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Organotransition-metal complexes of multidentate ligands

XIV *. Synthesis, structure and behavior in solution of some π-allyldicarbonyl complexes containing the pyrazole-derived bidentate ligands

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Abstract

The π-allyldicarbonyl complexes, [Mo(N–N)(CO)$_2$(π-allyl)Br], can be prepared either directly by the allyl bromination of [Mo(N–N)(CO)$_4$] (N–N = H$_2$CPz$_2$, H$_2$CPz$'_2$, PhHCPz$_2$, PhHCPz$'_2$; Pz = pyrazol-1-yl; Pz$'$ = 3,5-dimethylpyrazol-1-yl) or [Mo(PhHCPz$'_2$)(CO)$_3$] or indirectly by the reaction between [Mo(MeCN)$_2$(CO)$_2$(π-allyl)Br] and N–N. The products obtained from [Mo(PhHCpz$'_2$)(CO)$_4$] or from [Mo(PhHCPz$'_2$)(CO)$_3$] are identical, which supports the mechanism proposed previously for the allyl bromination of substituted metal carbonyl complexes. The single-crystal structure of [Mo(PhHCPz$'_2$)(CO)$_2$(π-allyl)Br] has been determined by X-ray diffraction, explaining why the central proton of the allyl group in this complex or [Mo(PhHCPz$_2$)(CO)$_2$(π-allyl)Br] is more upfield relative to those of other similar complexes in the ^{1}H NMR spectrum. Furthermore, the unique structural features help to confirm unequivocally the solvent-dependent coordination-stability of the pyrazole-derived bidentate ligands, N–N, in [Mo(N–N)(CO)$_2$(π-allyl)Br].

Introduction

The conformational effect of the six-membered boat-metallocycle in the Mo(N–N) fragment (N–N = H$_2$CPz$_2$, H$_2$CPz$'_2$, PhHCPz$_2$, or PhHCPz$'_2$; Pz = pyrazol-1-yl; Pz = 3,5-dimethylpyrazol-1-yl; Fig. 1) has recently led us to isolate the rare intramolecular η^2-arene compound, [Mo(PhHCPz$'_2$)(CO)$_3$] [2], and several paramagnetic, 16-electron species, [Mo(N–N)(CO)$_2$X$_2$] with X = Br or I [3]. Here we wish to report conclusive evidence showing that the stability of the metallacycle in

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* For Part XIII, see ref. 1.

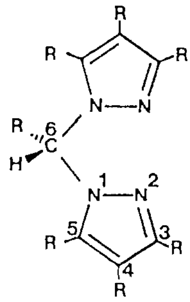

Fig. 1. Structure and numering scheme for N-N ligands: (i) 3-C-R = 4-C-R = 5-C-R = 6-C-R = H; N-N = H_2CPz_2. (ii) 3-C-R = 5-C-R = Me; 4-C-R = 6-C-R = H; N-N = $H_2CPz'_2$. (iii) 3-C-R = 4-C-R = 5-C-R = H; 6-C-R = Ph; N-N = $PhHCPz_2$. (iv) 3-C-R = 5-C-R = Me; 4-C-R = H; 6-C-R = Ph; N-N = $PhHCpz'_2$.

the π-allyldicarbonyl complexes, $[Mo(N-N)(CO)_2(\pi\text{-allyl})Br]$, in solution is dependent on the solvent used.

Results and discussion

The π-allyldicarbonyl complexes $[Mo(N-N)(CO)_2(\pi\text{-allyl})Br]$ (N-N = H_2CPz_2 (I), $H_2CPz'_2$ (II), $PhHCPz_2$ (III) and $PhHCPz'_2$ (IV)) can be obtained directly by the allyl bromination of $[Mo(N-N)(CO)_4]$ or $[Mo(PhHCPz'_2)(CO)_3]$ or indirectly by the reaction between $[Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br]$ and N-N (eq. 1).

$$\begin{tikzcd}
{[Mo(N-N)(CO)_4] + H_2C{=}CHCH_2Br} \arrow[r, "-2CO"] & {[Mo(N-N)(CO)_2(\pi\text{-allyl})Br]} \\
{[Mo(PhHCPz'_2)(CO)_3] + H_2C{=}CHCH_2Br} \arrow[ur, "-CO"] & \\
{[Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br] + N-N} \arrow[uur, "-2MeCN"'] &
\end{tikzcd} \qquad (1)$$

