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Organotransition-metal complexes of multidentate ligands

IX *. Synthesis and structure of hydridotris(benzotriazol-1-yl)borate derivatives of the group VI metal carbonyls

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Abstract

Potassium hydridotris(benzotriazol-1-yl)borate (KL) reacts with $[M(CO)_6]$ (M = Mo, W) to give $K[ML(CO)_3]$. Upon addition of electrophiles, the potassium salts and also $[Et_4N][ML(CO)_3]$ are converted readily into $[ML(CO)_3Br]$, $[ML(CO)_3I]$, $[ML(CO)_2(NO)]$ and $[ML(CO)_2(\pi\text{-allyl})]$. The solid-state structure of $[MoL(CO)_2(\pi\text{-allyl})]$ has been determined by X-ray diffraction, showing that the tridentate ligand (L^-) contains the more hindered B–N bonds and that the metal coordination occurs at the 2 position of the ring of the benzotriazolyl fragments of the ligand.

Introduction

Our success in the preparation and the structural characterization of several organotransition-metal complexes of the pyrazole-derived multidentates [1] has led to explore other multidentate ligands prepared from the different heterocyclic compounds and the corresponding derivatives of the group VI metal carbonyls [2]. The recent report by Lalor, Miller and Garvey [3] on the synthesis and reactivity of potassium hydridotris(benzotriazol-1-yl)borate (KL) has prompted us to provide details of our preparation and the applications of KL. We present here our evidence that clearly shows the geometrical structure of the uninegative nitrogen-tripod ligand, L^-, to have the more hindered B–N bonds, shown in I, rather than the less hindered B–N bonds, displayed in II.

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* For Part VIII, see ref. 1a.

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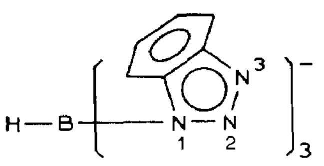
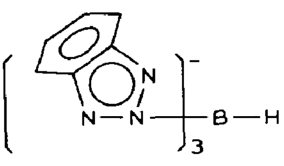


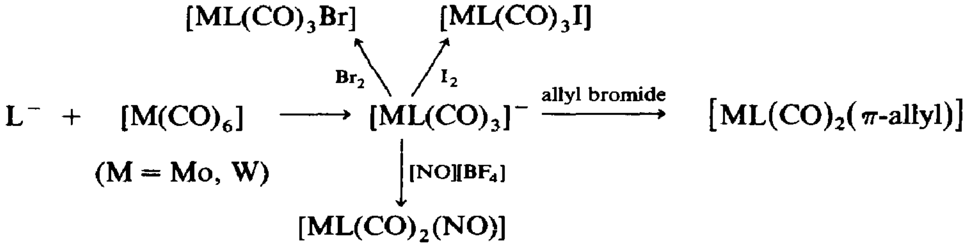
I



II

Results and discussion

A mixture of 1-*H*-benzotriazole and KBH_4 when heated gradually to 220°C results in the evolution of three moles of H_2, and work-up of the reaction mixture gives a white solid, analysis of which is consistent with potassium hydridotris(benzotriazol-1-yl)borate (KL). The L anion can replace the three mutually cis carbonyls of $[M(CO)_6]$ (M = Mo, W) to give $[ML(CO)_3]^-$. The addition of electrophiles to $K[ML(CO)_3]$ or $[Et_4N][ML(CO)_3]$ converts the salts readily into $[MoL(CO)_3Br]$ (**I**), $[WL(CO)_3Br]$ (**II**), $[MoL(CO)_3I]$ (**III**), $[WL(CO)_3I]$ (**IV**), $[MoL(CO)_2(NO)]$ (**V**), $[WL(CO)_2(NO)]$ (**VI**), $[MoL(CO)_2(\pi\text{-allyl})]$ (**VII**) and $[WL(CO)_2(\pi\text{-allyl})]$ (**VIII**) (Scheme 1).



Scheme 1

In Table 1 are listed the analytical data for, and the color and yields of KL and the complexes we have isolated. The spectroscopic data of KL and of all the ML complexes we have isolated are listed in Table 2. Since the salts $K[WL(CO)_3]$ and $[Et_4N][WL(CO)_3]$ are very air-sensitive, they were allowed to react with electrophiles in solution without prior isolation to give the neutral WL complexes. On the basis of our data and those for the analogous MoTp or MoTp′ complexes (Tp^- = hydridotris(pyrazol-1-yl)borate; Tp'^- = hydridotris(3,5-dimethylpyrazol-1-yl)borate) [4-6], as well as the solid-state structure of **VII** described below, both $[ML(CO)_2(NO)]$ and $[ML(CO)_2(\pi\text{-allyl})]$ have the structure depicted formally as **III** with L = NO and π-allyl, respectively, whereas $[ML(CO)_3X]$ (X = Br, I) has the geometry, **IV**, similar to that of $[MoTp(CO)_3Br]$. Since only one set of resonance signals can be assigned to benzotriazolyl carbons in the $^{13}C\{^1H\}$ NMR spectra of $[ML(CO)_2(\pi\text{-allyl})]$ and $[ML(CO)_3X]$, these complexes are probably fluxional in solution at room temperature.

