Journal of Organometallic Chemistry, 159 (1978) 289—298

STRUCTURAL CHARACTERIZATION OF A FOUR-ELECTRON DONATING, DOUBLY-BRIDGING ISOCYANIDE IN $(\mu\text{-}p\text{-}CH_3C_6H_4NC)Mn_2(Ph_2PCH_2PPh_2)_2(CO)_4$

LINDA S. BENNER, MARILYN M. OLMSTEAD and ALAN L. BALCH*
Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)
(Received April 19th, 1978)

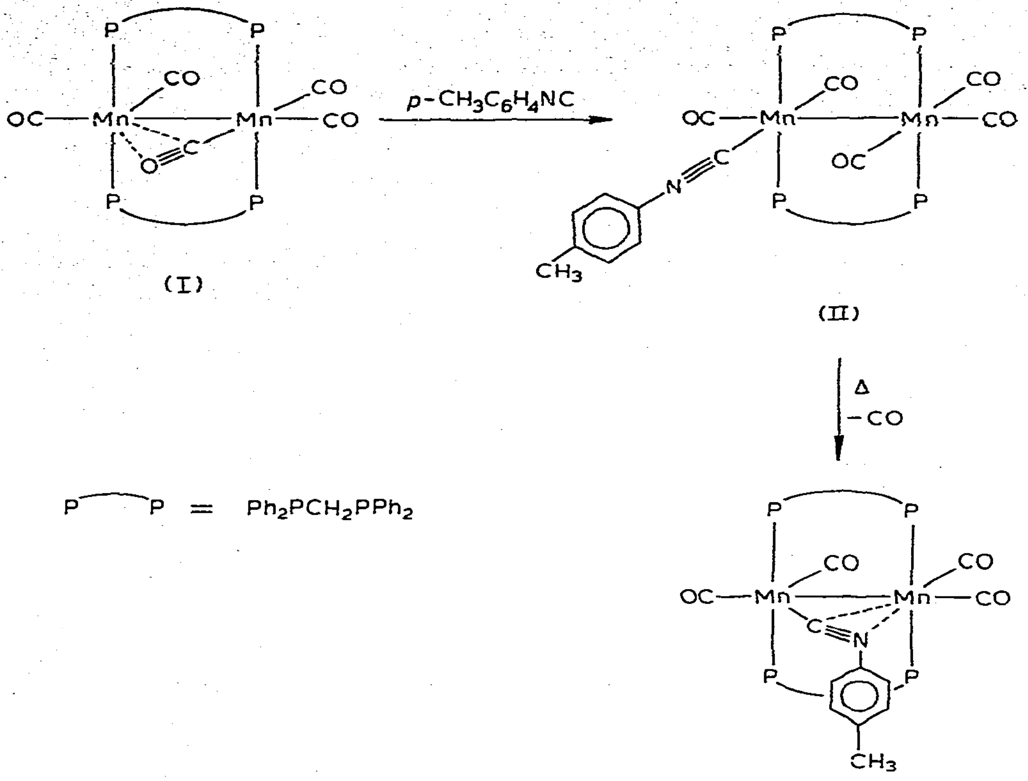
Summary

X-Ray crystallographic analysis of $(\mu\text{-}p\text{-}CH_3C_6H_4NC)Mn_2(Ph_2PCH_2PPh_2)_2(CO)_4$ is reported. The molecule consists of two manganese atoms joined by a single bond and bridged by two *trans* diphosphine ligands and the isocyanide. There are two terminal CO groups per Mn. The isocyanide carbon donates a pair of electrons to one Mn (Mn—C = 1.81 Å) while the C—N unit donates a second pair of electrons to the other Mn (Mn—N = 2.12 Å, Mn—C = 2.14 Å). The isocyanide is strongly bent with a C—N—C(phenyl) angle of 137°. The bonding of the isocyanide ligand is discussed.

Introduction

The ability of carbon monoxide, acetylides, and aminonitriles (cyanamides) to act as 4-electron, doubly-bridging ligands has been recently established. Compounds exhibiting this relatively rare mode of coordination involve both compounds where the metal atoms are directly bonded (e.g. $Mn_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}CO)(CO)_4$, [1,2], $Fe_2(CO)_6(\mu\text{-}C_2Ph)(\mu\text{-}PPh_2)$ [3], $(\eta^5\text{-}C_5H_5)_2Mo(CO)_4(\mu\text{-})NCNMe_2)$ [4]) and compounds where there is no direct metal—metal bond (e.g. $Ni_3(CO)_3(\mu\text{-}NCNC_5H_{10})_3$ [5,6], $(Ph_3P)Rh(C{\equiv}CC_6F_5)_5Ag_2(PPh_3)_2)$ [7,8].