Since $[Mo(PhHCPz'_2)(CO)_3]$ can be prepared by the decarbonylation of $[Mo(PhHCPz'_2)(CO)_4]$ [2], the fact that only one product, $[Mo(PhHCPz'_2)(CO)_2(\pi\text{-allyl})Br]$, is obtained directly from both $[Mo(PhHCPz'_2)(CO)_4]$ and $[Mo(PhHCPz'_2)(CO)_3]$ indicates that the initial loss of the carbonyl group *cis* to the bidentate ligand, N-N, in $[Mo(N-N)(CO)_4]$ occurs prior to the attachment of allyl bromide. The known chemistry of metal carbonyl complexes [4] would suggest η^2-bonding of the olefinic moiety rather than the bound bromine atom of C_3H_5Br for this attachment. Thus, the synthesis supports the mechanism proposed earlier for the allyl bromination of $[Mo(phen)(CO)_4]$ (phen = *o*-phenanthroline) on the basis of the related kinetic data [5]. Although two different geometrical isomers with the allyl group *cis* (cf. Fig. 2) and *trans* to the phenyl group of $PhHCPz'_2$ (or $PhHCPz_2$) are possible, the formation of only one single product with the *cis* allyl group by the reaction between $[Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br]$ (V) and $PhHCPz'_2$ (or $PhHCPz_2$) can be rationalized either by considering that there is only one stable conformation for $PhHCPz_2$ (or $PhHCPz'_2$) in solution or by supposing that the process leading to the *cis* orientation has a lower energy barrier than that giving the *trans* geometry.

In the ^1H NMR spectra of $[Mo(N-N)(CO)_2(\pi\text{-allyl})Br]$ in acetone-d_6, the central proton, H_c, of the allyl group resonates as a multiplet at 4.21 for I, 4.36 for II, 2.28 for III and 2.21 ppm for IV (Table 1). Compared with the characteristic H_c resonance range of 4–6.5 ppm [4], the H_c proton of either III or IV is quite upfield. In order to explain this NMR feature, the solid-state structure of IV was determined; an ORTEP plot of this structure is shown in Fig. 2. From Fig. 3, which contains a projection view of the allyl group from the phenyl plane, it is clear that the ring-current of the phenyl moiety shields H_c rather strongly relative to H_a (the *anti*-protons) or H_s (*syn*-protons) of the allyl group in III or IV so that the chemical shifts for H_a or H_s in the compounds (Table 1) are within the general range of the chemical shifts for H_a (1–3 ppm) and H_s (2–5 ppm) [4].

Since compound I has a better solubility in CD_3CN than that in acetone-d_6, the ^1H NMR spectrum of this compound was also measured in CD_3CN. To our surprise, the spectrum is more complicated than expected. We then measured the spectra of other three π-allyldicarbonyl complexes in CD_3CN and found similar features. From the structure of IV and the NMR spectra of V and the N–N ligand, we soon recognized that any spectrum for $[Mo(N-N)(CO)_2(\pi\text{-allyl})Br]$ measured in CD_3CN is the superposition of three species including $[Mo(N-N)(CO)_2(\pi\text{-allyl}(Br)]$, $[Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br]$ (V) and the free N–N ligand. In other words, $[Mo(N-N)(CO)_2(\pi\text{-allyl})Br]$ and CD_3CN are in equilibrium (eq. 2).

$$[Mo(N-N)(CO)_2(\pi\text{-allyl})Br] + 2\ MeCN \rightleftharpoons [Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br] + N-N \qquad (2)$$

(We did not measure the equilibrium constants due to the overlap of the resonance

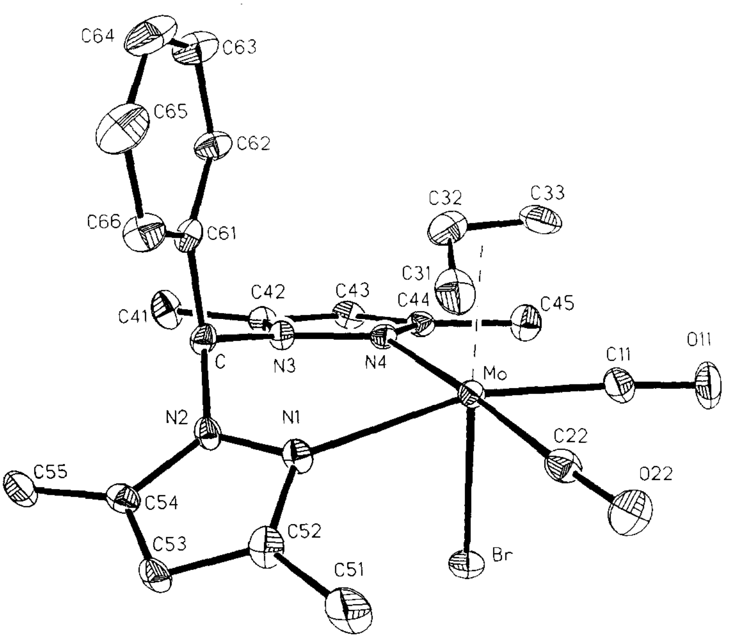

Fig. 2. Structure of $[Mo(PhHCPz'_2)(CO)_2(\pi\text{-allyl})Br]$ (IV) showing the atomic numering scheme and 50% probability thermal ellipsoids.