It is noteworthy that $[ML(CO)_2(\pi\text{-allyl})]$ and $[MoTp(CO)_2(\pi\text{-allyl})]$ can be obtained by a direct route by reaction of relevant anion with the allyl bromide, whereas the previously described complex $[MoTp'(CO)_2(\pi\text{-allyl})]$, cannot be obtained by a similar direct-allylation but can be obtained indirectly from the reaction of KTp′ with $[Mo(CH_3CN)_2(CO)_2(\pi\text{-allyl})Br]$ [5]. Thus, the nucleophilicities of the

Table 1

Analytical data for KL and the ML compounds

Compound	Analysis (found (calcd.) (%))			Color	Yield (%)
	C	H	N		
KL	53.57 (53.34)	3.45 (3.23)	31.50 (31.11)	white	93
[Et_4N][MoL(CO)$_3$]	51.18 (51.50)	4.90 (4.92)	20.68 (20.71)	orange-red	89
[MoL(CO)$_3$Br] (I)	39.88 (40.29)	2.29 (2.09)	19.76 (20.14)	yellow-brown	81
[WL(CO)$_3$Br] (II)	35.16 (35.32)	1.90 (1.84)	17.58 (17.66)	orange-yellow	89
[MoL(CO)$_3$I] (III)	37.22 (37.47)	2.03 (1.95)	18.69 (18.73)	red-brown	85
[WL(CO)$_3$I] (IV)	32.98 (33.14)	1.78 (1.72)	16.46 (16.57)	orange-red	88
[MoL(CO)$_2$(NO)]·$\frac{1}{2}H_2O$ (V)	43.26 (43.11)	2.53 (2.53)	24.89 (25.14)	orange-yellow	69
[WL(CO)$_2$(NO)]·$\frac{1}{2}H_2O$ (VI)	37.11 (37.22)	2.18 (2.18)	21.68 (21.73)	yellow-brown	68
[MoL(CO)$_2$(π-C_3H_5)] (VII)	49.01 (49.40)	3.29 (3.24)	22.35 (22.55)	orange-yellow	86
[WL(CO)$_2$(π-C_3H_5)] (VIII)	42.29 (42.69)	2.87 (2.80)	19.30 (19.48)	orange-yellow	85

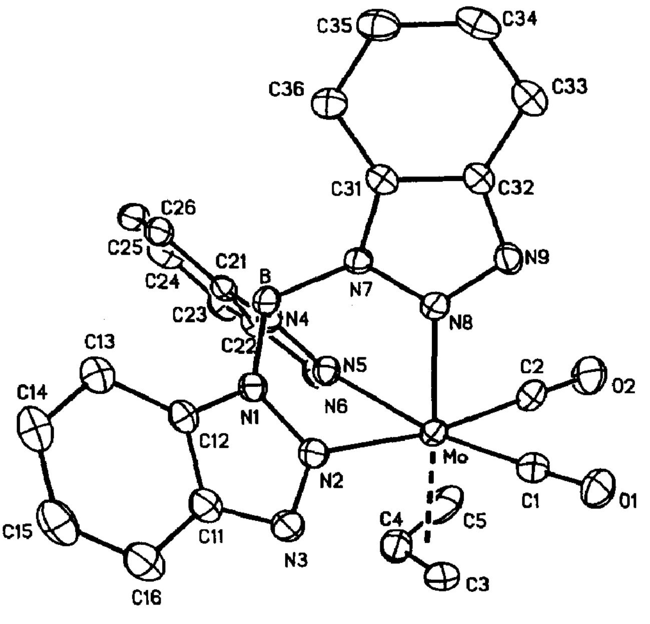


Fig. 1. Structure of [MoL(CO)$_2$(π-C_3H_5)] (VII) with numbering scheme. The probability ellipsoids are at the 50% level.

