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Structures and properties of molybdenum carbonyl complexes containing uninegative nitrogen-tripod ligands derived from heterocyclic compounds including 1-H-pyrazole and 1-H-1,2,4-triazole

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Abstract

The melt reaction between 1-H-1,2,4-triazole (HTz) and $NaBPh_4$ affords $Na(PhBTz_3)$ while a similar process between HTz and KBH_4 gives $K(HBTz_3)$. The uninegative L anion ($L = PhBTz_3$ or $HBTz_3$) reacts with $[Mo(CO)_6]$ to give $[MoL(CO)_3]^-$. Upon addition of electrophiles, $[MoL(CO)_2(\eta^3\text{-allyl})]$, $[MoL(CO)_2(NO)]$, $[MoL(CO)_3Br]$, and $[MoL(CO)_3I]$ are obtained. Two structures have been characterized by X-ray crystallography: $[NEt_4][Mo(HBPz_3)(CO)_3]$, orthorhombic, *Pbca*, $a = 15.832(3)$, $b = 15.799(4)$, $c = 19.388(5)$ Å, $Z = 8$, $R = 0.043$, $R_w = 0.031$ based on 2591 reflections with $I > 3.0\sigma(I)$; $[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]$, orthorhombic, *Pbca*, $a = 17.815(3)$, $b = 32.017(2)$, $c = 15.331(3)$ Å, $Z = 8$, $R = 0.044$, $R_w = 0.061$ based on 5743 reflections with $I > 2.0\sigma(I)$. Although comparison of the averaged $\nu(CO)$ values reveals the increasing order of the electron donativity as $HBBz_3^- < HBTz_3^-$, $PhBTz_3^- < HBPz_3^- < HBPz_3'^-$, $HBPz_3^{\star -} < HBPz_3''^-$, neither structural features nor reactivities show an appreciable substituent effect (*i.e.*, $HBTz_3^-$ *vs.* $HBPz_3^-$ and $HBTz_3^-$ *vs.* $PhBTz_3^-$). Neither is the 5-methyl-group effect for nickel pseudohalides suggested by Trofimenko *et al.* supported strongly by the solid-state structures of $[MoL'(CO)_3]^-$ ($L' = HBPz_3^-$, $HBPz_3'^-$, or $HBPz_3^{\star -}$; Pz′ = 3,5-dimethylpyrazol-1-yl; Pz* = 3-methylpyrazol-1-yl).

1. Introduction

Poly(pyrazolyl)borates have been used extensively as multidentate ligands in the syntheses of numerous organometallic and coordination compounds, since they were introduced in the 1960s [1]. There has been renewed interest arising from novel reactions such as activation of small molecules like H_2 [2], O_2 [3] or N_2 [4], induced by metal complexes without any carbonyl ligation, and of C–H bonds observed for quite a few metal carbonyl derivatives containing the tripodal tris(pyrazolyl)borates [5]. We and others have prepared similar ligands and collected structural and spectral data [6] as well as carrying out orbital analysis [7] and determining relative formation rates [8] of the carbonyl-containing complexes of all these tridentate ligands. The aim has been to get a clear picture of the electronic or steric factors determining the observed reactivity. The recent report by Trofimenko *et al.* [9] on the importance of the methyl group on the pyrazolyl ring-5 position of tris(pyrazolyl)borates in nickel pseudohalides therefore prompted us to determine the crystal structures of a known compound, $[Et_4N][Mo(HBPz_3)(CO)_3]$ [7a], and a new analogue, $[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]$, and to study related reactions of this complex and another analogue, $[NEt_4][Mo(PhBTz_3)(CO)_3]$, to understand if such an effect of 5-methyl-group is also present in metal carbonyl deriva-

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tives containing the ligands, where Pz is pyrazol-1-yl and Tz is 1,2,4-triazol-1-yl.

2. Experimental section

All operations were performed by the usual Schlenk techniques [10], using deoxygened, dry solvents and gases. IR spectra, calibrated with polystyrene, were recorded on a Hitachi Model 270-30 instrument. Abbreviations are vs, very strong; s, strong; m, medium; w, weak; and sh, shoulder. NMR spectra were obtained on Bruker WP-100 (^{1}H, 100 MHz) or Varian VXR-300 (^{1}H, 300 MHz) FT-NMR spectrometers. Chemical shifts (δ in ppm, J in Herz) are defined as positive downfield or negative upfield relative to internal $SiMe_4$ (TMS) standard. Abbreviations are s, singlet; d, doublet; br, unresolved multiplet or two overlapped singlets; tt, triplet of triplet; q, quartet. Elemental analyses were by the Microanalytical Service of the Department of Chemistry, National Cheng Kung University. $[NEt_4][Mo(HBPz_3)(CO)_3]$ was prepared by the established procedure [7a].

2.1. Preparation of $KHBTz_3$

A mixture of 1-H-1,2,4-triazole (HTz, 29.29 g, 424 mmol) and KBH_4 (5.72 g, 106 mmol) was heated slowly to 200°C until 7.8 l (318 mmol) of H_2 had evolved (wet test meter). The melt was poured into 100 ml of stirred tetrahydrofuran (THF) and the mixture cooled to room temperature. The white precipitate was collected and recrystallized from $MeOH/Et_2O$ to give the product (14.87 g, 55%). Anal. Found: C, 28.12; H, 2.87; N, 49.31. $C_6H_7BKN_9$ calc.: C, 28.25; H, 2.77; N, 49.42%. IR (KBr): ν(BH), 2484w cm^{-1}. ^{1}H NMR (25°C, dimethylsulfoxide-d_6, 100 MHz): protons at ring-3 and -5 positions, δ 8.13 (3H, s), 7.83 (3H, s).

2.2. Preparation of $NaPhBTz_3$

A mixture of $NaBPh_4$ (13.00 g, 38 mmol) and HTz (51.96 g, 753 mmol) was gradually heated to 250°C until *ca.* 8.1 g (104 mmol) of benzene had distilled from the melt. The mixture was then poured into 200 ml of THF and filtered immediately. The off-white solid residue was washed twice with 200 ml of THF and once with 30 ml of MeOH. The solid was then recrystallized from Me_2SO and air dried to give 10.7 g (89%) product. Anal. Found: C, 45.54; H, 3.45; N, 39.87. $C_{12}H_{11}BN_9Na$ calc.: C, 45.74; H, 3.53; N, 40.01%. ^{1}H NMR (25°C, dimethylsulfoxide-d_6, 100 MHz): protons at ring-3 and -5 positions, δ 7.90 (3H, s), 7.78 (3H, s); phenyl protons, 7.15 (5H, m).