Table 1

Spectroscopic data for the N–N ligands and the π-allyldicarbonyl complexes

Compound	IR [a], ν(CO), cm^{-1}	NMR [b], ppm						
		Solvent	3-C-R/5-C-R	4-C-R	6-C-R/6-C-H	H_a [c]	H_s [c]	H_c [c]
H_2CPz_2		CD_3CN	7.75(2 H, d)(2.4) [d], 7,47(2 H, d)(1.4)	6.27(2 H, t)	6.29(2 H, s)			
$H_2CPz'_2$		CD_3CN	2.40(6 H s), 2.41(6 H, s)	5.78(2 H, s)	5.95(2 H, s)			
$PhHCPz_2$		CD_3CN	7.64(2 H, d)(2.4), 7.58(2 H, d)(1.5)	6.34(2 H, t)	7.62(1 H, s), 7.38(3 H, m) [e], 7.05(2 H, m) [e]			
$PhHCPz'_2$		CD_3CN	2.11(6 H, br), 2.12(3 H, s), 2.13(3 H, s)	5.89(2 H, br)	7.58(1 H, s), 7.34(3 H, m), 7.01(2 H, m)			
	1934, 1826 (KBr)	CD_3CN	7.89(2 H, d)(2), 7.87(2 H, d)(2)	6.41(2 H, t)	8.25(1 H, d)(3), *(1 H)	1.37(2 H, d)(9.3)	3.53(2 H, d)(7.0)	4.25(1 H, m)
I	1944, 1842 (CH_2Cl_2) 1956, 1866, 1844(sh) (MeCN)	acetone-d_6	8.09(2 H, d)(2.6), 8.03(2 H, d)(2.6)	6.48 H, t)	7.85(1 H, d)(3), 7.45(1 H, d)(3)	1.32(2 H, d)(9.1)	3.50(2 H, br)	4.21(1 H, m)
	1922, 1828 (KBr)	CD_3CN	2.07(3 H, s), 2.18(3 H, s), 2.33(3 H, s), 2.45(3 H, s)	5.84(1 H, s), 5.87(1 H, s)	5.95(1 H, d)(15.7), 6.00(1 H, d)(15.7)	1.26(2 H, d)(9.2)	3.08(2 H, d)(5.6)	4.24(1 H, m)
II	1950, 1854 (CH_2Cl_2)	acetone-d_6	2.44(6 H, br) [f], 2.47(6 H, br) [f]	5.99(2 H, br) [f]	6.09(1 H, d)(15.7) [f], 6.29(1 H, d)(15.7) [f]	1.19(2 H, d)(8.9) [f]	3.08(2 H, d)(6.4) [f]	4.36(1 H, m) [f]

	1949, 1862 (MeCN)							
	1944, 1857 (KBr)	CD_3CN	8.20(2 H, d)(2.3), 7.96(2 H, br)	6.56(2 H, t)	8.43(1 H, s), 7.40(3 H, m), 6.01(2 H, m)	1.02(2 H, d)(9.0)	2.79(2 H, br)	2.30(1 H, m)
III	1950, 1860 (CH_2Cl_2)	acetone-d_6	8.38(1 H, d)(2.6), 8.37(1 H, d)(2.6), 8.01(2 H, br)	6.61(2 H, t)	8.31(1 H, s), 6.06(2 H, m)	0.96(2 H, d)(8.9) 7.41(3 H, m),	2.78(2 H, br)	2.28(1 H, m)
	1952, 1862 (MeCN)							
	1926, 1830 (KBr)	CD_3CN	2.19(6 H, br), 2.43(3 H, s),	6.19(2 H, br)	7.58(1 H, s), 7.43(3 H, m), 6.06(2 H, m)	1.00(2 H, d)	2.77(2 H, d)(6.6)	2.22(1 H, m) 2.52(3 H, s)
IV	1946, 1850 (CH_2Cl_2)	acetone-d_6	2.54(6 H, br), 2.57(6 H, s)	6.23(2 H, br)	7.61(1 H, s), 7.43(3 H, m), 6.11(2 H, m)	0.93(2 H, d)(9.3)	2.75(2 H, d)(6.6)	2.21(1 H, m)
	1954(sh), 1942, 1864, 1848(sh) (MeCN)	$CDCl_3$	2.42(6 H, br), 2.62(6 H, br)	6.12(2 H, br)	7.26(1 H, s), 7.36(3 H, m), 6.04(2 H, m)	1.07(2 H, d)(9.3)	2.81(2 H, d)(8.9)	2.14(1 H, m)
V	1946, 1830 (KBr) 1954, 1864 (MeCN)	CD_3CN				1.14(2 H, d)(9.3)	3.25(2 H, d)(6.2)	4.00(1 H, m)