We recently prepared the isocyanide complex $Mn_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}CNC_6H_4CH_3)(CO)_4$ (III) via eq. 1 [9]. The low CN stretching frequency (1661 cm^{-1}) of III indicated that a bridging isocyanide was present and we anticipated that this molecule possesses structure III which is analogous to that of I. However, on the basis of the available spectroscopic data, the alternate structures, IV, which is similar to that found in $Pd_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}CNCH_3)(CNCH_3)_2^{2+}$ [10], and V which is unprecedented, could not be wholely rejected. Consequently the present crystal structure determination was undertaken to ascertain the geometric details of the isocyanide bonding.

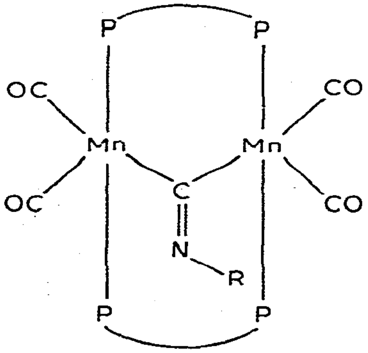


(I)

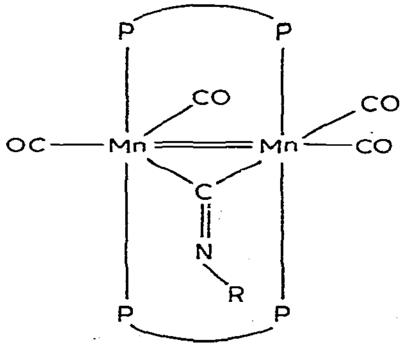
(II)

(III)

(1)



(IV)



(V)

Experimental

Data collection. Crystals of $Mn_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}p\text{-}CH_3C_6H_4NC)(CO)_4$ [9] were obtained as a dichloromethane solvate by slow diffusion of n-hexane into a dichloromethane solution of the complex. To prevent rapid solvent loss and subsequent crystal fracture, several crystals were coated with epoxy resin while still

TABLE 1

CRYSTAL DATA FOR $Mn_2(dpm)_2(\mu\text{-}p\text{-}CH_3C_6H_4NC)(CO)_4 \cdot 3\ CH_2Cl_2$

$Mn_2Cl_6P_4O_4NC_{65}H_{57}$	$V = 3101.27(68)$ Å^3
FW = 1362.7	$Z = 2$
$a = 14.6519(19)$ Å	Triclinic
$b = 14.8407(20)$ Å	Space Group $P\overline{1}$ (No. 2)
$c = 17.5287(20)$ Å	Mo-K_α Radiation
$\alpha = 69.881(10)^\circ$	μ(Mo-K_α) 8.3 cm^{-1}
$\beta = 83.360(11)^\circ$	D_{exp} (298 K) 1.4 g cm^{-3} [a]
$\gamma = 60.286(8)^\circ$	D_{calc} (150 K) 1.46 g cm^{-3}

[a] Since crystals tend to dissolve in the density standard, an accurate measurement could not be obtained.

in the mother liquor. A red-orange plate measuring 1.0 × 0.5 × 0.08 mm was selected for data collection and immediately mounted on the goniometer head under a nitrogen cold stream.

Intensity data were collected at 150 K on a Syntex $P2_1$ automated diffractometer using Mo-K_α radiation ($\lambda = 0.7107$ Å) and a graphite monochromator. A variable speed (0.5 to 30° min^{-1})ω scan of the most intense part of the peak and a 1° offset for background were used. The intensities of 2 standard reflections were measured every 198 reflections and showed only random fluctuation during data collection. Of the 7926 reflections measured with $2\theta \leqslant 45^\circ$, 6669 with $I_{net} > 3\sigma(I_{net})$ were used in final refinement. The data were corrected for Lorentz and polarization effects but not for absorption. Crystal data are reported in Table 1.

Solution and refinement. The crystallographic computer programs used in this work were furnished by Dr. H. Hope, except for Johnson's ORTEP-2 [11]. Cromer and Waber's atomic scattering factors [12a] were used and corrections for real and imaginary parts of anomalous scattering [12b] were made to manganese and chlorine.