Table 2

Spectroscopic data for KL and the ML compounds

Complex	IR ^{a}, cm^{-1}			NMR ^{b,c}, ppm	
	ν(CO)		ν(BH)	^{1}H	^{13}C{^{1}H}
	KBr	solution	KBr		
KL			2496(w)	7.99 (3 H, m)	
				7.93 (3 H, m)	
				7.49 (3 H, m)	
				7.30 (3 H, m)	
[Et$_4$N][MoL(CO)$_3$]	1906(s)	1908(s)	2492(w)	8.10 (3 H, d, J = 8.3 Hz)	229.7 (3 C, s) 112.4 (3 C, s)
	1775(vs)	1790(vs)		7.94 (3 H, d, J = 8.5 Hz)	146.4 (3 C, s)
				7.52 (3 H, dd)	138.7 (3 C, s)
				7.34 (3 H, dd)	128.2 (3 C, s)
				3.12 (8 H, q, J = 7.3 Hz)	125.1 (3 C, s)
				1.17 (12 H, tt)	118.3 (3 C, s)
(I)	2064(s)	2060(s)	2520(w)	8.30 (3 H, d, J = 8.8 Hz)	234.6 (3 C, s) 126.2 (3 C, s)
	1996(s)	1998(s)		8.08 (3 H, d, J = 8.7 Hz)	146.0 (3 C, s) 119.7 (3 C, s)
	1966(s)	1970(s)		7.71 (3 H, dd)	137.4 (3 C, s) 111.9 (3 C, s)
				7.51 (3 H, dd)	130.0 (3 C, s)
(II)	2056(s)	2056(s)	2536(w)	8.33 (3 H, d, J = 8.8 Hz)	206.1 (3 C, s) 127.4 (3 C, s)
	1982(s)	1972(s)		8.10 (3 H, d, J = 8.4 Hz)	147.1 (3 C, s) 120.0 (3 C, s)
	1942(s)	1944(s)		7.75 (3 H, dd)	138.4 (3 C, s)113.3 (3 C, s)
				7.55 (3 H, dd)	131.2 (3 C, s)
(III)	2060(s)	2056(s)	2524(w)	8.25 (3H, d, J = 8.6 Hz)	233.9 (3 C, s) 127.1 (3 C, s)
	1998(s)	1990(s)		8.06 (3 H, d, J = 7,9 hz)	146.7 (3 C, s) 120.0 (3 C, s)
	1960(s)	1964(s)		7.68 (3 H, dd)	138.3 (3 C, s) 113.3 (3 C, s)
				7.48 (3 H, dd)	130.9 (3 C, s)
(IV)	2040(s)	2044(s)	2528(w)	8.30 (3 H, d, J = 8.6 Hz)	206.1 (3 C, s) 127.4 (3 C, s)

	1960(s)	1970(s)		8.09 (3 H, d, $J = 8.8$ Hz)	147.1 (3 C, s) 120.1 (3 C, s)
	1942(s)	1944(s)		7.73 (3 H, dd)	138.4 (3 C, s) 113.4 (3 C, s)
				7.53 (3 H, dd)	131.2 (3 C, s)
(V)	2036(s)	2040(s)	2488(w)	8.05 (3 H, m)	220.9 (3 C, s) 129.7 (1 C, s) 119.6 (2 C, s)
	1952(s)	1962(s)		7.98 (3 H, m)	146.0 (2 C, s) 128.9 (2 C, s) 111.5 (1 C, s)
	1694(s) [d]	1694(s) [d]		7.57 (3 H, m)	145.3 (1 C, s) 125.9 (1 C, s) 111.2 (2 C, s)
				7.40 (3 H, s)	137.5 (2 C, s) 125.4 (2 C, s)
					136.8 (1 C, s) 119.8 (1 C, s)
(VI)	2024(s)	2028(s)	2492(w)	8.03 (3 H, m)	218.2 (2 C, s) 130.2 (1 C, s) 119.8 (2 C, s)
	1926(s)	1938(s)		7.98 (3 H, m)	146.2 (2 C, s) 129.4 (2 C, s) 111.5 (1 C, s)
	1690(s) [d]	1678(s) [d]		7.60 (3 H, m)	145.5 (1 C, s) 126.3 (1 C, s) 111.2 (2 C, s)
				7.40 (3 H, m)	137.3 (2 C, s) 125.7 (2 C, s)
					136.7 (1 C, s) 119.9 (1 C, s)
(VII)	1950(s)	1960(s)	2524(w)	7.97 (3 H, br)	224.8 (2 C, s) 74.3 (1 C, s)
	1870(s)	1874(s)		7.80 (3 H, d, $J = 8.9$ Hz)	145.2 (3 C, s) 62.8 (2 C, s)
				7.51 (3 H, dd)	137.3 (3 C, s)
				7.33 (3 H, dd)	128.9 (3 C, s)
				4.93 (2 H, d, $J = 6.4$ Hz)	125.1 (3 C, s)
				3.85 (1 H, m)	119.4 (3 C, s)
				2.00 (2 H, d, $J = 9.8$ Hz)	111.5 (3 C, s)
(VIII)	1936(s)	1950(s)	2532(w)	7.97 (3 H, br)	216.6 (2 C, s) 119.6 (3 C, s)
	1856(s)	1860(s)		7.90 (3 H, d, $J = 8.6$ Hz)	145.3 (3 C, s) 111.5 (3 C, s)
				7.53 (3 H, br)	137.2 (3 C, s) 66.7 (1 C, s)
				7.36 (3 H, dd)	129.1 (3 C, s) 55.2 (2 c, s)
				4.74 (2 H, d, $J = 6.2$ Hz)	125.4 (3 C, s)
				3.10 (1 H, m)	
				2.22 (2 H, d, $J = 9.0$ Hz)	