2.3. Preparation of $[NEt_4][Mo(HBTz_3)(CO)_3]$

A mixture of 1.98 g (7.7 mmol) of $KHBTz_3$ and 1.85 g (7.0 mmol) of $[Mo(CO)_6]$ in 50 ml of MeCN was stirred at reflux for 3.5 h to give a yellow solution. A de-aerated solution of 2.1 g of Et_4NBr in 150 ml of H_2O was then added to the solution to give the crystalline solid. The pale yellow solid was collected and washed twice with 20 ml of H_2O and three times with 10 ml of Et_2O and dried under vacuum; yield 3.06 g (83%). Anal. Found: C, 38.63; H, 5.21; N, 26.41. $C_{17}H_{27}BMoN_{10}O_3$ calc.: C, 38.80; H, 5.17; N, 26.62%. IR (KBr): ν(BH), 2523w; ν(CO), 1902s, 1774vs and IR (MeCN): ν(CO), 1906s, 1776vs cm^{-1}. ^{1}H NMR (25°C, acetone-d_6, 100 MHz): protons at ring-3 and -5 positions, δ 8.38 (3 H, s), 8.13 (3H, s); CH_2 of NEt_4^+, 3.47 (8H, q, J(H,H) = 7.2); CH_3 of NEt_4^+, 1.36 (12H, tt, J(N,H) = 1.9, J(H,H) = 7.2). A metathesis reaction between bis(triphenylphosphine)iminium chloride ($[N(PPh_3)_2]Cl$) and $K[Mo(HBTz_3)(CO)_3]$ in MeOH was also found to give $[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]$.

2.4. Preparation of $[NEt_4][Mo(PhBTz_3)(CO)_3]$

This yellow compound was obtained from $NaPhBTz_3$, $[Mo(CO)_6]$, and excess Et_4NBr by an analogous procedure; yield 80%. Anal. Found: C, 46.21; H, 5.46; N, 23.49. $C_{23}H_{31}BMoN_{10}O_3$ calc.: C, 45.86; H, 5.20; N, 23.25%. IR (KBr): ν(CO), 1904s, 1770vs and IR (MeCN): ν(CO), 1906s, 1774vs cm^{-1}. ^{1}H NMR (25°C, $CDCl_3$, 100 MHz): protons at ring-3 and -5 positions, δ 8.29 (3H, s), 8.09 (3H, s); Ph, 7.86 (2H, m), 7.56 (3H, m); CH_2 of NEt_4^+, 3.33 (8H, q, J(H,H) = 7.3); CH_3 of NEt_4^+, 1.38 (12H, tt, J(N,H) = 1.9, J(H,H) = 7.3).

2.5. Preparation of $[MoL(CO)_2(NO)]$ ($L = HBTz_3$, $PhBTz_3$)

To a stirred solution of 3.0 mmol of $M[MoL(CO)_3]$ (M = Na or K) prepared *in situ* in 30 ml of MeCN, $[NO][BF_4]$ (0.38 g, 3.3 mmol) was added in portions. Gas evolved briskly and when this stopped the solvent was removed under vacuum. Recrystallization from $MeOH/H_2O$ gave the orange yellow product $[Mo(HBTz_3)(CO)_2(NO)]$; yield 60–65%. Anal. Found: C, 23.64; H, 1.93; N, 34.37. $C_8H_7BMoN_{10}O_2 \cdot 1/2\ H_2O$ calc.: C, 23.70; H, 1.95; N, 34.60%. IR (KBr): ν(BH), 2544w; ν(CO), 2028s, 1936s; ν(NO), 1680s and IR (CH_2Cl_2): ν(CO), 2036s, 1950s; ν(NO), 1690s cm^{-1}. ^{1}H NMR (25°C, acetone-d_6, 100 MHz): protons at ring-3 and -5 positions, δ 8.67 (2H, s), 8.63 (2H, s), 8.58 (1H, s), 8.54 (1H, s). $[Mo(PhBTz_3)(CO)_2(NO)]$, Anal. Found: C, 35.04; H, 2.49; N, 29.13. $C_{14}H_{11}BMoN_{10}O_2 \cdot 1/2\ H_2O$ calc.: C, 34.81; H, 2.50; N, 29.00%. IR (KBr): ν(CO), 2028s, 1932s; ν(NO), 1680s and IR (CH_2Cl_2): ν(CO), 2036s, 1948s; ν(NO), 1680s cm^{-1}. ^{1}H NMR (25°C, $CDCl_3$, 300 MHz): protons at ring-3 and -5 positions, δ 8.29 (2H, s), 8.27 (2H, s), 8.07 (1H, s), 8.00 (1H, s); Ph, 7.82 (2H, m), 7.58 (3H, m). $^{13}C\{^1H\}$ NMR (25°C, $CDCl_3$, 75 MHz): CO, 221.9 (2 C); Carbon nuclei at ring-3 and

-5 positions, 155.4 (2 C), 155.2 (1 C), 149.7 (1 C), 149.5 (2 C); Ph, 133.8 (2 C), 130.3 (1 C), 129.4 (2 C) with one unobserved signal for the *ipso*-carbon nucleus of Ph.

2.6. Preparation of [MoL(CO)$_3$X] (X = Br, I)

A solution of 3.03 mmol of M[MoL(CO)$_3$] in 20 ml of MeOH was treated dropwise with a solution containing 3.40 mmol of Br_2 or I_2 in 5 ml of MeOH at −20°C with immediate formation of precipitate. The resulting suspension was stirred for 10 min and then filtered out. The product was washed twice with 15 ml of MeOH and dried under vacuum in 50–75% yield. [Mo(HBTz$_3$)(CO)$_3$I], orange-yellow. Anal. Found: C, 20.53; H, 1.46; N, 24.05. $C_9H_7BIMoN_9O_3$ calc.: C, 20.67; H, 1.35; N, 24.11%. IR (KBr): ν(BH), 2548w; ν(CO), 2044s, 1968s, 1934s and IR (CH_2Cl_2): ν(CO), 2044s, 1974s, 1942s cm^{-1}. ^{1}H NMR (25°C, $CDCl_3$, 100 MHz): protons at ring-3 and -5 positions, δ 8.74 (3H, s), 8.36 (3H, s). [Mo(PhBTz$_3$)(CO)$_3$Br], yellow-brown. Anal. Found: C, 32.50; H, 2.15; N, 22.74. $C_{15}H_{11}BBrMoN_9O_3$ calc.: C, 32.64; H, 2.01; N, 22.84%. IR (KBr): ν(CO), 2056s, 1996s, 1942s and IR (CH_2Cl_2): ν(CO), 2056s, 1984s, 1942s cm^{-1}. ^{1}H NMR (25°C, $CDCl_3$, 100 MHz): protons at ring-3 and -5 positions, δ 8.73 (3H, s), 8.62 (3H, s); Ph, 7.86 (2H, m), 7.66 (3H, m). [Mo(PhBTz$_3$)(CO)$_3$I], orange-yellow. Anal. Found: C, 30.21; H, 1.98; N, 21.15. $C_{15}H_{11}BIMoN_9O_3$ calc.: C, 30.08; H, 1.85; N, 21.05%. IR (KBr): ν(CO), 2036s, 1974s, 1948s and IR (CH_2Cl_2): ν(CO), 2044s, 1974s, 1940s cm^{-1}. ^{1}H NMR (25°C, $CDCl_3$, 100 MHz): protons at ring-3 and -5 positions, δ 8.37 (2H, s); Ph, 7.86 (2H, m), 7.65 (3H, m).