A sharpened three-dimensional Patterson map was used to locate the two manganese and four phosphorus atoms. An initial Fourier map calculated from these six atoms did not reveal the positions of additional atoms. Following two cycles of full-matrix least-squares refinement of the six heavy atoms, a second Fourier synthesis indicated the positions of three phenyl rings and three carbon monoxides. Refinement of these atoms and a subsequent Fourier map eventually allowed another thirty-one atoms to be located. The final twelve atoms of the complex were found by a difference Fourier. Two more cycles of isotopic refinement of seventy-three atoms brought R to 0.285 where $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$. A second difference Fourier revealed three molecules of dichloromethane. Thereafter, all eighty-two non-hydrogen atoms were used in the structure factor calculation. After partial refinement of the nine solvent atoms, the seventy-three atoms of the complex were refined isotropically to convergence at an R index of 0.111. * A total of eighteen cycles of full-matrix least-squares refinement

---

* The table of structure factors has been deposited as NAPS Document No. 03317 (37 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 9.25 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 2

FINAL ATOMIC FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FACTORS (Å^2)[a]

Atom	x/a	y/b	z/c	B_{iso}
Mn(1)	0.3000(1)	0.0919(1)	0.1720(1)	1.49(3)
Mn(2)	0.1784(1)	0.0562(1)	0.3136(1)	1.41(3)
P(1)	0.4391(2)	0.0408(2)	0.2522(1)	1.39(4)
P(2)	0.1681(2)	0.1375(2)	0.0849(1)	1.45(4)
P(3)	0.3059(2)	0.0102(2)	0.4021(1)	1.41(4)
P(4)	0.378(2)	0.1096(2)	0.2352(1)	1.33(4)
O(1)	0.0950(5)	−0.0637(5)	0.4459(4)	2.47(12)
O(2)	0.0736(5)	0.2796(5)	0.3266(4)	2.86(13)
O(3)	0.1989(5)	0.3177(5)	0.1753(4)	2.57(12)
O(4)	0.4293(5)	0.1145(5)	0.0317(4)	2.70(12)
N(1)	0.3374(6)	−0.0755(6)	0.2131(4)	2.13(13)
C(1)	0.1265(7)	−0.0123(7)	0.3939(5)	1.70(15)
C(2)	0.1144(7)	0.1925(7)	0.3216(5)	1.88(15)
C(3)	0.2385(7)	0.2278(7)	0.1743(5)	1.73(15)
C(4)	0.3767(7)	0.1060(7)	0.0871(5)	1.99(16)
C(5)	0.4122(6)	0.0418(7)	0.3580(5)	1.65(14)
C(6)	0.0352(7)	0.1844(7)	0.1254(5)	1.79(15)
C(7)	0.1314(7)	0.2572(7)	−0.0094(5)	1.74(15)
C(8)	0.1706(8)	0.3273(8)	−0.0214(6)	2.69(18)
C(9)	0.1359(8)	0.4208(9)	−0.0913(6)	3.30(20)
C(10)	0.0628(8)	0.4462(8)	−0.1487(6)	2.82(18)
C(11)	0.0265(8)	0.3707(8)	−0.1368(6)	2.84(18)
C(12)	0.0617(7)	0.2766(7)	−0.0691(6)	2.27(16)
C(13)	0.1897(6)	0.0300(7)	0.0450(5)	1.54(14)
C(14)	0.1250(7)	−0.0166(7)	0.0578(5)	2.27(16)
C(15)	0.1531(8)	−0.1069(8)	0.0331(6)	2.74(18)
C(16)	0.2473(8)	−0.1491(8)	−0.0066(6)	2.77(18)
C(17)	0.3094(7)	−0.0985(8)	−0.0214(6)	2.40(17)
C(18)	0.2816(7)	−0.0106(7)	0.0032(5)	2.17(16)
C(19)	0.0072(6)	0.0045(7)	0.2330(5)	1.61(14)
C(20)	−0.0883(7)	0.0356(7)	0.1947(5)	1.92(15)
C(21)	−0.1081(7)	−0.0449(7)	0.1892(5)	2.33(17)
C(22)	−0.0317(8)	−0.1555(8)	0.2210(6)	2.79(18)
C(23)	0.0635(8)	−0.1867(8)	0.2596(6)	2.66(18)
C(24)	0.0812(7)	−0.1061(7)	0.2664(5)	2.03(16)
C(25)	−0.0863(6)	0.2070(6)	0.2638(5)	1.35(14)
C(26)	−0.1317(8)	0.3191(8)	0.2263(6)	2.76(18)
C(27)	−0.2226(8)	0.3929(8)	0.2539(6)	2.89(18)
C(28)	−0.2681(7)	0.3511(8)	0.3214(6)	2.59(17)
C(29)	−0.2219(7)	0.2377(8)	0.3597(6)	2.54(17)
C(30)	−0.1341(7)	0.1674(8)	0.3306(6)	2.34(17)
C(31)	0.5062(6)	0.1233(7)	0.2251(5)	1.59(14)
C(32)	0.5969(7)	0.0865(7)	0.2721(5)	2.24(16)
C(33)	0.6511(7)	0.1449(8)	0.2540(6)	2.56(17)
C(34)	0.6147(7)	0.2418(8)	0.1883(6)	2.61(17)
C(35)	0.5246(7)	0.2801(8)	0.1399(6)	2.56(17)
C(36)	0.4711(7)	0.2206(7)	0.1589(5)	1.82(15)
C(37)	0.5512(6)	−0.0950(7)	0.2616(5)	1.70(15)
C(38)	0.5651(7)	−0.1890(7)	0.3228(5)	2.13(16)
C(39)	0.6464(8)	−0.2930(8)	0.3245(6)	2.72(18)
C(40)	0.7173(8)	−0.3006(8)	0.2649(6)	2.91(18)
C(41)	0.7062(8)	−0.2066(9)	0.2021(6)	3.22(20)
C(42)	0.6241(8)	−0.1049(8)	0.2004(6)	2.81(18)
C(43)	0.2616(6)	0.0799(7)	0.4788(5)	1.60(14)
C(44)	0.2980(7)	0.1464(7)	0.4885(5)	2.27(16)
C(45)	0.2612(8)	0.1954(8)	0.5488(6)	2.63(17)
C(46)	0.1882(8)	0.1778(8)	0.6009(6)	2.89(18)
C(47)	0.1503(7)	0.1121(8)	0.5911(6)	2.59(17)