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[a] In KBr disc or in solution using CH_2Cl_2 or MeCN as solvent. Abbreviation: sh, shoulder. [b] The chemical shifts are not assigned for the 3-C-R and 5-C-R protons. An asterisk represents a signal buried in other signals. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, a broad signal which may be either the unresolved multiplet or two combined singlets. [c] H_a, H_s and H_c represent the *anti-*, *syn-* and central-protons of the π-allyl group, respectively. [d] Coupling constant in hertz. [e] Phenyl protons. [f] Reported data [14].

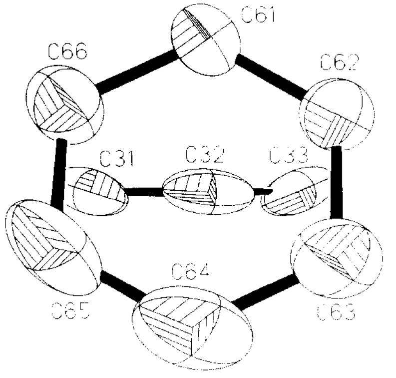

Fig. 3. Projection view of the π-allyl group from the phenyl plane in IV.

signals. However, the ^{1}H NMR signals observed in CD_3CN were assigned (Table 1) and the ratios — 0.39 for [V]/[I], 0.69 for [V]/[II], 0.72 for [V]/[III] and 1.06 for [V]/[IV] — were calculated based on the integrated area of resonance signals of H_a in [Mo(MeCN)$_2$(CO)$_2$(π-allyl)Br] (V) and that in [Mo(N–N)(CO)$_2$(π-allyl)Br]). Thus, although two sharp carbonyl-stretching bands are present at their specific positions for [Mo(N–N)(CO)$_2$(π-allyl)Br] in a KBr disc or in CH_2Cl_2, two ν(CO) bands or shoulders are found in identical positions within experimental error (ca. ± 5 cm^{-1}) to those of 1954 and 1864 cm^{-1} for [Mo(MeCN)$_2$(CO)$_2$(π-allyl)Br] in MeCN (Table 1).

The solid-state structure of [Mo(PhHCPz$'_2$)(CO)$_2$(π-allyl)Br] (IV)

The molecular structure of [Mo(PhHCpz$'_2$)(CO)$_2$(π-allyl)Br] (IV) is shown in Fig. 2 and pertinent crystallographic parameters are given in Tables 2–4. The molecule can be described as pseudooctahedral with the assumption that the allyl moiety occupies one coordination site. The molybdenum atom is surrounded by six ligands, viz. an allyl group, two terminally coordinated carbonyl groups, the bidentate ligand and a bromine atom.

The six-membered $\overline{\text{Mo–N(1)–N(2)–C–N(3)–N(4)}}$ metallacycle of the Mo(PhHCpz$'_2$) fragment in IV adopts a shallow boat form analogous to the metallocycle in [Mo(PhHCPz$'_2$)(CO)$_4$] [2] and that in [Mo(PhHCPz$'_2$)(CO)$_2$I$_2$] [3], but in contrast to the nearly planar five-membered $\overline{\text{Mo–N–C–C–N}}$ linkage of the Mo(phen) or Mo(bpy) (bpy = 2,2′-bipyridine) fragment observed in other π-allyldicarbonyl complexes, including [Mo(bpy)(CO)$_2$(π-allyl)(pyridine)][BF$_4$] (VI), [Mo(phen)(CO)$_2$(π-2-methylallyl)(NCS)] (VII), [Mo(bpy)(CO)$_2$(η^3-C$_4$Ph$_3$O)Br] (VIII) and [Mo(bpy)-(CO)$_2$(η^3-C$_3$Ph$_3$)Br] (IX) [6–8]. The fact that the distances between Mo and N(1) and N(4) in IV are 2.307(5) and 2.327(5) Å, respectively (Table 3), which are significantly longer than the Mo–N distances of 2.209(6), 2.290(5) in VI [6], 2.252(8), 2.255(8) in VII [7], 2.211(8), 2.233(8) in VIII and 2.223(19), 2.221(17) Å in IX [8], and that the Mo–Br bond length in IV is 2.649(1) Å (Table 3), which is slighly longer than that of 2.619(1) in VIII or that of 2.626(3) Å in IX [8], indicates that the nonbonded interactions between the two pyrazolyl rings sticking below the boat and the Br atom weaken the Mo(N–N) metallacycle more than the Mo–Br bond in I–IV so that acetonitriles capable of strongly coordinating the central metal

