3.545 Å and angle N–H···Cl2 = 178°, and these values compare favorably with previously reported NH to Cl hydrogen bonds.[49,52,53] The severely acute H···Cl–Sn angle (65°) is not unusual when halides are involved, for example, in the case of $Co(en)_3^{3+}$ where a chloride ion is hydrogen bonded to three of the ethylenediamine nitrogens of a trigonal face.[53]

The packing of the molecules is shown in Figure 2, in which it can be seen that there are no unusually close intermolecular contacts. The highly electronegative chlorine groups are quite well segregated from one another, as the molecules align themselves in chains parallel to the *b* axis. The perfectly staggered orientations of the disordered benzene ring are also shown.

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Registry No. 1b, 66141-46-6.

Supplementary Material Available: Tables of least-squares planes and out-of-plane distances (Table V) and torsion angles (Table VI) and a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Dealkylation and Reductive Coupling of *tert*-Butyl Isocyanide Ligands in Heptakis(*tert*-butyl isocyanide)molybdenum(II). Structure of Seven-Coordinate Cyanotetrakis(*tert*-butyl isocyanide)((*N*,*N*′-di-*tert*-butyldiamino)acetylene)molybdenum(II) Tetraphenylborate[1,2]

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The reaction of heptacoordinate $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$ with zinc in refluxing ethanol produces the $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)]^+$ cation in 27% yield. This new complex contains the coupled ligand product (*N*,*N*′-di-*tert*-butyldiamino)acetylene and coordinated cyanide ion that arises from dealkylation of *tert*-butyl isocyanide. An X-ray crystallographic study of the tetraphenylborate salt of cyanotetrakis(*tert*-butyl isocyanide)((*N*,*N*′-di-*tert*-butyldiamino)acetylene)molybdenum(II) has been carried out. The compound crystallizes in the orthorhombic space group *Pccn* with $Z = 4$. The unit cell dimensions are $a = 16.349$ (3) Å, $b = 19.724$ (3) Å, and $c = 17.752$ (4) Å. The molybdenum and cyanide C and N atoms lie on a crystallographically required twofold axis that passes through the midpoint of the acetylenic C–C bond. Unlike other $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)X]^+$ cations, where X = Br or I, the present structure more closely resembles pentagonal-bipyramidal rather than capped trigonal-prismatic idealized geometry. The two axial *tert*-butyl isocyanide ligands have Mo–C bond lengths of 2.121 (5) Å, and the corresponding C–Mo–C angle is 175.7 (3)°. The equatorial Mo–C bond lengths are 2.204 (6) Å for the cyanide ion, 2.143 (5) Å for the *tert*-butyl isocyanide groups, and 2.053 (4) Å for the bidentate coupled ligand. Other features of the coupled ligand geometry include a rather long acetylenic C–C bond of 1.402 (8) Å, C–N bond distances of 1.312 (5) and 1.472 (6) Å for the alkynyl and alkyl fragments, respectively, and respective C–C–N and C–N–C angles of 127.9 (3) and 128.5 (4)°. The HNCCNH unit is planar to within ±0.04 Å. Distortions of the cation are discussed in terms of hydrogen bonding and intramolecular steric interactions. Its molecular geometry and those of the other $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)X]^+$ cations are analyzed according to Kepert's ligand–ligand repulsion model for seven-coordinate stereochemistries.

Introduction

The reaction of the seven-coordinate $[Mo(CN\text{-}t\text{-}Bu)_6X]^+$ cations, X = Cl, Br, I, CN, with zinc in tetrahydrofuran produces $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)X]^+$ complexes in which two adjacent ligands have reductively coupled to form the coordinated (*N*,*N*′-di-*tert*-butyldiamino)acetylene molecule.[3,4] An attempt was made to extend this chemistry to the parent cation,[5] $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$. Surprisingly, the product was found to be $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)]^+$, in which not only reductive coupling but also dealkylation of one of the *tert*-butyl isocyanide ligands had occurred. The latter reaction, which has been independently verified in thermal decomposition studies of $[M(CN\text{-}t\text{-}Bu)_7]^{2+}$ (M = Mo, W) cations,[6] serves as a striking illustration of the propensity of metal-coordinated isocyanides, especially *tert*-butyl derivatives, to lose carbonium ions with concomitant formation of the metal–cyanide linkage.[7] Here we describe the synthesis and the crystal and molecular structure of the new complex, isolated as the tetraphenylborate salt. The results also contribute to the current information pool on the stereochemistry of seven-coordinate transition-metal complexes, a subject of considerable theoretical interest.[8,9] The

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stereochemistry of this new complex has been analyzed in terms of the ligand–ligand repulsion energy calculations of Kepert.[9]

Experimental Section

Preparation of $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)]^+$ Salts. A mixture of 977 mg (1 mmol) of $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$[5,6] and 788 mg (12 mmol) of zinc dust in 50 mL of 95% ethanol was heated at reflux for 5 days. The warm solution was filtered and concentrated to 25 mL. Water and ethanol (final volume ≈ 100 mL) were added to bring the boiling filtrate to the cloud point. The solution was cooled to room temperature and allowed to stand overnight. A 0.211-g (27%) crop of purple microcrystalline solid was collected by filtration.

Proton NMR spectra: in $CDCl_3$, δ 1.51 (s, 36 protons), 1.55 (s, 18 protons), 8.28 (br s, ~2 protons); in $C_6D_6/Me_2SO\text{-}d_6$, δ 1.19 (s):1.52 (s), 2:1, relative intensity.

^{13}C NMR spectra: in CD_2Cl_2 with added $Cr(acac)_3$,[10] δ 29.79, 57.52, 142.71, 158.42, 200.83 (see ref 3a for assignments; the 142.71-ppm resonance arises from the cyanide carbon atom).