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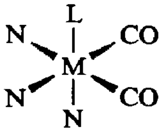
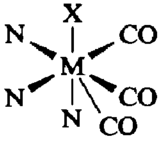
[a] In KBr discs or CH_2Cl_2 solution. Abbreviations: w. weak; s, strong; vs, very strong. [b] Spectra measured at 21° C; Chemical shifts in ppm from Me_4Si. Abbreviations: s, singlet; d, doublet; dd, doublet of doublet; tt, triplet of triplet; m, multiplet; br, broad singlet. [c] Solvents used for NMR spectra: CD_3CN for $[Et_4N][MoL(CO)_3]$ (^1H and ^{13}C); $CDCl_3$ for (V)–(VIII) (^1H and ^{13}C); acetone-d_6 for (I), (II), (IV) (^1H and ^{13}C); acetone-d_6 for (III) (^1H); CD_2Cl_2 for (III) ^{13}C). [e] ν(NO).

anions $[MoL(CO)_3]^-$ and $[MoTp(CO)_3]^-$ are comparable. Because many reactions are possible for $[MoTp(CO)_3]^-$ [7], we expect that $[MoL(CO)_3]^-$ and $[WL(CO)_3]^-$ to undergo as many if not more reactions.



III



IV

The solid-state structure of [MoL(CO)$_2$(π-allyl)] (VII)

Complex **VII** has 8 equivalent mononuclear units in the monoclinic unit cell. The molecular geometry, with numbering scheme, is depicted in the ORTEP drawing (Fig. 1). For further crystallographic details see Experimental and Table 3.

The fractional coordinates and anisotropic displacement coefficients of all the non-hydrogen atoms, and the selected bond lengths and angles for VII are given in Tables 4 and 5, respectively. Fractional atomic coordinates of all the hydrogen atoms (Table 6) and F_o vs. F_c (Table 7) are available from the authors.

The structure of **VII** consists of discrete units of $[MoL(CO)_2(\pi\text{-}C_3H_5)]$ as shown in Fig. 1. It has C_s symmetry within experimental error, with the mirror plane consisting of one benzotriazolyl fragment, the metal atom, and the central carbon

Table 3

Crystal data for $[MoL(CO)_2(\pi\text{-}C_3H_5)]$

Formula	$C_{23}H_{18}BMoN_9O_2$
Color	orange-yellow
$D_{calc.}$ (g/cm^3)	1.57
$D_{obs.}$ (g/cm^3)	1.58
Crystal size (mm)	0.4×0.2×0.2
Crystal system	monoclinic
Space group	*C2/c*
Cell dimensions:	
a (Å)	22.265(6)
b (Å)	16.711(5)
c (Å)	16.842(5)
β (°)	130.84(2)
V (Å^3)	4741(2)
Z (molecules/unit cell)	8
Data collection mode	$2\theta:\theta$
$2\theta_{max}$ (°)	50.0
h, *k*, *l* (quadrant collected)	±26, 16, 16
Radiation	Mo-K_α (λ = 0.71073 Å)
μ (mm^{-1})	0.578
Absorption correction	empirical
NO/NV [a,b]	2647/326
R^a, R_w [a]	0.035, 0.030
GOF [a]	1.35

[a] For the meaning of each term, see text. [b] No. of measurements = 4703, no. of independent reflections = 4029, no. of independent reflections with $I > 3\sigma(I)$ = 2647.