Table 2

Atomic coordinates ($\times 10^4$) and anisotropic displacement coefficients [a] (Å$^2 \times 10^3$) for [Mo(PhHCPz$'_2$)(CO)$_2$(π-allyl)Br] (IV)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	6131(1)	823(1)	8214(1)	28(1)	24(1)	33(1)	−1(1)	−3(1)	−1(1)
Br	6586(1)	742(1)	9988(1)	50(1)	45(1)	35(1)	2(1)	−6(1)	3(1)
O(11)	3426(5)	468(4)	8777(5)	31(3)	58(4)	118(5)	8(4)	3(4)	−12(3)
O(22)	5608(6)	−1270(4)	8195(5)	83(4)	26(3)	91(5)	−2(3)	−16(4)	−15(3)
N(1)	8254(5)	838(4)	8190(4)	29(3)	30(3)	45(3)	−9(3)	3(3)	5(3)
N(2)	8984(5)	1620(4)	8234(4)	26(3)	30(3)	44(3)	−5(3)	3(3)	3(2)
N(3)	7514(5)	2861(4)	8420(4)	28(3)	24(3)	40(3)	−3(2)	2(2)	2(2)
N(4)	6424(5)	2398(4)	8489(4)	30(3)	25(3)	35(3)	5(2)	0(2)	4(2)
C	8551(6)	2503(5)	7909(5)	34(4)	25(3)	40(4)	1(3)	4(3)	−5(3)
C(11)	4434(7)	651(5)	8563(6)	35(4)	32(4)	61(5)	−1(4)	−8(4)	1(3)
C(22)	5858(7)	−496(5)	8179(6)	43(4)	37(4)	43(4)	−6(4)	−9(4)	0(3)
C(31)	6376(8)	279(7)	6741(5)	54(5)	81(6)	35(4)	−18(5)	0(4)	−12(5)
C(32)	5936(9)	1181(6)	6762(6)	86(7)	55(5)	35(4)	5(4)	−17(5)	−38(5)
C(33)	4759(9)	1340(7)	7107(6)	67(6)	60(6)	53(5)	15(4)	−31(5)	−7(5)
C(41)	8473(7)	4410(5)	8766(6)	49(5)	39(4)	72(5)	−17(4)	−8(4)	−12(4)
C(42)	7454(7)	3726(5)	8795(5)	42(4)	24(3)	35(4)	−6(3)	−6(3)	−5(3)
C(43)	6294(6)	3801(5)	9140(5)	44(5)	28(3)	41(4)	−8(3)	−3(4)	12(3)
C(44)	5680(7)	2980(5)	8937(5)	34(4)	34(4)	37(4)	4(3)	0(3)	7(3)
C(45)	4387(7)	2749(6)	9194(6)	41(4)	43(5)	65(5)	−6(4)	10(4)	7(4)
C(51)	8606(8)	−851(6)	8459(8)	53(5)	31(4)	142(10)	8(6)	−10(6)	20(5)
C(52)	9026(7)	135(5)	8400(6)	40(4)	27(3)	64(5)	−12(4)	10(4)	6(3)
C(53)	10206(7)	471(5)	8545(6)	27(3)	32(4)	60(5)	−3(4)	−2(3)	12(3)
C(54)	10157(7)	1420(5)	8431(5)	37(4)	43(4)	32(4)	−3(3)	−3(3)	6(3)
C(55)	11147(7)	2115(6)	8479(6)	34(4)	52(5)	77(6)	4(4)	−12(5)	4(4)
C(61)	8402(7)	2572(5)	6873(5)	40(4)	31(3)	40(4)	0(3)	8(4)	−8(3)
C(62)	7687(8)	3241(5)	6492(5)	62(5)	34(4)	41(4)	7(3)	−1(4)	−2(4)
C(63)	7593(10)	3329(6)	5560(6)	90(7)	48(5)	46(5)	9(4)	−2(5)	−1(5)
C(64)	8220(11)	2724(8)	5012(7)	116(9)	74(7)	38(5)	9(5)	9(6)	−18(7)
C(65)	8935(11)	2029(7)	5378(7)	103(8)	76(7)	51(6)	−16(5)	30(6)	4(7)
C(66)	9023(9)	1946(6)	6312(6)	64(6)	52(5)	47(5)	−4(4)	7(5)	6(5)

[a] The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^2 \times U_{11} + \ldots + 2hka \times b \times U_{12})$.

atoms can compete with the chelate effect of the N–N bidentate ligands. Since a nearly quantitative yield of the product from the reaction between [Mo(MeCN)$_2$(CO)$_2$(π-allyl)Br] and N–N was obtained (cf. the experimental section), [Mo(N–N)(CO)$_2$(π-allyl)Br] and acetonitrile in solution are in equilibrium 2, and Le Châtelier's principle applies during the final workup in the synthesis of the product (i.e., as acetonitrile is removed under vacuum, the equilibrium shifts to the left and the product is finally obtained from the total conversion of [Mo(MeCN)$_2$(CO)$_2$(π-allyl)Br]).