Anal. Calcd for $C_{31}H_{56}N_7MoPF_6$: C, 48.50; H, 7.35; N, 12.77; Mo, 12.50; P, 4.03. Found: C, 47.09; H, 7.28; N, 12.21; Mo, 11.94; P, 4.35.

The tetraphenylborate salt was obtained by applying 240 mg of the hexafluorophosphate salt, dissolved in 325 mL of methanol, to a 2.5 × 11 cm column of MP50 cation-exchange resin (100–200 mesh, Na^+ form). Elution of the column with 75 mL of $Na[B(C_6H_5)_4]$, 0.1 g/L in methanol, gave a purple band that was diluted with water and extracted into ~125 mL of CH_2Cl_2. The organic phase was isolated, washed three times with water, dried over Na_2SO_4, and evaporated in vacuo to yield 165 mg of purple product. IR (KBr pellet): 3235 (w), 2975 (m), 2925 (w), 2180 (sh), 2135 (s), 1580 (m), 1475 (w), 1455 (w), 1430 (w), 1370 (m), 1262 (m), 1235 (w), 1200 (m), 1100 (m), 1035 (w), 800 (m), 735 (m), 600 (m) cm^{-1}. X-ray quality crystals were obtained by slow evaporation of an ethanolic solution of the tetraphenylborate salt.

Collection and Reduction of X-ray Data. The purple crystal used for the diffraction study had approximate dimensions of 0.4 mm × 0.4 mm × 0.16 mm. Its quality was checked, on the diffractometer, by taking open-counter ω scans of several strong low-angle reflections and was judged to be acceptable. Further details of the data collection and reduction appear in Table I and ref 11.

Determination and Refinement of the Structure. Study on the diffractometer suggested that the crystal belonged to the orthorhombic system, with systematic absences $0kl$ when $k \neq 2n$, $h0l$ when $h + l \neq 2n$, and $hk0$ when $k \neq 2n$. These conditions define the space group to be *Pbnb* (D_{2h}^{10}; No. 56, in a nonstandard setting).[12] The structure was solved with use of Patterson and Fourier maps. The transformation matrix (100, $00\bar{1}$, 010), applied to the *hkl* indices and cell constants, converted the space group to the standard setting *Pccn* to which all subsequent results and discussion are referred. Neutral atom scattering factors and anomalous dispersion corrections, for the nonhydrogen atoms, were obtained from ref 13. Scattering factors for the hydrogen atoms were those of Stewart et al.[14] All nonhydrogen atoms were refined anisotropically. There was no evidence for disorder in any part of the structure. Methyl hydrogen atoms were initially set up and refined as rigid groups (C–H = 0.95 Å; H–C–H = 109.5°), pivoting on their respective carbon atoms, with a common isotropic temperature factor that converged toward $U = 0.145$ Å^2. In the final cycles of refinement, these hydrogen atoms were included as invariants with all parameters fixed at the values obtained in the last cycle of rigid group refinement. Hydrogen atoms on the phenyl rings of the anion were placed in calculated positions (C–H = 0.95 Å) and were constrained to "ride" on the carbon atoms to which they are bound. A common isotropic temperature factor for these atoms converged at $U = 0.096$ (7) Å^2. The hydrogen atom, attached to N(41), was located in a difference Fourier map toward the final stages of refinement and has been successfully refined as H(41).

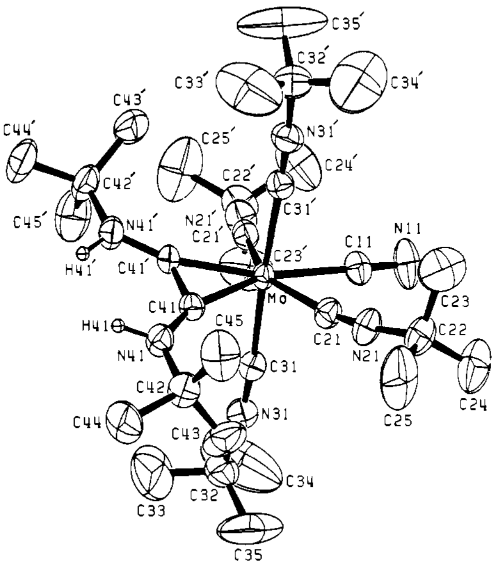

Figure 1. Geometry of the $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)]^+$ cation showing the atom labeling scheme. Thermal ellipsoids are depicted at the 40% probability level. Hydrogen atoms have been omitted for clarity. Primed atoms are related to those unprimed by a crystallographically required twofold axis through Mo, C(11), and N(11).

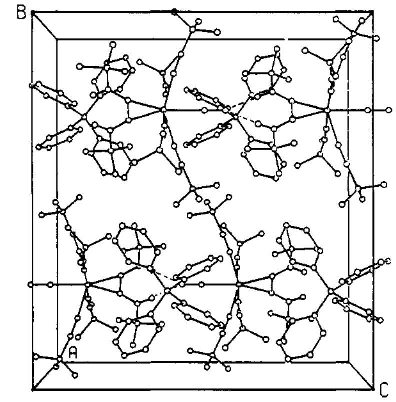

Figure 2. Unit cell packing diagram for $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)][B(C_6H_5)_4]$. Dashed lines represent hydrogen bonding interactions.

Full-matrix least-squares refinement of 297 variables, using SHELX-76,[15] converged to final residual indices[16] of $R_1 = 0.052$ and $R_2 = 0.057$. The function minimized in the least-squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.5193/[\sigma^2(F_o) + 0.000625F_o^2]$. In the final cycle of refinement, no parameter shifted by more than 0.007 of its estimated standard deviation. The largest peaks on a final difference Fourier map were 0.96, 0.88, and 0.74 e Å^{-3} located 1.00–1.16 Å from the Mo atom. All remaining peaks were <0.43 e Å^{-3}. The average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, $(\sin\theta)/\lambda$, $|h|$, $|k|$, or $|l|$ showed good consistency, and the weighting scheme was considered to be satisfactory.