2.7. Preparation of [MoL(CO)$_3$(η^3-allyl)]

To a suspension of 1.0 mmol of [Et_4N][MoL(CO)$_3$] in 20 ml of CH_2Cl_2 was added 1 ml of allyl bromide. The mixture was stirred at room temperature for 3 h and a transparent solution formed. A solution IR spectrum indicated the complete reaction. The solvent and excess allyl bromide were then removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave 80% of the orange-yellow solid. [Mo(HBTz$_3$)(CO)$_2$(η^3-allyl)], yellow. Anal. Found: C, 31.52; H, 3.04; N, 29.87. $C_{11}H_{12}BMoN_9O_2 \cdot 1/2\ H_2O$ calc.: C, 31.60; H, 3.14; N, 30.15%. IR (KBr): ν(CO), 1954s, 1856s and IR (CH_2Cl_2): ν(CO), 1960s, 1866s cm^{-1}. ^{1}H NMR (25°C,

TABLE 1. Crystal data for [NEt$_4$][Mo(HBPz$_3$)(CO)$_3$] and [N(PPh$_3$)$_2$][Mo(HBTz$_3$)(CO)$_3$]

Compound	[NEt$_4$][Mo(HBPz$_3$)(CO)$_3$]	[N(PPh$_3$)$_2$][Mo(HBTz$_3$)(CO)$_3$]
empirical formula	$C_{20}H_{30}BMoN_7O_3$	$C_{45}H_{37}BMoN_{10}O_3P_2$
colour	yellow	yellow
crystal size (mm)	0.60 × 0.40 × 0.34	0.30 × 0.40 × 0.50
space group	orthorhombic, *Pbca* (No. 61)	
unit cell dimensions *a*, *b*, *c*, Å	15.832(3), 15.799(4), 19.388(5)	17.815(3), 32.017(2), 15.331(3)
volume, Å^3	4850(2)	8745(2)
Z	8	8
D_{calc} g/cm^3	1.433	1.336
orientation rflns, range	13, 13° ≤ 2θ ≤ 24°	25, 79° ≤ 2θ ≤ 80°
data collected	−*h*, −*k*, −*l*	+*h*, +*k*, +*l*
abs cor	ψ scan	
abs coeff, mm^{-1}	0.56	3.62
abs. correction	not applied	applied
transm range	-	0.51–1.00
diffractometer used	Siemens R3m/V	Rigaku AFC-5R
radiation; λ, Å	Mo Kα, 0.7107	Cu Kα, 1.5418
temperature (K)	297	298
scan type	θ/2θ	
2θ range, deg	3–50	2–120
scan speed, deg/min	3–15	32
std rflns	3 std/50 rflns	3 std/300 rflns
decay; %	≤ 1	≤ 1
no. of unique rflns	4284	6492
no. of rflns used	2591 with $I > 3.0\sigma(I)$	5743 with $I > 2.0\sigma(I)$
max Δ/σ ratio	0.001	0.024
RR_ω S [a]	0.043, 0.031, 1.0	0.044, 0.061, 2.45
resid peak; e/Å^3	0.88	0.58
solution	direct method	Patterson synthesis

[a] See ref. [6a,11].

TABLE 2. Fractional atomic coordinates for $[NEt_4][Mo(HBPz_3)(CO)_3]$ and $[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]$

Atom	x	y	z
(a) $[NEt_4][Mo(HBPz_3)(CO)_3]$			
Mo	0.0605(1)	0.1414(1)	0.6669(1)
N	0.7863(3)	0.1205(2)	0.0996(2)
N(11)	0.0465(2)	0.1837(2)	0.5559(2)
N(12)	0.0833(2)	0.2571(2)	0.5328(2)
N(21)	0.1950(2)	0.1809(2)	0.6443(2)
N(22)	0.2134(2)	0.2520(2)	0.6075(2)
N(31)	0.0489(2)	0.2832(2)	0.6842(2)
N(32)	0.0898(3)	0.3397(2)	0.6429(2)
O(1)	0.0792(3)	0.1091(3)	0.8243(2)
O(2)	−0.1246(3)	0.0848(3)	0.6932(2)
O(3)	0.0947(3)	−0.0479(2)	0.6348(2)
B	0.1415(3)	0.3090(3)	0.5813(3)
C(1)	0.0745(3)	0.1201(3)	0.7640(2)
C(2)	−0.0552(3)	0.1093(3)	0.6823(2)
C(3)	0.0820(3)	0.0241(3)	0.6469(2)
C(4)	0.8502(4)	0.0511(4)	0.1075(3)
C(5)	0.7335(4)	0.1084(3)	0.0349(3)
C(6)	0.7279(4)	0.1214(5)	0.1603(3)
C(7)	0.8354(4)	0.2032(4)	0.0916(3)
C(8)	0.9091(5)	0.0375(5)	0.0481(4)
C(9)	0.6918(4)	0.0238(3)	0.0277(3)
C(10)	0.7702(5)	0.1398(8)	0.2295(3)
C(11)	0.7833(5)	0.2820(4)	0.0885(5)
C(13)	0.0628(3)	0.2698(3)	0.4665(2)
C(14)	0.0135(3)	0.2039(3)	0.4456(2)
C(15)	0.0049(3)	0.1520(3)	0.5025(2)
C(23)	0.2982(3)	0.2617(3)	0.6033(3)
C(24)	0.3349(3)	0.1949(4)	0.6374(3)
C(25)	0.2697(3)	0.1468(3)	0.6622(3)
C(33)	0.0799(3)	0.4181(3)	0.6690(3)
C(34)	0.0317(4)	0.4133(3)	0.7272(3)
C(35)	0.0135(3)	0.3283(3)	0.7348(2)
(b) $[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]$			
Mo	0.768202(17)	0.358777(10)	0.225822(20)
O(1)	0.85777(21)	0.29809(11)	0.1094(3)
O(2)	0.86708(18)	0.31898(11)	0.36971(21)
O(3)	0.89743(18)	0.42294(12)	0.22004(21)
C(1)	0.82347(23)	0.32118(13)	0.1528(3)
C(2)	0.82653(22)	0.33401(14)	0.3179(3)
C(3)	0.84902(21)	0.39863(14)	0.2203(3)
B	0.5818(3)	0.38246(16)	0.2040(3)
N(11)	0.68981(16)	0.40145(10)	0.30353(20)
N(12)	0.61598(17)	0.40568(20)	0.28172(20)
N(14)	0.63386(19)	0.44505(11)	0.39782(22)
N(21)	0.70055(17)	0.38732(10)	0.11510(20)
N(22)	0.62579(17)	0.39500(10)	0.12201(21)
N(24)	0.66076(22)	0.42104(13)	−0.00427(23)
N(31)	0.66240(19)	0.31915(10)	0.23788(22)
N(32)	0.59336(18)	0.33530(11)	0.22064(21)
N(34)	0.57576(24)	0.26899(12)	0.2532(3)
C(13)	0.58521(22)	0.43172(13)	0.3400(3)
C(15)	0.69744(24)	0.42556(12)	0.3728(3)
C(23)	0.60511(25)	0.41487(14)	0.0496(3)
C(25)	0.71823(25)	0.40276(14)	0.0381(3)
C(33)	0.5437(3)	0.30458(17)	0.2301(3)
C(35)	0.6486(3)	0.28004(15)	0.2573(3)
N	0.57170(18)	0.37501(11)	0.77408(19)
P(1)	0.50041(5)	0.35764(3)	0.82269(6)
P(2)	0.59836(5)	0.39014(3)	0.68135(6)