Although the Mo–Br and Mo–N bond lengths in IV (Table 3) are longer than the corresponding ones in VI–IX [6–8], the Mo–CO bond lengths of 1.930(8) and 1.924(7) Å in IV are not longer but shorter than those of 2.061(8), 1.911(8) in VI, 1.987(10), 1.950(10) in VII, 1.990(11), 2.005(12) in VIII and 1.992(24), 1.990(25) Å in IX [6–8]. Since the distance between Mo and the central carbon atom (C_c or C(32)) of the allyl group in IV, which is 2.200(8) Å, is much shorter than the Mo–C_c distances of 2.279(10) in VI, 2.274(13) in VII, 2.234(10) in VIII and 2.193(18) Å in

Table 3

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

Mo–Br	2.649(1)	Mo–N(1)	2.307(5)
Mo–N(4)	2.327(5)	Mo–C(11)	1.930(8)
Mo–C(22)	1.924(7)	Mo–C(31)	2.312(8)
Mo–C(32)	2.200(8)	Mo–C(33)	2.327(9)
O(11)–C(11)	1.169(10)	O(22)–C(22)	1.149(9)
N(1)–N(2)	1.380(8)	N(1)–C(52)	1.351(9)
N(2)–C	1.437(9)	N(2)–C(54)	1.338(9)
N(3)–N(4)	1.363(7)	N(3)–C	1.449(9)
N(3)–C(42)	1.364(9)	N(4)–C(44)	1.337(9)
C–C(61)	1.529(10)	C(31)–C(32)	1.385(13)
C(32)–C(33)	1.394(14)	C(41)–C(42)	1.483(10)
C(42)–C(43)	1.362(10)	C(43)–C(44)	1.390(10)
C(44)–C(45)	1.492(10)	C(51)–C(52)	1.494(11)
C(52)–C(53)	1.387(10)	C(53)–C(54)	1.379(10)
C(54)–C(55)	1.471(11)	C(61)–C(62)	1.358(11)
C(61)–C(66)	1.395(11)	C(62)–C(63)	1.376(11)
C(65)–C(66)	1.377(13)	C(65)–C(64)	1.377(15)
C(64)–C(63)	1.367(14)		
Br–Mo–N(1)	80.2(1)	Br–Mo–N(4)	81.3(1)
N(1)–Mo–N(4)	81.8(2)	Br–Mo–C(11)	85.0(2)
N(1)–Mo–C(11)	163.9(3)	N(4)–Mo–C(11)	102.2(3)
Br–Mo–C(22)	90.7(2)	N(1)–Mo–C(22)	99.4(3)
N(4)–Mo–C(22)	171.5(3)	C(11)–Mo–C(22)	74.5(3)
Br–Mo–C(31)	151.6(2)	N(1)–Mo–C(31)	82.7(3)
N(4)–Mo–C(31)	118.5(3)	C(11)–Mo–C(31)	108.2(3)
C(22)–Mo–C(31)	70.0(3)	Br–Mo–C(32)	167.9(2)
N(1)–Mo–C(32)	94.5(3)	N(4)–Mo–C(32)	87.3(3)
C(11)–Mo–C(32)	101.2(4)	C(22)–Mo–C(32)	101.0(3)
C(31)–Mo–C(32)	35.6(3)	Br–Mo–C(33)	144.9(2)
N(1)–Mo–C(33)	128.8(3)	N(4)–Mo–C(33)	84.0(3)
C(11)–Mo–C(33)	67.3(3)	C(22)–Mo–C(33)	101.4(3)
C(31)–Mo–C(33)	62.0(3)	C(32)–Mo–C(33)	35.7(3)
Mo–N(1)–N(2)	125.5(4)	Mo–N(1)–C(52)	127.6(5)
N(2)–N(1)–C(52)	104.2(5)	N(1)–N(2)–C	121.3(5)
N(1)–N(2)–C(54)	112.4(5)	C–N(2)–C(54)	125.0(6)
N(4)–N(3)–C	122.7(5)	N(4)–N(3)–C(42)	112.1(5)
C–N(3)–C(42)	124.9(6)	Mo–N(4)–N(3)	125.7(4)
Mo–N(4)–C(44)	127.8(4)	N(3)–N(4)–C(44)	104.8(5)
N(2)–C–N(3)	113.5(5)	N(2)–C–C(61)	114.9(6)
N(3)–C–C(61)	114.0(6)	Mo–C(11)–O(11)	174.4(7)
Mo–C(22)–O(22)	174.5(7)	Mo–C(31)–C(32)	67.7(5)
Mo–C(32)–C(31)	76.6(5)	Mo–C(32)–C(33)	77.1(5)
C(31)–C(32)–C(33)	118.6(8)	Mo–C(33)–C(32)	67.2(5)
N(3)–C(42)–C(41)	124.0(6)	N(3)–C(42)–C(43)	105.4(6)
C(41)–C(42)–C(43)	130.5(7)	C(42)–C(43)–C(44)	107.3(6)
N(4)–C(44)–C(43)	110.4(6)	N(4)–C(44)–C(45)	123.6(6)
C(43)–C(44)–C(45)	126.0(7)	N(1)–C(52)–C(51)	122.5(7)
N(1)–C(52)–C(53)	110.3(6)	C(51)–C(52)–C(53)	127.3(7)
C(52)–C(53)–C(54)	107.0(6)	N(2)–C(54)–C(53)	106.0(6)
N(2)–C(54)–C(55)	124.1(7)	C(53)–C(54)–C(55)	129.8(7)
C–C(61)–C(62)	121.0(6)	C–C(61)–C(66)	119.4(6)
C(62)–C(61)–C(66)	119.6(7)	C(61)–C(62)–C(63)	121.0(8)
C(66)–C(65)–C(64)	119.3(9)	C(61)–C(66)–C(65)	119.8(8)
C(65)–C(64)–C(63)	121.0(9)	C(62)–C(63)–C(64)	119.2(9)