(continued)

TABLE 2 (continued)

Atom	x/a	y/b	z/c	B_{iso}
C(48)	0.1873(7)	0.0625(7)	0.5312(5)	2.04(16)
C(49)	0.3786(7)	−0.1330(7)	0.4700(5)	1.89(15)
C(50)	0.3771(7)	−0.2174(7)	0.4525(5)	2.25(16)
C(51)	0.4386(8)	−0.3258(9)	0.5011(6)	3.16(19)
C(52)	0.5027(9)	−0.3515(9)	0.5692(7)	3.70(21)
C(53)	0.5010(9)	−0.2676(9)	0.5869(7)	3.57(21)
C(54)	0.4420(7)	−0.1587(7)	0.5376(5)	2.27(16)
C(55)	0.2712(7)	−0.0318(7)	0.2588(5)	2.02(16)
C(56)	0.3897(7)	−0.1785(7)	0.2016(5)	1.93(15)
C(57)	0.3628(8)	−0.2591(8)	0.2450(6)	2.83(18)
C(58)	0.4113(8)	−0.3582(9)	0.2297(6)	3.29(20)
C(59)	0.4847(9)	−0.3765(9)	0.1717(7)	3.46(20)
C(60)	0.5121(8)	−0.2962(9)	0.1305(6)	3.14(19)
C(61)	0.4652(7)	−0.1968(8)	0.1457(6)	2.39(17)
C(62)	0.5260(10)	−0.4813(11)	0.1497(8)	4.67(25)
C(63)	0.1355	0.6746	0.4904	6.40
C(64)	0.1215	0.4428	0.3987	5.95
C(65)	0.2335	0.5170	0.0950	5.70
Cl(1)	0.2503	0.6176	0.4397	7.54
Cl(2)	0.2284	0.6166	0.1296	6.69
Cl(3)	0.0148	0.5756	0.3670	6.76
Cl(4)	0.1169	0.5732	0.5623	6.89
Cl(5)	0.2160	0.4296	0.3275	8.21
Cl(6)	0.2738	0.5279	−0.0009	11.39

[a] Estimated standard deviations are given in parentheses. No e.s.d. are given for solvent atoms.

were utilized. Excluding solvent atoms, final atomic shifts were ⩽1/10 the corresponding e.s.d. except for C(28), C(41), C(51), and C(55) whose final shifts were <1/7 the e.s.d. The small amount of electron density observed in the final difference Fourier was clearly due to the heavier atoms. No effort was made to locate hydrogen atoms. Final atomic fractional coordinates and isotropic temperature coefficients, together with estimated standard deviations for all but the solvent atoms, are given in Table 2.