Results

Final nonhydrogen atom [except for H(41)] positional and thermal parameters, together with their estimated standard deviations, appear in Table II. Interatomic distances and

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(16) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table I. Experimental Details of the X-ray Diffraction Study of $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)][B(C_6H_5)_4]$

(A) Crystal Parameters[a] at 26 °C

a = 16.349 (3) Å
b = 19.724 (3) Å
c = 17.752 (4) Å
V = 5724 $Å^3$
mol wt 942.0
space group = *Pccn*
Z = 4
ρ(calcd) = 1.093 g cm^{-3}
ρ(obsd)[b] = 1.07 (1) g cm^{-3}

(B) Measurement of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα (λ_{α_1} = 0.709 30 Å, $\lambda_{\bar{\alpha}}$ = 0.710 73 Å) graphite monochromatized
takeoff angle: 2.0°
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan θ) mm
crystal-detector dist: 173 mm
scan technique: coupled ω(crystal)–2θ(counter)
scan width: variable, $\Delta\omega = (0.8 + 0.35 \tan\theta)^\circ$
scan rate: variable from 0.84 to 6.71° min^{-1} in ω
scan range: $3^\circ \leqslant 2\theta \leqslant 55^\circ$
prescan rejection limit: 1σ
prescan acceptance limit: 100σ
maximum counting time: 90 s
bkgd measments: moving crystal–moving detector, 25% added to scan width at both ends of each scan
stds: three reflctns $(\bar{8}0\bar{8})$, $(\bar{2}3\bar{9})$, and $(\bar{6}44)$, measured every 3600 s of X-ray exposure time, showed only random, statistical fluctuations
reorientation control: 3 stds recentered every 200 data; if position of any scattering vector deviated by more than 0.10° from its calculated position, new orientation matrix was calcd, based on the recentering of a further 22 reflctns
no. of reflctns collected: $[3^\circ \leqslant 2\theta \leqslant 25^\circ\ (+h,+k,-l)$; $3^\circ \leqslant 2\theta \leqslant 55^\circ\ (+h,+k,+l)]$; 7250 reflections, non-space-group extinguished

(C) Treatment of Intensity Data

reduction to F_o and $\sigma(F_o)$: correction for bkgd, attenuator, and Lorentz-polarization of monochromatized X-radiation as described previously[c]
abs cor: not applied; μ = 2.56 cm^{-1}
averaging: 338 equivalent pairs in the inner sphere ($2\theta \leqslant 25^\circ$); agreement factor R_{av} = 0.015
obsd data: 6574 unique reflctns of which the 2995 with $F_o > 4\sigma(F_o)$ were used in the structure solution and refinement

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30^\circ$. Reported here is the unit cell used in the final refinement. The unit cell used for data collection, reduction, and structure solution is described in the text. [b] By suspension in aqueous NaI. [c] Reference 11.

angles, with standard deviations, are given in Table III. A listing of final observed and calculated structure factor amplitudes, hydrogen atom positional parameters, and the results of least-squares plane calculations are available as Tables S1–S3, respectively.[17] Figure 1 shows the geometry of the cation and the atom labeling scheme. Figure 2 depicts the unit cell packing.

Discussion

Description of the Structure. The structure consists of discrete seven-coordinate $[MoL_4L'(CN)]^+$ cations (where L = CN-*t*-Bu, L′ = *t*-BuHNCCNH-*t*-Bu) and $[B(C_6H_5)_4]^-$ anions in a ratio of 1:1. In the cations (Figure 1), each molybdenum atom is bonded to four unidentate *t*-BuNC ligands, one unidentate cyanide ligand, and a bidentate (*N*,*N*′-di-*tert*-butyldiamino)acetylene "coupled" ligand. The last two ligands arise, respectively, from the thermal decomposition[6] and reductive coupling[3] reactions of coordinated *tert*-butyl isocyanide ligands in the MoL_7^{2+} cation.

A crystallographically required twofold axis passes through atoms Mo, C(11), N(11), and the midpoint of the C(41)—C(41′) bond. The Mo–C distances to the *t*-BuNC ligands [Mo–C(21) = 2.143 (5) Å; Mo–C(31) = 2.121 (5) Å] are similar to those observed in the previously reported[3a,4] $[MoL_4L'X]^+$ cations; the Mo–C distances average 2.120 Å in $[MoL_4L'I]I$, 2.122 Å in $[MoL_4L'I](PF_6)$, and 2.13 Å in $[MoL_4L'Br]_2(ZnBr_4)$. The Mo–C distances to the cyanide ion [Mo–C(11) = 2.204 (6) Å] can be compared to the Mo–CN distances in the Na^+ and K^+ salts of $[Mo(CN)_7]^{5-}$.[18] In $Na_5[Mo(CN)_7]\cdot10H_2O$, one of the Mo–CN distances is significantly longer, 2.201 (7) Å, than the average of the others, 2.137 Å. The long Mo–C distance was attributed to the fact that this cyanide ion is involved in three close contacts to Na^+ ions. In $K_5[Mo(CN)_7]\cdot H_2O$, all Mo–CN distances are similar (average = 2.14 Å), there being no close contacts to K^+. In the present compound, the Mo–CN distance compares favorably with the long Mo–CN distance in $Na_5[Mo(CN)_7]\cdot10H_2O$ presumably because N(11) is hydrogen bonded to the two hydrogen atoms of the coupled ligand in the lattice at ($^1/_2 - x$, y, $^1/_2 + z$) (Figure 2) [N(11)···H(41) = 2.05 (5) Å]. Similar hydrogen-bonding interactions were also observed in previous structural studies of $[MoL_4L'X]^+$ compounds.[4] In the complex $[Mo(CN\text{-}t\text{-}Bu)_6(CN)](PF_6)$,[2] there is again a long Mo–CN distance [2.191 (9) Å]. The cyanide ion in this complex is not involved in any hydrogen-bonding contacts although the long Mo–CN distance is consistent with the idea that weaker bonding occurs at the capping position in the capped trigonal prism.[19] The Mo–C distance to the coupled ligand [Mo–C(41) = 2.053 (4) Å] is not significantly different from those observed in the other $[MoL_4L'X]^+$ cations, the average values being 2.044 (8) Å in $[MoL_4L'I]I$, 2.026 (8) Å in $[MoL_4L'I](PF_6)$, and 2.03 (2) Å in $[MoL_4L'Br]_2(ZnBr_4)$. The closest interionic contact in the present structure, apart from the hydrogen-bonding interactions, is 3.46 (1) Å between C(35) and C(65), the latter atom being at ($-x$, $1 - y$, $1 - z$).