Table 4

Crystal data for IV

Empirical formula	$C_{22}H_{25}N_4O_2BrMo$
Color; habit	yellow chunks
Crystal size (mm)	$0.5 \times 0.5 \times 0.4$
Space group	orthorhombic, $P2_12_12_1$
Unit cell dimensions	$a = 10.866(3)$ Å $b = 14.410(3)$ Å $c = 14.657(3)$ Å
Volume	2295(1) Å
Z	4
Formula weight	553.3
Density (calc.)	1.601 g/cm^3
Absorption coefficient	2.306 mm^{-1}
$F(000)$	1112
Diffractometer used	Nicolet R3m/V
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature (K)	297
Monochromator	highly oriented graphite crystal
2θ range	2.0 to 50.0 °
Scan type	$\theta/2\theta$
Scan speed	Variable; 3.26 to 14.65 °/min. in ω
Scan range (ω)	1.02° plus K_α-separation
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard reflections	3 measured every 50 reflections
Index ranges	$0 \leqslant h \leqslant 12$, $-17 \leqslant k \leqslant 0$, $-17 \leqslant 1 \leqslant 0$
Reflections collected	2365 ($1964 > 3.0\sigma(I)$)
Independent reflections	2315 ($1944 > 3.0\sigma(I)$)
Extinction correction	$\chi = 0.00018(8)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Final R indices (obs. data)	$R = 3.37\%$, $R_w = 3.54\%$
Goodness-of-fit	1.10
Largest and mean Δ/σ	0.054, 0.000
Data-to-parameter ratio	7.1 : 1
Largest difference peak	0.67 e Å^{-3}
Largest difference hole	−0.57 e Å^{-3}

IX whereas the distances between Mo and the terminal carbon atoms (C_t or C(31), C(33)) of the allyl group in IV, which are 2.312(8), 2.327(9) Å, respectively, are within the range of the Mo–C_t distances of 2.204–2.350 Å in VI–IX, the C_c atom of the negative allyl anion in the Mo^{II} complex, IV, apparently donates more electron density toward the central metal atom in this complex than those in VI–IX. The bond angles, formed from the carbonyls, C(11)O(11) and C(22)O(22), the central Mo atom and the C(32) atom of the allyl group in IV, are not 90° but 101.2(4)° for C(11)–Mo–C(32) and 101.0(3)° for C(22)–Mo–C(32) (Table 4), probably help the better back-donation of electron density from Mo to the carbonyls through the overlap of orbitals with suitable symmetry [4].

Experimental

All operations were performed by the usual Schlenk techniques [9], using deoxygenated, dry solvents and gases. IR spectra, calibrated with polystyrene, were recorded on a Hitachi Model 270-30 instrument; NMR spectra were obtained on a Bruker WP-100 (^1H, 100 MHz) FT-NMR spectrometer. Proton chemical shifts (δ in ppm, J in hertz) are positive downfield or negative upfield relative to internal $SiMe_4$ (TMS) standard. Elemental analysis results were obtained by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

The ligands, H_2CPz_2, $H_2CPz'_2$, $PhHCPz_2$, and $PhHCPz'_2$, were prepared as described previously [10–13]. The complexes, $[Mo(H_2CPz_2)(CO)_4]$, $[Mo(H_2CPz'_2)(CO)_4]$, $[Mo(PhHCPz_2)(CO)_4]$, $[Mo(PhHCPz'_2)(CO)_4]$ and $[Mo(PhHCPz'_2)(CO)_3]$, were prepared by literature methods [2,12–15]. The allyldicarbonyl complexes, I–IV, can be prepared by the following two methods (methods 1 and 2) while IV can also be prepared using the third method (method 3). Any method used can afford the complexes in the nearly quantitative conversion. The IR and NMR data are collected in Table 1.