Results and discussion

The molecular structure of III, which has no crystallographically imposed symmetry, is shown in Fig. 1. Thus the molecule has the structure we originally thought most probable. The unit cell contains two molecules of III and six dichloromethane molecules with no intermolecular contacts less than the sum of the van der Waals radii. Important interatomic distances and angles are listed in Tables 3 and 4.

The Mn—Mn distance of 2.936 Å indicates that these two atoms are joined by a single bond. This bond length may be compared with the Mn—Mn bond length in $Mn_2(CO)_{10}$ (2.923 Å) [13] and in the carbonyl bridged complex, I, (2.934 Å) [2]. The two bridging phosphine ligands lie in mutually *trans* positions with the four phosphorus and two manganese atoms sitting in a plane. The lengths of the Mn—P bonds are unexceptional and fall within a more narrow range than found for I [2]. Additionally the metals are coordinated by four terminal carbonyl ligands and the bridging isocyanide. These five ligands and the

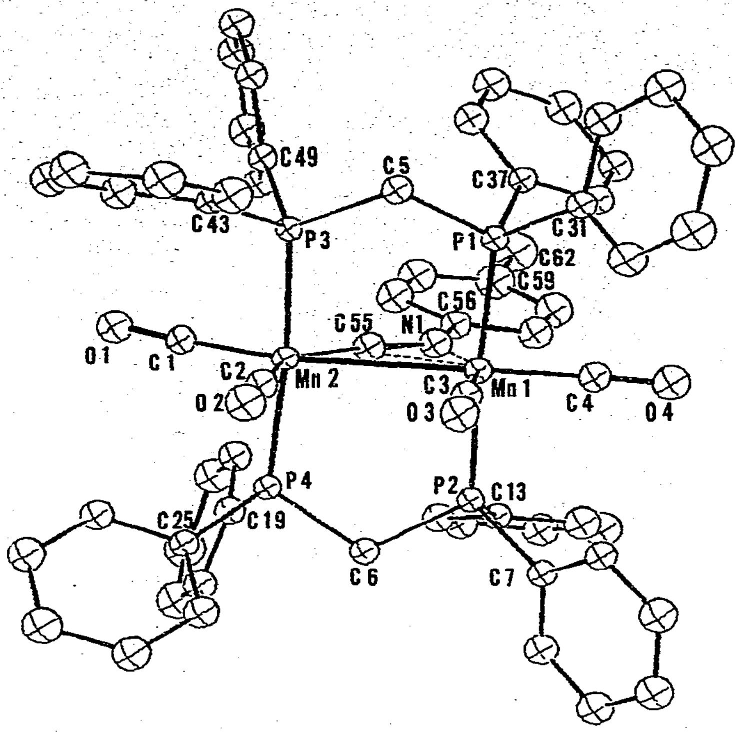


Fig. 1. An ORTEP drawing of $Mn_2dpm_2(\mu\text{-}CNC_6H_4CH_3)(CO)_4$ showing 50% thermal ellipsoids.

two manganese atoms lie in a plane which is perpendicular to the Mn_2P_4 plane. The equations of these least-squares planes along with the atom distances from the planes are reported in Table 5. The plane containing the bridging isocyanide and the terminal carbonyl ligands is shown in Fig. 2.