The dimensions of the coupled ligand in the present complex are, in general, the same as those determined in the other $[MoL_4L'X]^+$ cations. The C(41)–C(41′) distance of 1.402 (8) Å is, however, significantly larger than the same distance in these cations where the largest distance is 1.358 (10) Å in $[MoL_4L'I](PF_6)$. In $[MoL_4L'I]I$ and $[MoL_4L'I](PF_6)$, none of the six atoms (NCCN, Mo, or X) deviates more than 0.01 Å from the mean plane through them. In $[MoL_4L'I]I$, the hydrogen atoms of the coupled ligand are displaced 0.3 and 0.05 Å on either side of this plane with an H···H distance of 2.08 (10) Å. In $[MoL_4L'I](PF_6)$, the hydrogen atoms are 0.1 and 0.2 Å out of the NCCN plane and on the same side. The H···H distance is similar, being 2.34 (9) Å. Hydrogen atoms were not located in the less accurately determined structure containing the two crystallographically independent $[MoL_4L'Br]^+$ cations. In the present compounds, the NCCN atoms are not quite as planar. Atom C(41) lies 0.030 Å from the NCCN plane and N(41) deviates 0.014 Å on the opposite side. Atoms Mo, C(11), and N(11) are required to lie exactly in this plane. Atom H(41) of the coupled ligand lies 0.038 Å from the NCCN plane, on the same side as C(41). The H···H distance of 2.11 (10) Å is not significantly different from those mentioned above. If the plane through C(41), Mo, C(11), and N(11) is considered, N(41) is 0.077 Å out of this plane and H(41) is almost in the plane with a deviation of 0.007 Å.

The boron atom of each tetraphenylborate anion lies on a crystallographic twofold axis. This axis is coincident with a C_2 axis of the anion, and no disorder is present. The B–C distances in the present compound are not significantly different from those observed elsewhere,[20,21] and the mean C-