TABLE 2 (continued)

Atom	x	y	z
C(11A)	0.42665(21)	0.34011(12)	0.75135(25)
C(12A)	0.36684(24)	0.36588(13)	0.7303(3)
C(13A)	0.31556(24)	0.35315(16)	0.6688(3)
C(14A)	0.3221(3)	0.31546(16)	0.6297(3)
C(15A)	0.3800(3)	0.28931(15)	0.6503(3)
C(16A)	0.43369(24)	0.30130(13)	0.7097(3)
C(21A)	0.52782(20)	0.31596(11)	0.89428(23)
C(22A)	0.48024(22)	0.28335(13)	0.9150(3)
C(23A)	0.5030(3)	0.25358(14)	0.9749(3)
C(24A)	0.5723(3)	0.25653(14)	1.0159(3)
C(25A)	0.61946(25)	0.28945(15)	0.9944(3)
C(26A)	0.59880(22)	0.31875(13)	0.9336(3)
C(31A)	0.46075(21)	0.39757(12)	0.8922(3)
C(32A)	0.42227(23)	0.38681(14)	0.9678(3)
C(33A)	0.3948(3)	0.41744(18)	1.0220(3)
C(34A)	0.4032(3)	0.45917(18)	0.9994(4)
C(35A)	0.4401(3)	0.46999(15)	0.9253(4)
C(36A)	0.4706(3)	0.43920(14)	0.8715(3)
C(11B)	0.66079(21)	0.43399(11)	0.69529(24)
C(12B)	0.6854(3)	0.44430(13)	0.7776(3)
C(13B)	0.7386(3)	0.47630(17)	0.7872(3)
C(14B)	0.7645(3)	0.49703(18)	0.7153(3)
C(15B)	0.7379(3)	0.48764(15)	0.6337(3)
C(16B)	0.6863(3)	0.45574(13)	0.6232(3)
C(21B)	0.52588(20)	0.40671(12)	0.60781(24)
C(22B)	0.50061(24)	0.44766(13)	0.6093(3)
C(23B)	0.4455(3)	0.46060(14)	0.5532(3)
C(24B)	0.41488(24)	0.43302(15)	0.4946(3)
C(25B)	0.43835(25)	0.39220(14)	0.4929(3)
C(26B)	0.49287(22)	0.37841(13)	0.5496(3)
C(31B)	0.65403(21)	0.35116(11)	0.62641(25)
C(32B)	0.6677(3)	0.35375(13)	0.5372(3)
C(33B)	0.7172(3)	0.32699(16)	0.4986(3)
C(34B)	0.7545(3)	0.29757(15)	0.5472(3)
C(35B)	0.74118(25)	0.29431(14)	0.6336(3)
C(36B)	0.69001(23)	0.32088(13)	0.6750(3)

$CDCl_3$, 100 MHz): protons at ring-3 and -5 positions, δ 8.35 (3H, br), 8.22 (3H, br); the central proton of allyl, 3.78 (1H, s); the *syn*-protons of allyl, 3.73 (2H, br); the *anti*-protons of allyl, 1.66 (2H, d, J(H,H) = 7.8). $[Mo(PhBTz_3)(CO)_2(\eta^3\text{-allyl})]$, yellow. Anal. Found: C, 41.80; H, 3.35; N, 25.83. $C_{17}H_{16}BMoN_9O_2$ calc.: C, 42.09; H, 3.32; N, 25.99%. IR (KBr): ν(CO), 1954s, 1856s, and IR (CH_2Cl_2): ν(CO), 1960s, 1866s cm^{-1}. ^1H NMR (25°C, $CDCl_3$, 100 MHz): protons at ring-3 and -5 positions, δ 8.39 (3H, br), 7.98 (3H, br); Ph, 7.80 (2H, m), 7.62 (3H, m); the central proton of allyl, 3.87 (1H, s); the *syn*-protons of allyl, 3.76 (2H, br); the *anti*-protons of allyl, 1.67 (2H, d, J(H,H) = 7.8).

