14)	108·1 (4)	C(33)—C(34)—C(35)	106·2 (4)
N(12)—C(13)—C(16)	123·7 (5)	C(33)—C(34)—C(37)	127·3 (6)
C(14)—C(13)—C(16)	128·2 (5)	C(35)—C(34)—C(37)	126·5 (6)
C(13)—C(14)—C(15)	105·6 (4)	N(31)—C(35)—C(34)	109·7 (5)
C(13)—C(14)—C(17)	128·5 (5)	N(31)—C(35)—C(38)	122·0 (5)
C(15)—C(14)—C(17)	125·9 (5)	C(34)—C(35)—C(38)	128·3 (5)
N(11)—C(15)—C(14)	110·1 (5)	N(12)—B—N(22)	109·5 (4)
N(11)—C(15)—C(18)	121·8 (5)	N(12)—B—N(32)	108·8 (4)
C(14)—C(15)—C(18)	128·1 (5)	N(22)—B—N(32)	109·2 (4)

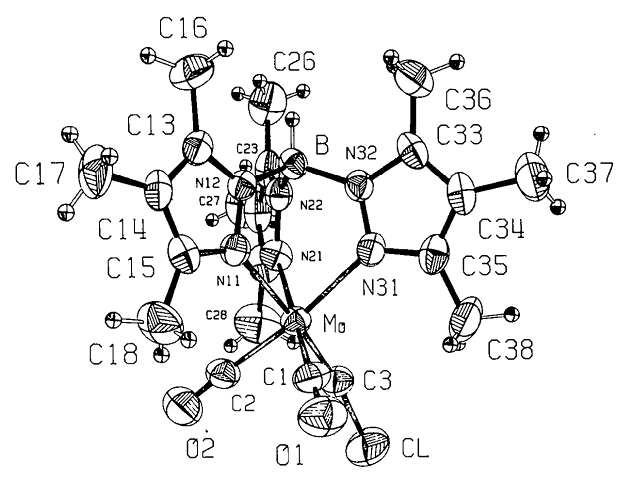

Fig. 1. A view of molecule (IV). Ellipsoids are at the 50% probability level except for H atoms (spheres of arbitrary size).

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52196 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

density peak heights or thermal parameters) for any mutual disorder of C—Cl or C—O groups. The bond lengths and bond angles within the hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate ligand resemble closely those of the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand in complex (II) and show no unexpected features. The arrangement of the two carbonyl ligands [mean Mo—C 1·978 (5), mean C—O 1·163 (7) Å, mean Mo—C—O 175·3 (5), C(1)—Mo—C(2) 87·9 (3)°] is very similar to that found in complex (II) [mean Mo—C 1·992 (5), mean C—O 1·150 (6) Å, mean Mo—C—O 177·7 (5), C(1)—Mo—(2) 89·0 (2)°].

The chloromethylidyne ligand is bonded to molybdenum with Mo—C(3) 1·798 (5) and C(3)—Cl 1·680 (6) Å. The molybdenum–C(methylidyne) separation is thus essentially identical to that in the η^1-organothiomethylidyne complex (II). The much longer Mo—C(methylidyne) bond reported for (I) may be an artefact of some residual disordering of carbonyl and chloromethylidyne ligands in the crystal of that complex. The Cl—C(methylidyne) separation in (IV), 1·680 (6) Å, is close to the value (1·69 Å) calculated from the sum of the covalent radii of *sp*-carbon and chlorine (Cotton & Wilkinson, 1976). Whereas the η^1-organothiomethylidyne ligands in complexes (II) and (III) bond to the metal in an essentially linear fashion [*M*—C—S 179·5 (2) and 174·2 (6)° respectively] the Mo—C(3)—Cl fragment in (IV) is distinctly angular [165·7 (4)°]; this non-linearity probably arises from the effects of crystal packing forces. Thus, intermolecular distance calculations show that with the non-linear model, the Cl atom makes two contacts with neighbouring molecules Cl···C(18) (at $\frac{1}{2}-x,\ -\frac{1}{2}+y,\ z$) 3·887 (6) and Cl···C(26) (at $1-x,\ -y,\ -\frac{1}{2}+z$) 3·728 (6) Å; these distances are in accord with the van der Waals radii sum for Cl and C(methyl) of approximately 3·8 Å. However, when the Cl atom is positioned geometrically so that the Mo—C—Cl bond is linear, the resulting Cl···C(18) and Cl···C(26) intermolecular contacts are reduced to 3·493 (6) and 3·501 (6) Å respectively, significantly less than the sum of the van der Waals radii.

The chloromethylidyne ligand in (IV) exerts a marked *trans* effect (the Mo—N bond *trans* to the ligand being *ca* 0·039 Å longer than those *trans* to CO) but the effect is less pronounced than that in (II) where the *trans* bond-lengthening is of the order of 0·074 Å.

In the crystal of (IV) the molecules are separated by normal van der Waals distances and show no unusual intermolecular contacts.

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Structure of Caesium Picrate

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Abstract. $\mathrm{Cs[C_6H_2N_3O_7]}$, $M_r = 361{\cdot}00$, monoclinic, $P2_1/c$, $a = 10{\cdot}811\,(1)$, $b = 4{\cdot}7011\,(4)$, $c = 19{\cdot}404\,(1)$ Å, $\beta = 101{\cdot}41\,(1)°$, $V = 966{\cdot}7\,(1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}48$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 38{\cdot}3$ cm^{-1}, $F(000) = 680$, $T = 295$ K, $R = 0{\cdot}025$ for 1831 observed reflections with $I > 2{\cdot}5\sigma(I)$. In the

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