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Table II. Final Positional and Thermal Parameters for the Atoms of $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)][B(C_6H_5)_4]$[a,b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.25	0.75	0.38176 (2)	0.0426 (3)	0.0383 (3)	0.0260 (2)	0.0034 (4)	0.00	0.00
N(11)	0.25	0.75	0.5697 (3)	0.144 (7)	0.091 (5)	0.029 (3)	−0.010 (6)	0.00	0.00
N(21)	0.1875 (3)	0.9004 (2)	0.4354 (2)	0.077 (4)	0.047 (3)	0.057 (3)	0.010 (3)	0.014 (2)	−0.003 (2)
N(31)	0.0727 (3)	0.6743 (2)	0.3843 (2)	0.051 (3)	0.066 (3)	0.058 (3)	−0.006 (2)	0.003 (3)	−0.002 (2)
N(41)	0.1844 (3)	0.8038 (2)	0.2149 (2)	0.062 (3)	0.060 (3)	0.036 (2)	0.014 (3)	−0.001 (2)	0.005 (2)
C(11)	0.25	0.75	0.5059 (3)	0.063 (5)	0.042 (4)	0.045 (3)	−0.014 (5)	0.00	0.00
C(21)	0.2048 (3)	0.8481 (3)	0.4126 (3)	0.052 (3)	0.051 (3)	0.040 (3)	0.003 (3)	0.005 (3)	0.004 (2)
C(22)	0.1758 (4)	0.9672 (3)	0.4695 (3)	0.086 (5)	0.043 (3)	0.074 (4)	0.006 (3)	0.021 (4)	−0.011 (3)
C(23)	0.2597 (5)	0.9956 (4)	0.4875 (5)	0.107 (6)	0.072 (4)	0.174 (7)	−0.014 (5)	0.017 (6)	−0.025 (5)
C(24)	0.1310 (5)	0.9566 (3)	0.5434 (4)	0.159 (8)	0.082 (5)	0.095 (5)	−0.025 (5)	0.044 (5)	−0.032 (4)
C(25)	0.1288 (6)	1.0107 (4)	0.4165 (4)	0.239 (10)	0.077 (5)	0.110 (6)	0.087 (6)	−0.019 (6)	−0.027 (4)
C(31)	0.1336 (3)	0.7027 (2)	0.3862 (3)	0.051 (3)	0.044 (3)	0.044 (3)	0.002 (2)	0.004 (3)	−0.001 (2)
C(32)	−0.0006 (4)	0.6342 (3)	0.3739 (4)	0.061 (4)	0.063 (4)	0.083 (4)	−0.012 (3)	−0.005 (4)	−0.013 (4)
C(33)	0.0017 (6)	0.6017 (5)	0.3001 (5)	0.159 (9)	0.221 (10)	0.171 (9)	−0.096 (8)	0.019 (7)	−0.100 (8)
C(34)	0.0018 (7)	0.5773 (6)	0.4298 (7)	0.194 (11)	0.190 (11)	0.312 (16)	−0.131 (10)	−0.099 (11)	0.115 (11)
C(35)	−0.0728 (5)	0.6747 (5)	0.3859 (7)	0.052 (5)	0.155 (9)	0.419 (18)	−0.001 (5)	−0.006 (8)	−0.147 (10)
C(41)	0.2211 (3)	0.7763 (2)	0.2730 (2)	0.044 (3)	0.047 (3)	0.031 (2)	0.000 (2)	−0.0022 (18)	0.0060 (19)
C(42)	0.1239 (4)	0.8591 (3)	0.2141 (3)	0.076 (4)	0.070 (4)	0.051 (3)	0.030 (4)	−0.009 (3)	0.009 (3)
C(43)	0.0565 (4)	0.8457 (4)	0.2703 (4)	0.072 (5)	0.158 (7)	0.081 (5)	0.052 (5)	0.009 (4)	0.028 (5)
C(44)	0.0895 (4)	0.8605 (3)	0.1335 (3)	0.108 (5)	0.114 (6)	0.059 (4)	0.034 (4)	−0.027 (4)	0.014 (3)
C(45)	0.1686 (5)	0.9252 (3)	0.2298 (4)	0.155 (7)	0.072 (5)	0.088 (5)	0.022 (5)	−0.014 (5)	0.010 (4)
H(41)	0.206 (3)	0.789 (3)	0.169 (3)	U_{iso} = 0.081 (18) Å^2					
B	0.25	0.25	0.3910 (4)	0.049 (4)	0.059 (5)	0.055 (4)	−0.001 (7)	0.00	0.00
C(51)	0.2200 (3)	0.3149 (3)	0.3391 (3)	0.046 (3)	0.070 (4)	0.056 (3)	−0.004 (3)	0.000 (3)	0.006 (3)
C(52)	0.2572 (4)	0.3322 (4)	0.2726 (4)	0.082 (5)	0.157 (7)	0.107 (5)	0.056 (5)	0.031 (5)	0.062 (5)
C(53)	0.2360 (5)	0.3903 (5)	0.2322 (4)	0.096 (6)	0.176 (8)	0.112 (5)	0.046 (6)	0.033 (5)	0.084 (6)
C(54)	0.1773 (4)	0.4315 (4)	0.2562 (5)	0.078 (5)	0.087 (5)	0.117 (6)	−0.003 (4)	−0.021 (5)	0.047 (5)
C(55)	0.1404 (4)	0.4173 (3)	0.3210 (4)	0.079 (5)	0.049 (4)	0.109 (5)	0.005 (4)	−0.008 (4)	0.003 (4)
C(56)	0.1622 (4)	0.3599 (3)	0.3624 (3)	0.074 (4)	0.053 (3)	0.067 (4)	−0.008 (3)	0.004 (3)	−0.003 (3)
C(61)	0.1741 (4)	0.2200 (3)	0.4413 (3)	0.073 (4)	0.037 (3)	0.059 (3)	0.006 (3)	0.016 (3)	−0.005 (3)
C(62)	0.0951 (4)	0.2174 (3)	0.4145 (4)	0.073 (5)	0.054 (4)	0.083 (4)	−0.010 (4)	0.016 (4)	−0.007 (3)
C(63)	0.0294 (4)	0.1900 (3)	0.4546 (5)	0.076 (5)	0.068 (5)	0.124 (6)	−0.022 (4)	0.023 (5)	−0.011 (4)
C(64)	0.0433 (6)	0.1632 (3)	0.5252 (5)	0.132 (8)	0.052 (4)	0.127 (7)	−0.017 (5)	0.072 (6)	−0.017 (4)
C(65)	0.1210 (5)	0.1634 (3)	0.5530 (4)	0.130 (7)	0.070 (5)	0.086 (5)	0.009 (5)	0.052 (6)	0.008 (4)
C(66)	0.1850 (4)	0.1896 (3)	0.5126 (3)	0.091 (5)	0.055 (4)	0.075 (4)	0.017 (4)	0.019 (4)	0.008 (3)

[a] Atoms of the cation are labeled as indicated in Figure 1. Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter. [b] H(41) is bound to N(41). Other hydrogen atom positional parameters are presented in Table S2. Anisotropic temperature factors are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. Methyl group hydrogen atoms were included in the refinement with a fixed isotropic temperature factor of $U = 0.145$ Å^2. Hydrogens of the anion were refined with a common isotropic temperature factor that converged at $U = 0.096$ (7) Å^2.

(ring)–C(ring) distance of 1.373 (8) Å also agrees well with that previously reported. The distortion of the phenyl rings from regular hexagons is also observed in the present compound as it has been previously.[20,21] The C–C–C angles at the carbon attached to boron (denoted α in ref 21) average 114.3 (6)°. The C–C–C angles adjacent to these (denoted β in ref 21) average 123.0 (7)°, while remaining C–C–C ring angles average 120.0 (8)°. The boron atom lies 0.04 and 0.11 Å out of the plane of the phenyl rings which is, again, not unusual.