Table 4

Atomic coordinates ($\times 10^4$) and anisotropic displacement coefficients [a] ($Å^2 \times 10^3$) for $[MoL(CO)_2(\pi\text{-}C_3H_5)]$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	2288(1)	5621(1)	4020(1)	55(1)	39(1)	68(1)	−1(1)	45(1)	2(1)
O(1)	1894(2)	7228(2)	2854(3)	79(2)	53(2)	94(3)	22(2)	47(2)	11(2)
O(2)	3543(2)	6761(2)	5831(3)	93(3)	76(3)	89(3)	−33(2)	52(2)	−12(2)
C(1)	2026(2)	6622(3)	3278(4)	50(3)	54(3)	69(3)	0(3)	35(3)	1(2)
C(2)	3086(3)	6319(3)	5184(4)	73(3)	47(3)	77(4)	−7(3)	52(3)	5(2)
C(3)	1057(3)	6079(3)	3357(5)	67(3)	70(4)	145(6)	−20(4)	74(4)	−2(3)
C(4)	1375(4)	5522(3)	4161(6)	110(5)	58(4)	166(6)	−11(4)	120(5)	−10(3)
C(5)	2038(4)	5768(3)	5147(5)	149(6)	74(4)	137(5)	7(4)	124(5)	23(4)
N(1)	1863(2)	4144(2)	2521(3)	47(2)	41(2)	51(2)	4(2)	33(2)	−1(2)
N(2)	1527(2)	4778(2)	2607(3)	51(2)	44(2)	61(2)	6(2)	36(2)	1(2)
N(3)	762(2)	4827(2)	1791(3)	50(2)	49(2)	64(3)	12(2)	80(2)	5(2)
N(4)	2923(2)	3830(2)	4432(2)	48(2)	35(2)	48(2)	0(2)	33(2)	0(2)
N(5)	2763(2)	4406(4)	4836(3)	59(2)	44(2)	52(2)	0(2)	39(2)	−3(2)
N(6)	2971(2)	4179(2)	5730(3)	64(2)	54(3)	56(2)	−4(2)	43(2)	−10(2)
N(7)	3236(2)	4665(2)	3521(2)	45(2)	43(2)	48(2)	0(2)	34(2)	1(1)
N(8)	3142(2)	5392(2)	3786(3)	50(2)	43(2)	57(2)	1(2)	37(2)	1(2)
N(9)	3655(2)	5912(2)	3943(3)	54(2)	43(2)	58(2)	0(2)	37(2)	−7(2)
B	2746(3)	3953(3)	3388(3)	50(3)	37(3)	52(3)	4(2)	34(3)	1(2)
C(11)	600(2)	4203(2)	1150(3)	49(3)	52(3)	48(3)	14(2)	26(2)	−5(2)
C(12)	1284(2)	3767(2)	1600(3)	51(3)	46(2)	42(3)	5(2)	30(2)	−8(2)
C(13)	1288(3)	3075(3)	1131(3)	64(3)	60(3)	52(3)	−2(2)	41(3)	−10(2)
C(14)	571(3)	2867(3)	177(4)	80(4)	70(3)	56(3)	−9(3)	43(3)	−26(3)
C(15)	−114(3)	3321(3)	−291(4)	68(4)	87(4)	47(3)	5(3)	24(3)	−24(3)
C(16)	−119(3)	3979(3)	175(4)	58(3)	69(3)	68(4)	22(3)	31(3)	−3(3)
C(21)	3257(2)	3207(2)	5107(3)	40(2)	42(2)	45(3)	2(2)	27(2)	−6(2)
C(22)	3284(2)	3425(3)	5926(3)	46(2)	51(3)	44(3)	−1(2)	28(2)	−11(2)
C(23)	3606(2)	2908(3)	6774(3)	56(3)	74(3)	50(3)	6(3)	32(3)	−13(3)
C(24)	3909(3)	2205(3)	6767(4)	60(3)	81(4)	75(4)	35(3)	41(3)	7(3)
C(25)	3884(3)	1992(3)	5952(4)	59(3)	52(3)	90(4)	24(3)	48(3)	11(2)
C(26)	3560(2)	2473(2)	5100(3)	53(3)	49(3)	62(3)	8(2)	37(2)	2(2)
C(31)	3834(2)	4719(2)	3507(3)	42(2)	54(3)	33(2)	4(2)	24(2)	−3(2)
C(32)	4100(2)	5511(2)	3779(3)	45(2)	51(3)	39(2)	4(2)	27(2)	−2(2)
C(33)	4741(2)	5766(3)	3859(3)	50(2)	69(3)	48(3)	1(2)	29(2)	−12(2)
C(34)	5070(3)	5216(3)	3653(3)	50(3)	104(4)	54(3)	−1(3)	37(2)	−11(3)
C(35)	4799(2)	4421(3)	3382(3)	59(3)	95(4)	55(3)	−8(3)	42(2)	1(3)
C(36)	4181(2)	4159(3)	3297(3)	54(2)	65(3)	45(3)	−1(2)	36(2)	2(2)