Method 1. The orange-yellow complexes, I, III and IV, can be prepared by following a similar procedure to that for preparation of II [15]. The new compounds were further recrystallized from CH_2Cl_2. I: Anal. Found: C, 34.27; H, 3.10; N, 13.27. $C_{12}H_{13}BrMoN_4O_2$ calc.: C, 34.23; H, 3.11; N, 13.30%. III with one molecule of CH_2Cl_2: Anal. Found: C, 39.12; H, 3.41; N, 9.59. $C_{19}H_{10}Cl_2BrMoN_4O_2$ calc.: C, 39.20; H, 3.29; N, 9.62%. IV: Anal. Found: C, 47.73; H, 4.64; N, 10.20. $C_{22}H_{25}BrMoN_4O_2$ calc.: C, 47.76; H, 4.55; N, 10.13%.

Method 2. A solution of one mmol of $[Mo(MeCN)_2(CO)_2(\pi\text{-allyl})Br]$ [16] in 20 ml of MeCN was added to one mmol of N–N. The mixture was stirred for one hour and the solvent was removed under vacuum to give the product, I–IV.

Method 3. A solution of one mmol of $[Mo(PhHCPz'_2)(CO)_3]$ [2] dissolved in 50 ml of CH_2Cl_2 was treated with excess allyl bromide (ca. 0.5 ml). The mixture was stirred for one hour. Removal of the solvent and excess allyl bromide gave a solid residue. The product was recrystallized from CH_2Cl_2/hexane to give 0.55 g (95%) of IV.

X-Ray diffraction study of $[Mo(PhHCPz'_2)(CO)_2(\pi\text{-allyl})Br]$ (IV). The crystals of IV were grown from CH_2Cl_2/hexane at room temperature. General operating procedures and listings of programs were previously given [17]. Absorption correction was performed on this structure using ψ scans. Final coordinates of the non-hydrogen atoms (Table 2), selected bond lengths and bond angles (Table 3), and the related crystal data (Table 4) are reported. The H-atom coordinates and structural factors are available from the authors.

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References

1 K.-B. Shiu and C.-J. Chang, J. Organomet. Chem., 395 (1990) C47.

2 K.-B. Shiu, C.-C. Chou, S.-L. Wang and S.-C. Wei, Organometallics, 9 (1990) 286; 9 (1990) 2632.

3 (a) K.-B. Shiu, K.-S. Loiou, S.-L. Wang, C.P. Cheng, F.-J. Wu, J. Organomet. Chem., 359 (1989) C1; (b) K.-B. Shiu, K.-S. Liou, S.-L. Wang and S.-C. Wei, Organometallics, 9 (1990) 669.

4 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke (Eds.), Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.

5 J.-L. Rousche and G.R. Dobson, J. Organomet. Chem., 150 (1978) 239.

6 R.H. Fenn and A.J. Graham, J. Organomet. Chem., 37 (1972) 137.

7 A.J. Grahan and R.H. Fenn, J. Organomet. Chem., 25 (1970) 173.

8 M.G.B. Drew, B.J. Brisdon and A. Day, J. Chem. Soc., Dalton Trans., (1981) 1310.

9 D.F. Shriver (Ed.), Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969.

10 S. Julia, P. Sala, J. Mazo, M. Sancho, C. Ochoa, J. Elguero, J.-P. Fayet and M.-C. Vertut, Heterocycl. Chem., 19 (1982) 1141.

11 A.R. Katritzky, A.E. Abdel-Rahman, D.E. Leahy and O.A. Schwarz, Tetrahedron, 39 (1983) 4133.

12 K.-S. Liou, M.Sc. Thesis, National Cheng Kung University, Tainan, Taiwan, June 1988.

13 C.-C. Chou, M.Sc. Thesis, National Cheng Kung University, Tainan, Taiwan, June, 1989.

14 K.-B. Shiu and C.-J. Chang, J. Chin. Chem. Soc. (Taipei), 34 (1987) 297.

15 G. Gioia Lobbia and F. Bonati, J. Organomet. Chem., 366 (1989) 121.

16 B.J. Brisdon and M. Cartwright, J. Organomet. Chem., 164 (1979) 83.

17 K.-B. Shiu, F.-M. Shen, S.-L. Wang and S.-C. Wei, J. Organomet. Chem., 372 (1989) 251.