Comparison with Other Seven-Coordinate Stereochemistries. For seven-coordinate complexes of stoichiometry [metal(bidentate ligand)(unidentate ligand)$_5]^{x\pm}$, ligand–ligand repulsion energy calculations[9,22] predict that, when the normalized bite of the bidentate ligand lies between 0.7 and 1.1, two minima of comparable energy appear on the potential energy surface. The "normalized bite" of a bidentate ligand is defined as b = AB/MA = AB/MB (Figure 3). One of these minima is a capped trigonal prism (CTP), called stereochemistry A, and the other is a pentagonal bipyramid (PB) (Figure 3), called stereochemistry B.[9,22] Until the $[MoL_4L'X]^+$ cations were structurally characterized,[4] no examples of stereochemistry A (CTP) existed in the literature. A few examples of stereochemistry B (PB), with bidentate ligands of small bite, were known.[9,22,23]

From Table IV it can be seen that the angular coordinates (Figure 3) of the cations in the complexes $[MoL_4L'I]I$, $[MoL_4L'I](PF_6)$, and molecule 1 of $[MoL_4L'Br]_2(ZnBr_4)$ agree quite well with the calculated values of stereochemistry A (CTP) for b = 0.7. Molecule 2 of $[MoL_4L'Br]_2(ZnBr_4)$ agrees less well with the calculated values. In particular, the values of θ_C, θ_D, θ_E, and θ_F deviate by an average of +12°, suggesting that the four *t*-BuNC ligands are rotated by this amount relative to the coupled ligand. Also, ϕ_C, ϕ_D, ϕ_E, and ϕ_F deviate from the calculated values: ϕ_C and ϕ_E deviate by an average of +2° and ϕ_D and ϕ_F by an average of +5°. This distortion arises from the rotation (by +12°) of the four *t*-BuNC ligands, leading to increased repulsions between ligands F and D and the coupled ligand. These two *t*-BuNC groups are therefore forced toward ligand G, distorting their ϕ values in the manner observed. There is a similar but smaller distortion for the compound $[pyH][TaCl_4(py)(PhCCPh)]$.[24] The values of θ_C, θ_D, θ_E, and θ_F are larger than the calculated values by an average of +6°, suggesting a rotation, by this amount, of the four Cl ligands relative to the PhCCPh ligand. Again, the ligands that rotate toward the bidentate ligand are distorted further toward the unique ligand than are the other two ligands. The average deviation from the calculated ϕ values are small, however, being +2° for ϕ_D and ϕ_F and +1° for ϕ_C and ϕ_E. The reasons for this distortion from the calculated values

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Table III. Interatomic Distances (Å) and Angles (Deg) for $[\mathrm{Mo(CN}\text{-}t\text{-}\mathrm{Bu)_4}(t\text{-}\mathrm{BuHNCCNH}\text{-}t\text{-}\mathrm{Bu)(CN)}][\mathrm{B(C_6H_5)_4}]$[a]

	Coordination Sphere		
Mo–C(11)	2.204 (6)	Mo–C(31)	2.121 (5)
Mo–C(21)	2.143 (5)	Mo–C(41)	2.053 (4)
C(11)–Mo–C(21)	75.2 (1)	C(21)–Mo–C(31′)	84.5 (2)
C(11)–Mo–C(31)	87.9 (1)	C(21)–Mo–C(41′)	123.2 (2)
C(11)–Mo–C(41)	160.0 (1)	C(31)–Mo–C(41)	86.5 (2)
C(21)–Mo–C(31)	94.4 (2)	C(31)–Mo–C(31′)	175.7 (3)
C(21)–Mo–C(41)	86.2 (2)	C(31)–Mo–C(41′)	97.5 (2)
C(21)–Mo–C(21′)	150.4 (3)	C(41)–Mo–C(41′)	39.9 (2)
	Ligand Geometry		
N(11)–C(11)	1.132 (7)	N(41)–C(41)	1.312 (5)
N(11)···H(41)[b]	2.05 (5)	N(41)–C(42)	1.472 (6)
N(11)···N(41)[b]	2.988 (6)	N(41)–H(41)	0.94 (5)
N(21)–C(21)	1.143 (5)	C(41)–C(41′)	1.402 (8)
N(21)–C(22)	1.464 (6)	H···H′	2.11 (10)
N(31)–C(31)	1.143 (6)	mean C–C(methyl)	1.498 (8)
N(31)–C(32)	1.448 (6)	range C–C(methyl)	1.44–1.54
C(21)–N(21)–C(22)	172.6 (6)	Mo–C(41)–N(41)	161.7 (4)
C(31)–N(31)–C(32)	173.2 (5)	Mo–C(41)–C(41′)	70.0 (1)
C(41)–N(41)–C(42)	128.5 (4)	N(41)–C(41)–C(41′)	127.9 (3)
C(41)–N(41)–H(41)	113 (3)	N(41)–H(41)···N(11)[c]	175 (5)
C(42)–N(41)–H(41)	118 (3)	mean N–C–C(methyl)	108.5 (5)
Mo–C(11)–N(11)	180.0	range N–C–C(methyl)	105.6–110.9
Mo–C(21)–N(21)	172.0 (5)		
Mo–C(31)–N(31)	174.9 (4)	mean C(methyl)–C–C(methyl)	110.4 (6)
		range C(methyl)–C–C(methyl)	105.4–112.8
	Anion Geometry		
C(51)–C(52)	1.370 (7)	C(61)–C(62)	1.377 (7)
C(51)–C(56)	1.360 (7)	C(61)–C(66)	1.412 (7)
C(51)–B	1.652 (7)	C(61)–B	1.639 (7)
C(52)–C(53)	1.396 (9)	C(62)–C(63)	1.399 (8)
C(53)–C(54)	1.328 (8)	C(63)–C(64)	1.378 (9)
C(54)–C(55)	1.330 (8)	C(64)–C(65)	1.364 (9)
C(55)–C(56)	1.397 (7)	C(65)–C(66)	1.370 (8)
C(52)–C(51)–C(56)	114.1 (6)	C(66)–C(61)–B	123.1 (6)
C(52)–C(51)–B	122.8 (5)	C(61)–C(62)–C(63)	123.9 (7)
C(56)–C(51)–B	122.8 (5)	C(62)–C(63)–C(64)	119.1 (8)
C(51)–C(52)–C(53)	122.5 (7)	C(63)–C(64)–C(65)	118.8 (8)
C(52)–C(53)–C(54)	121.1 (7)	C(64)–C(65)–C(66)	121.5 (8)
C(53)–C(54)–C(55)	118.5 (7)	C(61)–C(66)–C(65)	122.3 (7)
C(54)–C(55)–C(56)	120.6 (7)	C(51)–B–C(61)	111.1 (3)
C(51)–C(56)–C(55)	123.1 (6)	C(51)–B–C(51′)	112.2 (6)
C(62)–C(61)–C(66)	114.4 (6)	C(51)–B–C(61′)	104.4 (3)
C(62)–C(61)–B	122.3 (5)	C(61)–B–C(61′)	114.0 (6)

[a] See footnote *a*, Table II. Values reported have not been corrected for thermal motion. Primed atoms are related to those unprimed by twofold symmetry. [b] Atom is at $(^1/_2 - x, y, {}^1/_2 + z)$. [c] Atom is at $(^1/_2 - x, y, -^1/_2 + z)$.