[a] The anisotropic displacement coefficients take the form: $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5

Selected bond lengths (Å) and bond angles (°)

Mo–C(1)	1.936(5)	Mo–C(2)	1.951(4)	Mo–C(3)	2.311(6)
Mo–C(4)	2.200(11)	Mo–C(5)	2.313(11)	Mo–N(2)	2.290(3)
Mo–N(5)	2.287(3)	Mo–N(8)	2.213(5)	O(1)–C(1)	1.161(6)
O(2)–C(2)	1.147(5)	C(3)–C(4)	1.395(10)	C(4)–C(5)	1.378(8)
N(1)–N(2)	1.359(6)	N(1)–B	1.532(5)	N(1)–C(12)	1.360(4)
N(2)–N(3)	1.316(4)	N(3)–C(11)	1.369(6)	N(4)–N(5)	1.354(6)
N(4)–B	1.543(8)	N(4)–C(21)	1.351(5)	N(5)–N(6)	1.309(6)
N(6)–C(22)	1.371(5)	N(7)–C(31)	1.349(7)	N(7)–N(8)	1.358(5)
N(7)–B	1.528(6)	N(8)–N(9)	1.318(6)	N(9)–C(32)	1.367(7)
C(11)–C(16)	1.401(5)	C(21)–C(26)	1.404(6)	C(31)–C(36)	1.398(8)
C(11)–C(12)	1.383(6)	C(21)–C(22)	1.390(8)	C(31)–C(32)	1.399(5)
C(12)–C(13)	1.404(7)	C(22)–C(23)	1.401(7)	C(32)–C(33)	1.408(8)
C(13)–C(14)	1.376(5)	C(23)–C(24)	1.359(8)	C(33)–C(34)	1.355(8)
C(14)–C(15)	1.395(8)	C(24)–C(25)	1.383(11)	C(34)–C(35)	1.406(7)
C(15)–C(16)	1.356(9)	C(25)–C(26)	1.367(7)	C(35)–C(36)	1.361(8)

C(1)–Mo–C(2)	79.8(2)	C(3)–C(4)–C(5)	115.8(5)
C(1)–Mo–N(2)	98.9(2)	C(2)–Mo–N(2)	168.7(3)
C(1)–Mo–N(5)	168.7(2)	C(2)–Mo–N(5)	99.7(1)
N(2)–Mo–N(5)	79.4(1)	C(1)–Mo–N(8)	88.0(2)
C(2)–Mo–N(8)	87.6(2)	N(2)–Mo–N(8)	81.2(2)
N(5)–Mo–N(8)	80.7(2)	Mo–C(1)–O(1)	177.9(4)
Mo–C(2)–O(2)	176.5(5)	N(2)–N(1)–B	120.9(3)
N(2)–N(1)–C(12)	107.8(3)	B–N(1)–C(12)	131.2(4)
Mo–N(2)–N(1)	120.4(2)	Mo–N(2)–N(3)	128.3(3)
N(1)–N(2)–N(3)	111.3(3)	N(2)–N(3)–C(11)	105.7(4)
N(5)–N(4)–B	121.5(3)	N(5)–N(4)–C(21)	107.8(4)
B–N(4)–C(21)	130.6(4)	Mo–N(5)–N(4)	119.9(3)
Mo–N(5)–N(6)	128.7(3)	N(4)–N(5)–N(6)	111.1(3)
N(5)–N(6)–C(22)	106.6(4)	N(8)–N(7)–B	119.6(5)
N(8)–N(7)–C(31)	108.2(3)	B–N(7)–C(31)	131.9(4)
Mo–N(8)–N(7)	123.4(3)	Mo–N(8)–N(9)	125.7(3)
N(7)–N(8)–N(9)	110.8(4)	N(8)–N(9)–C(32)	106.5(3)
N(1)–B–N(4)	109.0(5)	N(1)–B–N(7)	109.1(3)
N(4)–B–N(7)	108.1(3)	N(3)–C(11)–C(12)	109.9(3)
N(3)–C(11)–C(16)	129.6(5)	C(12)–C(11)–C(16)	120.5(5)
N(1)–C(12)–C(11)	105.3(4)	N(1)–C(12)–C(13)	132.3(4)
C(11)–C(12)–C(13)	122.3(3)	C(12)–C(13)–C(14)	115.8(4)
C(13)–C(14)–C(15)	121.8(5)	C(14)–C(15)–C(16)	122.2(4)
C(11)–C(16)–C(15)	117.3(5)	N(4)–C(21)–C(22)	106.0(4)
N(4)–C(22)–C(21)	132.1(5)	C(22)–C(21)–C(26)	121.8(4)
N(6)–C(22)–C(21)	108.4(4)	N(6)–C(22)–C(23)	130.7(5)
C(21)–C(22)–C(23)	120.8(4)	C(22)–C(23)–C(24)	116.7(6)
C(23)–C(24)–C(25)	122.3(5)	C(24)–C(25)–C(26)	122.8(5)
C(21)–C(26)–C(25)	115.6(6)	N(7)–C(31)–C(32)	105.6(4)
N(7)–C(31)–C(36)	132.4(4)	C(32)–C(31)–C(36)	122.0(5)
N(9)–C(32)–C(31)	108.8(4)	N(9)–C(32)–C(33)	130.9(4)
C(31)–C(32)–C(33)	120.3(5)	C(32)–C(33)–C(34)	116.9(4)
C(33)–C(34)–C(35)	122.4(6)	C(34)–C(35)–C(36)	121.8(6)
C(31)–C(36)–C(35)	116.5(4)		