TABLE 3

IMPORTANT INTERATOMIC DISTANCES (Å) [a,b]

Mn(1)—Mn(2)	2.936(2)	P(1)—P(3)	3.129(3)
Mn(1)—P(1)	2.259(3)	P(2)—P(4)	3.103(3)
Mn(1)—P(2)	2.278(3)	P(1)—C(5)	1.85(1)
Mn(2)—P(3)	2.245(3)	P(3)—C(5)	1.86(1)
Mn(2)—P(4)	2.247(3)	P(2)—C(6)	1.86(1)
Mn(2)—C(1)	1.77(1)	P(4)—C(6)	1.86(1)
Mn(2)—C(2)	1.81(1)	P(1)—C(31)	1.84(1)
Mn(1)—C(3)	1.77(1)	P(1)—C(37)	1.83(1)
Mn(1)—C(4)	1.78(1)	P(2)—C(7)	1.85(1)
Mn(2)—C(55)	1.81(1)	P(2)—C(13)	1.83(1)
Mn(1)—C(55)	2.14(1)	P(3)—C(43)	1.84(1)
Mn(1)—N(1)	2.12(1)	P(3)—C(49)	1.84(1)
C(1)—O(1)	1.18(1)	P(4)—C(19)	1.84(1)
C(2)—O(2)	1.16(1)	P(4)—C(25)	1.82(1)
C(3)—O(3)	1.17(1)	N(1)—C(55)	1.25(1)
C(4)—O(4)	1.18(1)	N(1)—C(56)	1.41(1)
		C(59)—C(62)	1.54(2)

[a] Estimated standard deviations given in parentheses. [b] Phenyl C—C and dichloromethane C—Cl distances are normal and are not reported.

TABLE 4

IMPORTANT INTERATOMIC ANGLES (DEGREES)[a]

Mn(2)—Mn(1)—P(1)	91.8(1)	Mn(1)—Mn(2)—P(3)	93.1(1)	Mn(1)—P(1)—C(5)	116.3(4)
Mn(2)—Mn(1)—P(2)	91.5(1)	Mn(1)—Mn(2)—P(4)	92.6(1)	Mn(1)—P(1)—C(31)	119.4(3)
P(1)—Mn(1)—P(2)	175.9(1)	P(3)—Mn(2)—P(4)	173.5(1)	Mn(1)—P(1)—C(37)	115.0(3)
Mn(2)—Mn(1)—C(3)	84.0(3)	Mn(1)—Mn(2)—C(1)	159.3(3)	C(5)—P(1)—C(31)	97.9(4)
Mn(2)—Mn(1)—C(4)	177.0(4)	Mn(1)—Mn(2)—C(2)	98.8(3)	C(5)—P(1)—C(37)	105.5(4)
Mn(2)—Mn(1)—C(55)	37.8(3)	Mn(1)—Mn(2)—C(55)	46.3(3)	C(31)—P(1)—C(37)	100.1(5)
Mn(2)—Mn(1)—N(1)	71.9(2)	P(3)—Mn(2)—C(1)	89.0(3)	Mn(1)—P(2)—C(6)	115.4(3)
P(1)—Mn(1)—C(3)	91.5(3)	P(3)—Mn(2)—C(2)	87.4(3)	Mn(1)—P(2)—C(7)	118.8(4)
P(1)—Mn(1)—C(4)	87.9(3)	P(4)—Mn(2)—C(1)	86.9(3)	Mn(1)—P(2)—C(13)	115.3(3)
P(2)—Mn(1)—C(3)	91.3(3)	P(4)—Mn(2)—C(2)	88.5(3)	C(6)—P(2)—C(7)	97.0(5)
P(2)—Mn(1)—C(4)	88.6(3)	P(3)—Mn(2)—C(55)	92.3(3)	C(6)—P(2)—C(13)	106.1(5)
P(1)—Mn(1)—C(55)	90.2(3)	P(4)—Mn(2)—C(55)	94.0(3)	C(7)—P(2)—C(13)	101.6(4)
P(1)—Mn(1)—N(1)	88.0(3)	C(1)—Mn(2)—C(55)	112.8(5)	Mn(2)—P(3)—C(5)	116.2(3)
P(2)—Mn(1)—C(55)	91.0(3)	C(2)—Mn(2)—C(55)	145.1(5)	Mn(2)—P(3)—C(43)	115.2(3)
P(2)—Mn(1)—N(1)	90.8(2)	C(1)—Mn(2)—C(2)	102.1(5)	Mn(2)—P(3)—C(49)	118.9(4)
N(1)—Mn(1)—C(55)	34.1(4)	Mn(1)—C(3)—O(3)	179.2(9)	C(5)—P(3)—C(43)	101.4(5)
C(3)—Mn(1)—C(55)	121.8(4)	Mn(1)—C(4)—O(4)	178.7(9)	C(5)—P(3)—C(49)	103.1(5)
C(3)—Mn(1)—N(1)	155.9(4)	Mn(2)—C(1)—O(1)	175.8(9)	C(43)—P(3)—C(49)	99.2(4)
C(3)—Mn(1)—C(4)	99.0(5)	Mn(2)—C(2)—O(2)	179.8(8)	Mn(2)—P(4)—C(6)	116.6(4)
C(4)—Mn(1)—C(55)	139.2(5)	P(1)—C(5)—P(3)	115.0(5)	Mn(2)—P(4)—C(19)	118.4(3)
C(4)—Mn(1)—N(1)	105.1(4)	P(2)—C(6)—P(4)	113.3(5)	Mn(2)—P(4)—C(25)	113.5(3)
Mn(1)—C(55)—Mn(2)	95.9(5)	Mn(1)—N(1)—C(55)	73.6(6)	C(6)—P(4)—C(19)	102.5(4)
Mn(1)—C(55)—N(1)	72.3(6)	Mn(1)—N(1)—C(56)	149.0(6)	C(6)—P(4)—C(25)	101.6(4)
Mn(2)—C(55)—N(1)	168.1(9)	C(55)—N(1)—C(56)	137.2(9)	C(19)—P(4)—C(25)	101.7(5)