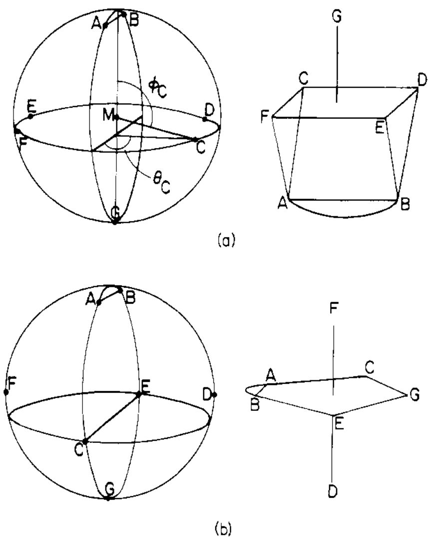

Figure 3. Axes used to define the stereochemistry of [metal(bidentate)(unidentate)$_5$]$^{x\pm}$ complexes: (a) stereochemistry A, capped trigonal prism (b = 0.7–1.1); (b) stereochemistry B, pentagonal bipyramid (b = 0.7–1.1). b is defined in footnote *a* of Table IV. This figure and the nomenclature closely follow that of ref 22. The metal atom (M) is at the center of the sphere.

are not clear although the distortions are consistent with calculations suggesting that the energy barrier between stereochemistry A (CTP) and stereochemistry B (PB) is minimal.[9]

The situation with the present compound is very different. The distortion from stereochemistry A (CTP) is quite marked. The values of θ_C, θ_D, θ_E, and θ_F deviate by an average of −26° from the calculated values, suggesting a large twist of the four *t*-BuNC ligands relative to the coupled ligand. This twist is toward the formation of stereochemistry B (PB). If the twist in this plane were an average of −45° from the calculated values for stereochemistry A, the structure would correspond to that calculated for stereochemistry B (PB) (Table IV). Again, the values of the deviations from the calculated values of ϕ_C, ϕ_D, ϕ_E, and ϕ_F suggest interaction with the bidentate ligand. The average deviation of ϕ_C and ϕ_E is +8° as these *t*-BuNC ligands are forced away from the bidentate ligand towards the $\mathrm{CN^-}$ ligand. Interestingly, the average deviation of ϕ_D and ϕ_F is now −5°, revealing that these two *t*-BuNC ligands move toward the bidentate ligand as rotation occurs. This result is that expected for distortion toward the PB stereochemistry (Figure 3).

Inspection of Figure 21 of ref 9 shows that the present compound lies in the trough connecting stereochemistry A and stereochemistry B, being slightly closer to the latter. The cation is prevented from attaining perfect pentagonal-bipyramidal geometry by intramolecular contacts. Specifically,

Table IV. Calculated and Experimental Angular Coordinates (Deg) for Selected Complexes with b = 0.7–1.1[a]

	b	ϕ_A	ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	ϕ_F	θ_F	ϕ_G	θ_G	ref
calcd angular coordinates for stereochemistry A[b]	0.7	20.5	97	46	97	134	97	226	97	314	180	*c*	22
	0.8	23.6	97	47	98	134	98	226	97	313	180		22
	1.0	30.0	98	52	100	137	98	232	100	317	180		22
calcd angular coordinates for stereochemistry B[b]	0.7	20.5	100	0	93	90	100	180	93	270	180		22
	0.8	23.6	102	0	92	90	102	180	92	270	180		22
	1.0	30.0	105	0	91	90	105	180	91	270	180		22
$[\mathrm{MoL_4L'I}]\mathrm{I}$[d]	0.66	19.3	101	46	100	131	101	224	100	315	179		4
$[\mathrm{MoL_4L'I}](\mathrm{PF_6})$[d]	0.67	19.6	101	45	99	131	101	223	100	313	180		4
$[\mathrm{MoL_4L'Br}]^+$ (molecule 1)[d]	0.66	19.4	101	45	97	131	101	227	100	313	179		4
(molecule 2)[d]	0.66	19.2	100	59	102	144	98	240	103	326	178		4
$[\mathrm{pyH}][\mathrm{TaCl_4(py)(PhCCPh)}]$[e]	0.64	18.7	98	54	100	140	98	232	99	320	180		24
$[\mathrm{MoL_4L'(CN)}][\mathrm{B(C_6H_5)_4}]$[f]	0.68	20.0	105	22	92	106	105	202	92	286	179		*h*
$[\mathrm{MoCl(CO)_2}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{P(OMe)_3})_2]$[g]	1.02	30.6	106	6	101	88	105	189	79	270	157	91	25

[a] The "normalized bite" of a bidentate ligand, b, is defined as AB/MA = AB/MB (Figure 3); L and L′ are defined in the text. [b] See Figure 3. [c] θ_G has no meaning when ϕ_G = 180°. [d] C(1) occupies site A (Figure 3); halogen occupies site G. [e] C(20) occupies site A; (py) occupies site G. [f] C(41) occupies site A; $\mathrm{CN^-}$ occupies site G. [g] C(3) occupies site A; C(5) occupies site G. [h] This work.