2.8. X-Ray diffraction study of $[NEt_4][Mo(HBPz_3)(CO)_3]$ and $[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]$

All the single crystals were grown from CH_2Cl_2/hexane at room temperature. General procedures and listings of programs were previously given [6a,11]. Absorption correction was performed on the structures

TABLE 3. Selected bond lengths (Å) and angles (°) for $\mathrm{[NEt_4][Mo(HBPz_3)(CO)_3]}$ and $\mathrm{[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]}$

(a) $\mathrm{[NEt_4][Mo(HBPz_3)(CO)_3]}$

(i) Bond lengths

N–C(4)	1.500(7)	C(4)–C(8)	1.497(9)
N–C(5)	1.520(7)	C(5)–C(9)	1.498(8)
N–C(6)	1.497(7)	C(6)–C(10)	1.527(9)
N–C(7)	1.528(7)	C(7)–C(11)	1.495(9)

	n = 1	n = 2	n = 3
Mo–C(n)	1.926(4)	1.924(5)	1.925(5)
Mo–N(n1)	2.263(3)	2.261(4)	2.272(4)
B–N(n2)	1.551(6)	1.537(6)	1.527(6)
C(n)–O(n)	1.167(6)	1.184(7)	1.177(6)
N(n1)–N(n2)	1.373(5)	1.362(5)	1.362(5)
N(n2)–C(n3)	1.341(6)	1.355(6)	1.348(6)
C(n3)–C(n4)	1.363(7)	1.373(8)	1.365(8)
C(n4)–C(n5)	1.382(7)	1.370(7)	1.381(7)
C(n5)–N(n1)	1.326(6)	1.346(6)	1.337(6)

(ii) Bond angles

C(4)–N–C(5)	111.3(4)	C(6)–N–C(7)	112.7(5)
C(4)–N–C(6)	110.1(4)	N–C(4)–C(8)	116.5(5)
C(4)–N–C(7)	107.0(4)	N–C(5)–C(9)	115.6(5)
C(5)–N–C(6)	108.0(4)	N–C(6)–C(10)	114.9(5)
C(5)–N–C(7)	107.7(4)	N–C(7)–C(11)	115.8(5)
C(1)–Mo–C(2)	84.9(2)	C(1)–Mo–N(11)	172.9(2)
C(1)–Mo–C(3)	90.4(2)	C(1)–Mo–N(21)	97.4(2)
C(2)–Mo–C(3)	86.8(2)	C(1)–Mo–N(31)	92.1(1)
N(11)–Mo–N(21)	80.0(1)	C(2)–Mo–N(11)	97.6(2)
N(11)–Mo–N(31)	80.9(1)	C(2)–Mo–N(21)	117.6(2)
N(21)–Mo–N(31)	80.4(1)	C(2)–Mo–N(31)	99.2(2)
N(12)–B–N(22)	109.3(4)	C(3)–Mo–N(11)	96.4(2)
N(12)–B–N(32)	108.9(4)	C(3)–Mo–N(21)	93.5(2)
N(22)–B–N(32)	109.0(4)	C(3)–Mo–N(31)	173.6(2)

	n = 1	n = 2	n = 3
Mo–N(n1)–N(n2)	121.2(3)	122.0(3)	121.4(3)
Mo–N(n1)–C(n5)	132.8(3)	131.8(3)	131.9(3)
Mo–C(n)–O(n)	176.7(5)	176.0(4)	179.7(5)
B–N(n2)–N(n1)	120.0(3)	119.9(4)	120.4(3)
B–N(n2)–C(n3)	130.2(4)	130.4(4)	130.4(4)
N(n1)–N(n2)–C(n3)	109.7(4)	109.6(4)	109.1(4)
N(n2)–C(n3)–C(n4)	108.0(4)	107.7(5)	108.9(4)
C(n3)–C(n4)–C(n5)	105.8(4)	106.1(5)	105.0(5)
C(n4)–C(n5)–N(n1)	110.6(4)	110.4(5)	110.6(4)
N(n2)–N(n1)–C(n5)	106.0(3)	106.2(4)	106.4(4)

(b) $\mathrm{[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]}$

(i) Bond lengths

N–P(1)	1.574(3)	C(32A)–C(33A)	1.375(6)
N–P(2)	1.575(3)	C(33A)–C(34A)	1.388(8)
P(1)–C(11A)	1.799(4)	C(34A)–C(35A)	1.359(9)
P(1)–C(21A)	1.796(4)	C(35A)–C(36A)	1.394(7)
P(1)–C(31A)	1.808(4)	C(11B)–C(12B)	1.376(5)
P(2)–C(11B)	1.804(4)	C(11B)–C(16B)	1.383(5)
P(2)–C(21B)	1.794(4)	C(12B)–C(13B)	1.403(6)
P(2)–C(31B)	1.803(4)	C(13B)–C(14B)	1.367(8)
C(11A)–C(12A)	1.386(6)	C(14B)–C(15B)	1.372(7)
		C(15B)–C(16B)	1.384(6)
C(11A)–C(16A)	1.403(6)	C(21B)–C(22B)	1.386(6)
C(12A)–C(13A)	1.374(6)	C(21B)–C(26B)	1.402(5)
C(13A)–C(14A)	1.353(7)	C(22B)–C(23B)	1.370(6)
C(14A)–C(15A)	1.367(7)	C(23B)–C(24B)	1.373(7)
C(15A)–C(16A)	1.375(6)	C(24B)–C(25B)	1.373(7)

TABLE 3 (continued)