atom of the allyl group. Several important features were unambiguously found: (1) the tridentate ligand, L^-, occupies three facial sites in a pseudo-octahedron as expected; (2) the ligand has a structure containing the more-hindered B–N bonds; and (3) the metal–ligand coordination occurs through the nitrogen atom at the 2-position of the ring of the benzotriazolyl fragments.

The Mo separations (Table 5) from the coordinated N atoms, viz., N(8), N(5), and N(2), are 2.213(5), 2.287(3), and 2.290(3) Å, respectively, indicating that the longer Mo–N distances occur when there is a carbonyl group trans to the nitrogen atom. A similar pattern was previously reported for the π-allyl complexes, $[Mo(PhBPz_3)(CO)_2(\pi\text{-}C_3H_5)]$ and $[Mo(PhBPz_3)(CO)_2(\eta^3\text{-}C_7H_7)]$ [8]. This pattern probably reflects the stronger π-acidity of the carbonyls relative to that of the π-allyl group. In the $[Mo(PhBPz_3)(CO)_2(\pi\text{-}C_3H_5)]$ structure, the two Mo–CO distances are 1.908(7) and 1.928(6) Å, which are relatively short when compared with those of 1.936(5) Å for Mo–C(1)O(1) and 1.951(4) Å for Mo–C(2)O(2) in **VII**, showing that L^- is a weaker σ-donor than $PhBPz_3^-$. Because Tp^-, Tp'^-, and $PhBPz_3^-$, are similar the electron-donating ability of L^- should be much less than that of either Tp^- or Tp'^-. This deduction is reasonable and finds support from the variation in the weighted ν(CO) average values which are 1806 cm^{-1} for $[Et_4N][MoTp(CO)_3]$, 1798 cm^{-1} for $[Et_4N][MoTp'(CO)_3]$ [5a], and 1834 cm^{-1} for $[Et_4N][MoL(CO)_3]$ measured in acetonitrile.

Experimental

All operations were carried out under N_2 by standard Schlenk and vacuum-line techniques. Organic solvents were dried by standard procedures and distilled under N_2 before use. IR spectra, calibrated with polystyrene, were recorded on a Hitachi 270-30 model instrument. NMR spectra were obtained on a Bruker AM-400 (^1H, 400; ^{13}C, 100.6 MHz) FT NMR spectrometer using internal deuterium lock solvents and tetramethylsilane standard. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

Preparation of potassium hydridotris(benzotriazol-l-yl)borate, KL

A mixture of 1-*H*-benzotriazole (20 g, 166 mmol) and KBH_4 (2.29 g, 42 mmol) was heated slowly to 220 °C and maintained at that temperature until 3.15 l (126 mmol) of H_2 had evolved (wet test meter). The mixture was worked up as described by Trofimenko [9]. Further recrystallization from CH_3OH/toluene gave 15.6 g (93%) of the white solid.

Preparation of $K[ML(CO)_3]$ and $[Et_4N][ML(CO)_3]$ (M = Mo, W)

A mixture of 2.03 g (5.0 mmol) of KL and 1.32 g (5.0 mmol) of $[Mo(CO)_6]$ in 50 ml of CH_3CN was stirred at reflux for 3 h to give a deep orange-red solution. A solution IR spectrum showed two ν(CO) bands at 1910s and 1796vs cm^{-1} confirming the conversion of $[Mo(CO)_6]$ into $K[MoL(CO)_3]$. A deaerated solution of 1.47 g of Et_4NCl in 130 ml of H_2O was then added to the solution to give orange-red crystals. These were collected and washed twice with 20 ml of H_2O and three times with 10 ml of ether and then dried under vacuum; yield 3.01 g (89%).