[a] Estimated standard deviations given in parentheses.

TABLE 5

EQUATIONS OF LEAST-SQUARE PLANES[a] AND DISTANCES (Å) OF ATOMS FROM THESE PLANES

Plane	Defining atoms	Distances (Å)					
I	Mn(1), Mn(2), P(1),	Mn(1)	0.0314	P(1)	−0.0038	P(3)	0.0085
	P(2), P(3), P(4)	Mn(2)	−0.0412	P(2)	−0.0255	P(4)	0.0306
II	Mn(1), Mn(2), C(1),	Mn(1)	−0.0053	O(1)	−0.0673	C(56)	0.0314
	C(2), C(3), C(4)	Mn(2)	0.0036	O(2)	0.0402	C(57)	−0.1900
	C(55)	C(1)	−0.0315	O(3)	−0.0225	C(58)	−0.2907
		C(2)	0.0270	O(4)	0.0266	C(59)	−0.1846
		C(3)	−0.0185	O(5)	0.0636	C(60)	0.0664
		C(4)	−0.0026	N(1)	0.0314	C(61)	0.1854
		C(55)	0.0273			C(62)	−0.4703
III	C(56), C(57), C(58),	C(56)	−0.0136	C(58)	0.0097	C(60)	0.0021
	C(59), C(60), C(61)	C(57)	0.0033	C(59)	−0.0123	C(61)	0.0109
						C(61)	−0.1747

Plane I: $2.0728x + 13.7616y + 4.7313z - 2.6681 = 0$
Plane II: $11.5636x + 4.9357y + 11.2328z - 5.8591 = 0$
Plane III: $10.0370x + 2.9693y + 12.1286z - 5.8410 = 0$

Dihedral angle between Plane I and Plane II: 90.1°
Dihedral angle between plane II and Plane III: 9.9°

[a] Equations have the form $Ax + By + Cz - D = 0$ where x, y, and z are fractional triclinic coordinates.

The four terminal carbonyl ligands are all essentially linear with M—C—O angles ranging from 176 to 180°. The M—C bond lengths to the carbonyl ligands range from 1.77 to 1.81 Å and the C—O distances range from 1.16 to 1.18 Å. Thus, the individual metal—carbonyl bonds are quite normal.

On the other hand, the isocyanide ligand is splayed between the two metals in an uncharacteristic fashion. The Mn(2)—C—N unit is slightly bent (Mn—C—N angle 168°) while the C—N—C(phenyl) portion is decidedly bent (C—N—C angle 137°). In contrast to other complexes containing both bridging and terminal isocyanide or carbonyl ligands, the Mn(2)—C(55) distance of 1.81 Å in III is not significantly longer than the terminal M—C distances. The isocyanide carbon C(55) and nitrogen N(1) are equidistant from Mn(1), (Mn(1)—C(55), 2.14 Å; Mn(1)—N(1), 2.12 Å). This observation contrasts with the geometry of the bridging carbonyl in I for which the corresponding Mn—C distance (2.01 Å) is reported to be shorter than the Mn—O distance (2.29 Å) [2]. The isocyanide C—N distance in III is longer than the carbonyl C—O distances in III, longer than observed for terminal isocyanide ligands, as long as the C—N distance in other bridging isocyanide ligands [14]. The phenyl ring of the isocyanide ligand is nearly coplanar with the plane formed by the two manganese atoms, the carbonyl ligands, and the isocyanide CN. The dihedral angle between these two planes is only 9.9°.