C(21A)–C(22A)	1.382(5)	C(25B)–C(26B)	1.376(6)
C(21A)–C(26A)	1.404(5)	C(31B)–C(32B)	1.392(6)
C(22A)–C(23A)	1.384(6)	C(31B)–C(36B)	1.381(5)
C(23A)–C(24A)	1.389(7)	C(32B)–C(33B)	1.364(6)
C(24A)–C(25A)	1.387(7)	C(33B)–C(34B)	1.372(7)
C(25A)–C(26A)	1.372(6)	C(34B)–C(35B)	1.350(7)
C(31A)–C(32A)	1.391(6)	C(35B)–C(36B)	1.399(6)
C(31A)–C(36A)	1.381(6)		
	n = 1	*n* = 2	*n* = 3
Mo–C(*n*)	1.917(4)	1.924(4)	1.926(4)
Mo–N(*n*1)	2.288(3)	2.274(3)	2.279(3)
B–N(*n*2)	1.530(6)	1.535(6)	1.545(6)
C(*n*)–O(*n*)	1.167(5)	1.176(5)	1.162(5)
N(*n*1)–N(*n*2)	1.364(4)	1.359(4)	1.360(5)
N(*n*2)–C(*n*3)	1.340(5)	1.332(5)	1.331(6)
C(*n*3)–N(*n*4)	1.311(5)	1.305(6)	1.322(7)
N(*n*4)–C(*n*5)	1.349(5)	1.346(6)	1.346(7)
C(*n*5)–N(*n*1)	1.320(5)	1.318(5)	1.311(6)
(ii) Bond angles			
C(1)–Mo–C(2)	83.84(18)	C(1)–Mo–N(11)	173.13(15)
C(1)–Mo–C(3)	90.37(18)	C(1)–Mo–N(21)	95.07(16)
C(2)–Mo–C(3)	84.35(18)	C(1)–Mo–N(31)	97.04(15)
N(11)–Mo–N(21)	79.93(11)	C(2)–Mo–N(11)	101.15(14)
N(11)–Mo–N(31)	77.61(11)	C(2)–Mo–N(21)	178.91(14)
N(21)–Mo–N(31)	81.14(12)	C(2)–Mo–N(31)	99.07(15)
N(12)–B–N(22)	107.9(3)	C(3)–Mo–N(11)	94.79(15)
N(12)–B–N(32)	107.1(3)	C(3)–Mo–N(21)	95.58(14)
N(22)–B–N(32)	108.8(3)	C(3)–Mo–N(31)	172.11(15)
N–P(2)–C(11B)	108.56(17)	P(1)–C(31A)–C(36A)	119.9(3)
N–P(2)–C(21B)	116.17(17)	C(32A)–C(31A)–C(36A)	119.5(4)
N–P(2)–C(31B)	112.01(18)	C(31A)–C(32A)–C(33A)	120.2(4)
C(11B)–P(2)–C(21B)	106.74(18)	C(32A)–C(33A)–C(34A)	119.9(5)
C(11B)–P(2)–C(31B)	104.77(17)	C(33A)–C(34A)–C(35A)	120.4(4)
C(21B)–P(2)–C(31B)	107.88(18)	C(34A)–C(35A)–C(36A)	120.2(5)
P(1)–C(11A)–C(12A)	121.2(3)	C(31A)–C(36A)–C(35A)	119.9(4)
P(1)–C(11A)–C(16A)	119.2(3)	P(2)–C(11B)–C(12B)	119.4(3)
C(12A)–C(11A)–C(16A)	119.3(4)	P(2)–C(11B)–C(16B)	120.0(3)
C(11A)–C(12A)–C(13A)	119.6(4)	C(12B)–C(11B)–C(16B)	120.5(4)
C(12A)–C(13A)–C(14A)	120.8(4)	C(11B)–C(12B)–C(13B)	119.0(4)
C(13A)–C(14A)–C(15A)	120.6(4)	C(12B)–C(13B)–C(14B)	119.9(4)
C(14A)–C(15A)–C(16A)	120.5(4)	C(13B)–C(14B)–C(15B)	120.8(4)
C(11A)–C(16A)–C(15A)	119.1(4)	C(14B)–C(15B)–C(16B)	119.8(4)
P(1)–C(21A)–C(22A)	122.4(3)	C(11B)–C(16B)–C(15B)	199.8(4)
P(1)–C(21A)–C(26A)	117.4(3)	P(2)–C(21B)–C(22B)	120.2(3)
C(22A)–C(21A)–C(26A)	120.1(3)	P(2)–C(21B)–C(26B)	120.7(3)
C(21A)–C(22A)–C(23A)	119.5(4)	C(22B)–C(21B)–C(26B)	119.1(3)
C(22A)–C(23A)–C(24A)	120.9(4)	C(21B)–C(22B)–C(23B)	120.6(4)
P(1)–N–P(2)	141.19(21)	C(22B)–C(23B)–C(24B)	120.1(4)
N–P(1)–C(11A)	114.31(17)	C(23B)–C(24B)–C(25B)	120.2(4)
N–P(1)–C(21A)	109.42(17)	C(24B)–C(25B)–C(26B)	120.6(4)
N–P(1)–C(31A)	110.14(18)	C(21B)–C(26B)–C(25B)	119.4(4)
C(11A)–P(1)–C(21A)	109.77(18)	P(2)–C(31B)–C(32B)	121.0(3)
C(11A)–P(1)–C(31A)	107.06(17)	P(2)–C(31B)–C(36B)	119.3(3)
C(21A)–P(1)–C(31A)	105.77(18)	C(32B)–C(31B)–C(36B)	119.4(4)
C(23A)–C(24A)–C(25A)	118.8(4)	C(31B)–C(32B)–C(33B)	120.1(4)
C(24A)–C(25A)–C(26A)	121.2(4)	C(32B)–C(33B)–C(34B)	120.6(4)
C(21A)–C(26A)–C(25A)	119.3(4)	C(33B)–C(34B)–C(35B)	120.0(4)
P(1)–C(31A)–C(32A)	120.6(3)	C(34B)–C(35B)–C(36B)	120.9(4)
		C(31B)–C(36B)–C(35B)	118.9(4)

TABLE 3 (continued)

	n = 1	*n* = 2	*n* = 3
Mo–N(*n*1)–N(*n*2)	122.29(23)	121.35(22)	121.36(23)
Mo–N(*n*1)–C(*n*5)	133.9(3)	134.8(3)	134.9(3)
Mo–C(*n*)–O(*n*)	178.9(4)	174.6(3)	177.6(4)
B–N(*n*2)–N(*n*1)	121.1(3)	121.7(3)	121.6(3)
B–N(*n*2)–C(*n*3)	131.8(3)	131.2(3)	130.7(4)
N(*n*1)–N(*n*2)–C(*n*3)	107.0(3)	107.0(3)	107.4(4)
N(*n*2)–C(*n*3)–N(*n*4)	112.9(4)	112.5(3)	112.3(4)
C(*n*3)–N(*n*4)–C(*n*5)	101.9(4)	102.3(3)	101.7(4)
N(*n*4)–C(*n*5)–N(*n*1)	114.4(4)	114.4(4)	115.0(5)
N(*n*2)–N(*n*1)–C(*n*5)	103.7(3)	103.8(3)	103.7(4)

using ψ scans. Related crystal data (Table 1), final coordinates of the non-hydrogen atoms (Table 2), and selected bond lengths and bond angles (Table 3) are reported. The anisotropic displacement coefficients of the atoms, the H-atom coordinates and structural factors are available from the authors. The ORTEP plots for anions, $[Mo(HBPz_3)(CO)_3]^-$ and $[Mo(HBTz_3)(CO)_3]^-$ were all quite similar and are shown as one plot (Fig. 1).