there is a close contact of 2.656 (5) Å between C(21) and H(432). Similar limiting intramolecular C···H contacts of ca. 2.6 Å occur in $[MoL_4L'I]I$ and $[MoL_4L'I](PF_6)$ between methyl hydrogen atoms of the "coupled" ligand and the C≡N moieties of the four *t*-BuNC ligands forming the capped face. The difference between the present compound and the CTP complexes lies in the angles between the capping ligand and the four ligands of the capped face (vide supra). In the CTP complexes, these four angles in each complex are close to 80°. In the present compound, the similar angle involving ligands 3 and 3', angle C(11)–Mo–C(31), opens up to 87.9° and that involving ligands 2 and 2', angle C(11)–Mo–C(21), closes to ca. 75.2°. The implications in the present compound are that if this 75° angle could close up further (i.e., ligands 2 and 2' move closer to the cyanide ligand), the four ligands 3, 3', 2, and 2' could rotate such that 2 and 2' were now in the plane of the coupled ligand and the stereochemistry would be pentagonal bipyramidal (stereochemistry B).

Intramolecular repulsions, due to bulky $P(OMe)_3$ groups, were invoked to rationalize the deviation of the recently determined structure[25] of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(P(OMe)_3)_2]$ from a regular pentagonal bipyramid (Table IV). The reason why the present compound does not have the less hindered capped trigonal-prismatic geometry adopted by the other $[MoL_4L'X]^+$ cations is not clear but obviously may be electronic in origin.

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Registry No. $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)][B(C_6H_5)_4]$, 78963-11-8; $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)](PF_6)$, 78891-51-7; $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$, 41982-05-2.

Supplementary Material Available: Tables S1–S3 reporting respectively final observed and calculated structure factors, hydrogen atom positional parameters, and least-squares planes (16 pages). Ordering information is given on any current masthead page.

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Synthesis and X-ray Crystal Structure of $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-\cdot{}^1/_3CH_2Cl_2$: A Complex Containing the Bridging Formazanido(3–) Ligand[1]

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The reaction between $CHFBr_2$ and the dinitrogen-derived hydrazido(2–) complex $[WBr(dppe)_2N_2H_2]^+Br^-$, in the presence of $[Ph_2I]^+Br^-$ and aqueous base, yields a cationic, binuclear complex $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$. This complex has been isolated as its bromide, hexafluorophosphate, and Reineckate salts, and a single-crystal X-ray study of the latter confirms that the cation contains a formazanido(3–) ligand, $[N_2CHN_2]^{3-}$, bridging two tungsten atoms in a seven-atom chain. Crystals of $[[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+[Cr(NH_3)_2(NCS)_4]^-\cdot{}^1/_3CH_2Cl_2]$ are monoclinic, space group $P2_1/n$, with $Z = 4$, $a = 19.089$ (3) Å, $b = 44.263$ (4) Å, $c = 13.807$ (2) Å, $\beta = 104.4$ (1)°, and $V = 11299.5$ Å^3. The structure was refined by blocked full-matrix least squares, with the phenyl rings treated as rigid bodies, to a final R value of 0.082 and R_w of 0.083 for the 5918 unique observed reflections $[I > 3\sigma(I)]$.

Introduction

It has recently been shown that reactions of the dinitrogen-derived hydrazido(2–) complex $[WBr(dppe)_2N_2H_2]^+Br^-$ with organic solvents, in the presence of diphenyliodonium bromide and aqueous base, often lead to products in which solvent-drived radicals have added to the nitrogen-containing ligand. Such products include the formyldiazenido complex $[WBr(dppe)_2N_2CHO]$ (from CH_2Cl_2 or $CHBr_3$)[3] and the cationic dichlorodiazomethane complex $[WBr(dppe)_2(N_2CCl_2)]^+$ (from $CHCl_3$ or $CBrCl_3$)[4], which are thought to arise by the sequence of ionic and radical reactions typified in Scheme I.

We now report that when the above reaction is carried out using dibromofluoromethane as the organic phase, small amounts of $[WBr(dppe)_2N_2CHO]$ are again formed, but the major product is the bromide salt of a complex cation which we have characterized spectroscopically and crystallographically as a binuclear species containing the bridging formazanido(3–) ligand $[\mu\text{-}N_2CHN_2]^{3-}$. Part of this work has been described in a preliminary communication.[5]

Experimental Section

Infrared spectra were obtained with a Perkin-Elmer PE197 spectrometer, and ^1H and ^{31}P NMR spectra were recorded on a JEOL XL100 FT instrument. Fluorodibromomethane was purchased from Fluorochem Ltd., and diphenyliodonium bromide from Lancaster Synthesis Ltd. The hydrazido(2–) complex[6] $[WBr(dppe)_2N_2H_2]^+Br^-$ was prepared by protonation of $[W(dppe)_2(N_2)_2]$ with aqueous hydrobromic acid in dichloromethane.[3] Unless otherwise specified, no special precautions were taken to exclude atmospheric oxygen or moisture.

Preparation of $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+Br^-\cdot3CH_2Cl_2$. The hydrazido(2–) complex $[WBr(dppe)_2N_2H_2]^+Br^-$ (2.00 g, 1.71 mmol) and diphenyliodonium bromide (0.70 g, 1.93 mmol) were suspended in $CHFBr_2$ (25 cm^3) and degassed aqueous potassium carbonate (20 cm^3 of a 5% solution) was added. The mixture was stirred vigorously under nitrogen for 45 min and then treated with diethyl ether (200 cm^3). The resulting dark olive green precipitate was filtered off, washed

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[1] dppe = 1,2-bis(diphenylphospino)ethane.

[2] (a) ICI Corporate Laboratory. (b) The Polytechnic of North London.

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