A similar procedure was used to make $K[WL(CO)_3]$ and $[Et_4N][WL(CO)_3]$

(ν(CO): 1900s, 1788vs cm^{-1} in CH_3CN) except that a longer time (ca. 48 h) was needed to convert [W(CO)$_6$] completely into K[WL(CO)$_3$] and [Et$_4$N][WL(CO)$_3$]. If [W(CH$_3$CN)$_3$(CO$_3$] [10] is used in place of [W(CO)$_6$], about 2 h is sufficient for completion. Since both K[WL(CO)$_3$] and [Et$_4$N][WL(CO)$_3$] are very air-sensitive, the salts were not isolated for further characterization but were treated with electrophiles to give the neutral WL complexes by the same procedure as described below for the preparation of the molybdenum analogue.

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

A solution of [Et$_4$N][MoL(CO)$_3$[(0.68 g, 1.0 mmol) in 40 ml of CH_3CN was treated dropwise with a solution containing 1.1 mmol of Br_2 or I_2 in 10 ml of CH_3CN at room temperature. After all the halide had been added, the solvent was removed under vacuum. Recrystallization from CH_2Cl_2/CH_3OH gave I in 81% yield, and III in 85% yield.

Preparation of MoL(CO)$_2$(NO) (V)

To a solution of [Et$_4$N][MoL(CO)$_3$] (0.68 g, 1.0 mmol) in CH_3CN (30 ml) was added portionwise with [NO][BF$_4$] (0.17 g, 1.5 mmol). The mixture was stirred at room temperature for 30 min. The solvent was then removed to give a yellow solid. The solid was recrystallized from CH_2Cl_2/CH_3OH to give 0.38 g (69%) of V.

Preparation of [MoL(CO)$_2$(π-allyl)] (VII)

To a suspension of [Et$_4$N][MoL(CO)$_3$] (0.56 g, 0.83 mmol) in 20 ml of CH_3CN was added 2 ml of allyl bromide. The mixture was stirred at room temperature for 17 h and the solvent and excess allyl bromide were then removed under vacuum. Recrystallization from CH_2Cl_2/CH_3OH gave 0.40 g (86%) of the orange-yellow solid.

X-Ray diffraction study of [MoL(CO)$_2$(π-allyl)] (VII)

Details of crystal data and intensity collection for VII are listed in Table 3. An orange-yellow crystal of approximate dimensions 0.4 × 0.2 × 0.2 mm, grown from CH_2Cl_2/hexane at room temperature, was mounted on a Nicolet *R3m/V* diffractometer equipped with a graphite monochromator. Seventeen independent reflections with $10.06 \leq 2\theta \leq 24.50°$ were used for the least-squares determination of the cell constants. Reflections *hkl* in the 2θ range of 2.0 to 50.0° were collected with $-26 \leq h \leq 26$, $0 \leq k \leq 16$, $0 \leq l \leq 16$. Three standard reflections taken every 50 reflections revealed no signs of crystal deterioration. Systematic absences (*hkl*, $h + k = 2n = 1$ and $h0l$, $l = 2n + 1$) indicate space group *Cc* or *C*2/*c*. The observed density of 1.58 g/cm^3 (by flotation) indicates the number of formula units in the unit cell to be eight. The space group *C*2/*c* was confirmed by successive refinements. The structure was solved by standard Patterson and Fourier methods (SHELXTL PLUS 86) [11] (transmission factor: min. 0.886 and max. 0.925). Hydrogen atoms were placed at idealized positions (C–H = 0.96 Å and B–H = 1.00 Å) with a fixed isotropic displacement parameter of 0.08 Å^2. The refinements converged with $R = 0.035$ and $R_w = 0.030$ based on 2647 observed reflections with $I > 3.0\sigma(I)$ ($R = \Sigma || F_o | - | F_c || / \Sigma | F_o |$, $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_0 |^2]^{1/2}$, $w = (\sigma^2(F) + 0.0001F^2)^{-1}$). Goodness-of-fit (GOF) = 1.35 (GOF = $[\Sigma(w | F_o | - | F_c |)^2/(NO - NV)]^{1/2}$, NO = number of observed reflections, NV =

number of variables). $(\Delta/\sigma)_{max}$ in the final refinement cycle was 0.072. The maximum height in the final difference map was 0.23 e/Å^3.

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