3. Results and discussion

The $KHBTz_3$ salt can be obtained in an analogous way to the preparation of $KHBPz_3$ [12] from the melt reaction of KBH_4 in excess HTz at 200°C. Although a similar reaction between $NaBPh_4$ and HPz at high temperatures gives only the disubstituted product $NaPh_2BPz_2$ [13], the reaction between $NaBPh_4$ and HTz first affords $NaPh_2BTz_2$ [14] and then $NaPhBTz_3$, reflecting the proton of HTz being more acidic than that of HPz [15]. The L anion ($L^- = HBTz_3^-$ or $PhBTz_3^-$) can replace the three mutually *cis*-carbonyls of $[Mo(CO)_6]$ in a similar way to $HBPz_3^-$, $HBPz'^-_3$ [17], $HBPz''^-_3$ [8], $HBBz_3^-$ [6a], or $HBPz^{\star -}_3$ [16] (Pz′ = 3,5-dimethylpyrazol-1-yl; Pz″ = 3,4,5-trimethylpyrazol-1-yl; Pz* = 3-methylpyrazol-1-yl; Bz = benzotriazol-1-yl) to give $[MoL(CO)_3]^-$. The addition of electrophiles to $M[MoL(CO)_3]$ (M = Na or K) or $[Et_4N][MoL(CO)_3]$ converts the salts readily into $[MoL(CO)_3X]$ (X = Br or I), $[MoL(CO)_2(NO)]$, and $[MoL(CO)_2(\eta^3\text{-allyl})]$ (Scheme 1). Apparently, the reaction chemistry of $[Mo(HBTz_3)(CO)_3]^-$ or $[Mo(PhBTz_3)(CO)_3]^-$ is quite similar to that of $[Mo(HBPz_3)(CO)_3]^-$, $[Mo(HBPz'_3)(CO)_3]^-$ [1] or $[Mo(HBBz_3)(CO)_3]^-$ [6a] towards the electrophiles we used in this study.

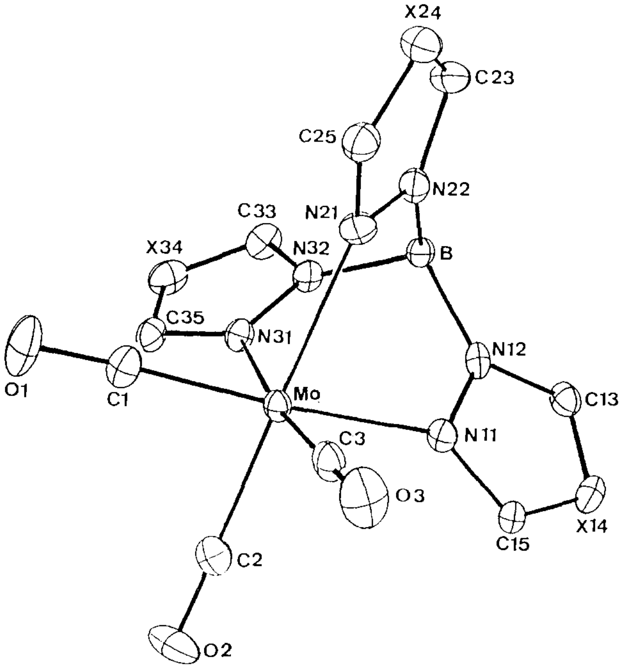
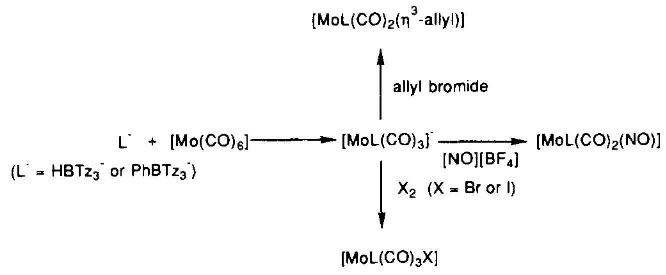


Fig. 1. ORTEP plot for anions, $[Mo(HBPz_3)(CO)_3]^-$ (X = C) and $[Mo(HBTz_3)(CO)_3]^-$ (X = N), showing the numbering scheme. The ellipsoids were drawn at the 50% probability level.

All the anions, $[MoL'(CO)_3]^-$ ($L' = HBPz_3^-$, $HBPz'^-_3$, $HBPz''^-_3$, $HBPz^{\star -}_3$, $HBBz_3^-$, $HBTz_3^-$, or $PhBTz_3^-$; Pz″ = 3,4,5-trimethylpyrazol-1-yl), belong to the point group of C_{3v} and display one strong (A_1) and one very strong (E) carbonyl stretching bands in solution. The averaged $\nu(CO)$ values taken as $1/3\ \nu(A_1) + 2/3\ \nu(E)$ for the anions measured in MeCN are calculated as follows: $L' = HBBz_3^-$, 1834 cm^{-1} [6a]; $HBPz_3^-$, 1806 cm^{-1}; $HBPz'^-_3$, 1798 cm^{-1} [17]; $HBPz''^-_3$,



Scheme 1.

1793 cm^{-1} [8]; $HBPz^{*}_3{}^-$, 1799 cm^{-1} [16]; $HBTz_3^-$, 1819 cm^{-1}; and $PhBTz_3^-$, 1818 cm^{-1}, indicating the increasing order of electron donating power as $HBBz_3^-$ < $HBTz_3^-$, $PhBTz_3^-$ < $HBPz_3^-$ < $HBPz'_3{}^-$, $HBPz^{*}_3{}^-$ < $HBPz''_3{}^-$. The weaker donating ability of $HBTz_3^-$ compared with that of $HBPz_3^-$ is compatible with HTz being more acidic than HPz [15]. From these values, it is clear that (1) the replacement of the hydrogen atom on the boron atom by a phenyl group in $HBTz_3^-$ (to give $PhBTz_3^-$) or the replacement of the hydrogen atoms on the pyrazolyl ring-5 position with the methyl groups in $HBPz^{*}_3{}^-$ (to give $HBPz'_3{}^-$) does not change at all the donating ability of the relevant ligands; (2) the substitution of the hydrogen atoms on pyrazolyl ring-3, -4, or -5 position with methyl groups, converting from $HBPz_3^-$ to $HBPz'_3{}^-$ or $HBPz''_3{}^-$ increases the ability slightly and (3) the replacement of the CH atoms on pyrazolyl ring-3 or -4 position by a nitrogen atom in making Bz or Tz, respectively, do weaken this ability. As reported earlier [6a], the complete reaction between $[Mo(HBBz_3)(CO)_3]^-$ and allyl bromide needs about 17 h while a similar reaction takes only about 3 h for $[Mo(HBTz_3)(CO)_3]^-$ or $[Mo(PhBTz_3)(CO)_3]^-$, showing that the much weaker donativity of $HBBz_3^-$ retards more strongly the oxidative allyl bromination of $[MoL(CO)_3]^-$ (L^- = $HBTz_3^-$, $PhBTz_3^-$ or $HBBz_3^-$) than $HBTz_3^-$ or $PhBTz_3^-$. Thus, the replacement of the CH atoms on the ring-3 position by a nitrogen atom has a stronger effect than the substitution on the ring-4 position.

In order further to compare the relevant structure features of $[MoL'(CO)_3]^-$ (L' = $HBPz_3^-$, $HBPz'_3{}^-$, $HBTz_3^-$, or $HBPz^{*}_3{}^-$), we determined the solid-state structures of $[NEt_4][Mo(HBPz_3)(CO)_3]$ (**1**) and $[N(PPh_3)_2][Mo(HBTz_3)(CO)_3]$ (**4**). The two anions are isostructural (Fig. 1), as expected, to $[NEt_4][Mo(HBPz'_3)(CO)_3]$ (**3**) [19] and $[NEt_4][Mo(HBPz^{*}_3)(CO)_3]$ (**2**) [16]. To our surprise, **1** and **4** are even X-ray isomorphous in a space group of *Pbca*. Apparently, the cone angles of $HBPz_3^-$ and $HBTz_3^-$ should be similar and the two similar anions $[Mo(HBPz_3)(CO)_3]^-$ and $[Mo(HBTz_3)(CO)_3]^-$ being larger than the cations NEt_4^+ or $N(PPh_3)_2^+$ determines the packing habit in the crystal [18]. As the methyl groups replace the hydrogen atoms symmetrically at the pyrazolyl ring-3 and -5 positions, converting $HBPz_3^-$ into $HBPz'_3{}^-$, this changes the habit to the space group of lower symmetry ($Pna2_1$) for $[NEt_4][Mo(HBPz'_3)(CO)_3]$ [19] and the less symmetric replacement of the hydrogen atoms, at the ring-3 position only, by methyl groups in the process of formation of $HBPz^{*}_3{}^-$ from $HBPz_3^-$ results in the space group of much lower symmetry ($P2_1$) for $[NEt_4][Mo(HBPz^{*}_3)(CO)_3]$ [16].

Some averaged bond lengths and angles calculated from the structures of anions $[MoL'(CO)_3]^-$ (L' = $HBPz_3^-$, $HBPz'_3{}^-$, $HBTz_3^-$, or $HBPz^{*}_3{}^-$) are listed in Table 4. From this table, it is clear that the angle C(n)–Mo–C(n′) of 84.4° in **3** is smaller than that of 88.0° in **1**, reflecting the different steric encumbrances (the cone angle is measured as 180 or 184° for $HBPz_3^-$ and 224 or 225° for $HBPz'_3{}^-$ [20,21]). Since the angle, C(n)–Mo–C(n′), is 85.3° in **2** (Table 4), it is reasonable to assume that the cone angle of $HBPz^{*}_3{}^-$ is less than that of $HBPz'_3{}^-$ though larger than in $HBPz_3^-$. However, the angle should be used with caution as the Mo–N(n1) and Mo–C(n) distances may be different. The angle of 86.2° in **4**, larger than that in **1**, cannot be used to infer that the cone angle for $HBTz_3^-$ is larger than that for $HBPz_3^-$, rather it has something to do with the longer Mo–N distance (Mo–N = 2.280 Å in **4** *vs.* 2.265 Å in **1** and Mo–C = 1.922 Å in **4** *vs.* 1.925 Å in **1**), which may reflect the donativity of $HBtz_3^-$ being

TABLE 4. Averaged bond lengths (Å) and angles (°) for $[MoL'(CO)_3]^-$

L^-	$HBPz_3$	$HBPz^{*}_3{}^-$	$HBPz'_3{}^-$	$HBTz_3^-$
Mo–C(*n*)	1.925 [1] [a]	1.928 [10]	1.941 [4]	1.922 [5]
C(*n*)–O(*n*)	1.176 [9]	1.168 [14]	1.167 [5]	1.168 [7]
Mo–N(*n*1)	2.265 [6]	2.285 [5]	2.263 [5]	2.280 [7]
B–N(*n*2)	1.538 [12]	1.532 [8]	1.535 [11]	1.537 [8]
N(*n*1)–N(*n*2)	1.366 [6]	1.363 [5]	1.376 [11]	1.361 [4]
N(*n*2)–C(*n*3)	1.348 [7]	1.346 [17]	1.365 [9]	1.334 [5]
C(*n*3)–X(*n*4) [b]	1.367 [5]	1.356 [20]	1.351 [10]	1.313 [9]
X(*n*4)–C(*n*5)	1.378 [7]	1.391 [15]	1.388 [27]	1.347 [2]
C(*n*5)–N(*n*1)	1.336 [10]	1.335 [6]	1.341 [29]	1.316 [5]
N(*n*1)–Mo–N(*n*′1)	80.4 [5]	81.0 [8]	81.3 [11]	79.6 [18]
N(*n*2)–B–N(*n*′2)	109.1 [2]	109.0 [7]	109.2 [3]	107.9 [9]
C(*n*)–Mo–C(*n*′)	88.0 [29]	85.3 [10]	84.4 [11]	86.2 [36]
Reference	this work	[16]	[19]	this work

[a] Standard deviations in square brackets were calculated by $\sigma = (\Sigma(x - \bar{x})^2/(N-1))^{1/2}$. N = the number of data used; [b] X = C for anions with L' = $HBPz_3^-$, $HBPz^{*}_3{}^-$ or $HBPz'_3{}^-$ and X = N for for $HBTz_3^-$.

weaker than that of $HBPz_3^-$, as observed in the larger averaged carbonyl-stretching value stated above. The Mo–N distance is 2.285 Å in **2** but 2.263 Å in **3**, giving only weak support to the 5-methyl-group effect for nickel pseudohalides suggested by Trofimenko *et al.* [9], whereby the presumed nonbonded repulsive interactions among the methyl groups at the ring-5 position are alleviated by tightening of the "bite" of the tridentate ligands around the metal atom with shortening Mo–N distances. It is probably true from the similarity of the Mo–N distances of 2.265 Å in **1** and 2.263 Å in **3** that the averaged value of 2.264 Å from the two may represent the closest distance between the tripodal ligand and the metal atom in **1–4**. Thus, if the 5-methyl-group effect is present at all in metal compounds, this effect should be manifested more clearly in the four-coordinate complexes such as the nickel compounds used by these other workers [9] compared with that in the six-coordinate compounds used in this paper.

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