The geometry of the bridging isocyanide in III clearly indicates that it behaves as a four-electron ligand by donating two electrons to each manganese. As a result each manganese atom acquires an 18-electron configuration. Compound III represents the first example of such a bridging isocyanide. The most striking feature about the bridging ligand is the degree to which it is bent. The bending can be compared to that observed for the isoelectronic acetylide ligands which

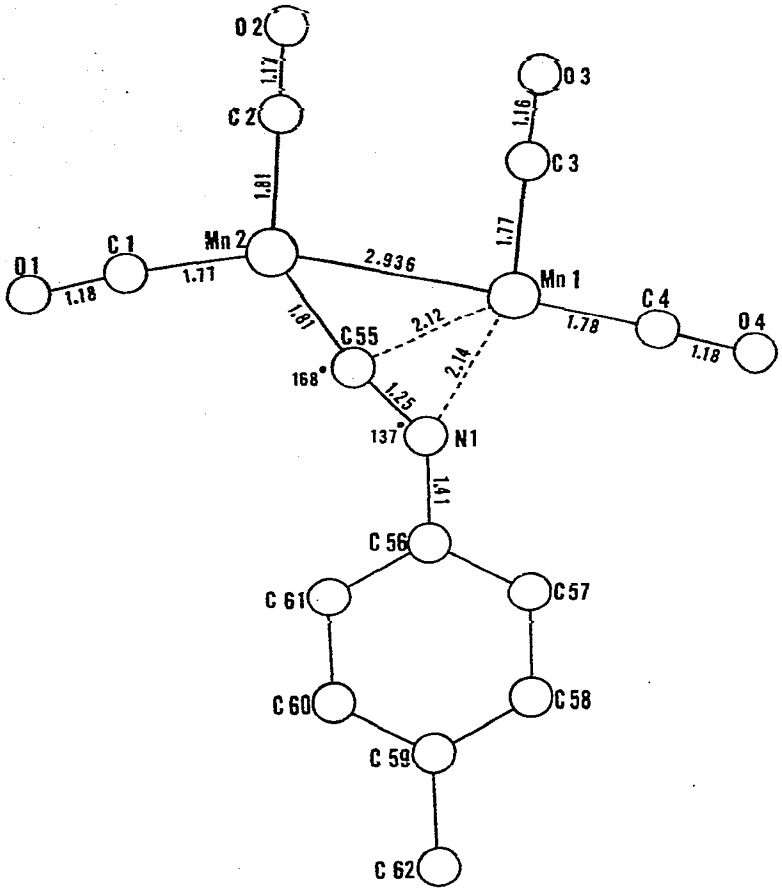


Fig. 2. Bond distances and angles in the $Mn_2(\mu\text{-}CNC_6H_4CH_3)(CO)_4$ plane.

bridge two metals. In these cases the bending of the originally linear $C{-}C{\equiv}C$ portion never exceeds 22° [3,15—18]. We propose the following account of the metal ligand bonding to explain the structural features of this bridging isocyanide. A typical terminal isocyanide ligand may be described in terms of the valence bond structures $M{-}C{\equiv}N{-}R$ (VI) and $M{=}C{=}N{-}R$ (VII).

In the present case the Mn(2)—isocyanide bond involves donation of the carbon lone pair to the manganese with the structure VII contributing heavily to the formation of that bond. This explains the shortness of the Mn(2)—C(55) bond and length of the C(55)—N(1) bond. The isocyanide donates an additional pair of electrons to Mn(1). This can be viewed as a donation of the nitrogen lone pair of structure VII or, alternatively, as a donation of the in-plane π-bond of structure VI. Since the C—N—C(phenyl) angle is 137°, structure VII must make a significant contribution to this bond. In this context we point out the existence of terminal isocyanide ligands in $Mo(Ph_2PCH_2CH_2PPh_2)_2(CNCH_3)_2$ [20] which are strongly bent due to significant participation of structure VII in bonding. In order to maintain conjugation with the isocyanide group and enhance metal—ligand back-bonding, the phenyl ring of the isocyanide ligand is constrained to lie near the plane of the Mn_2CN unit.

The orientations of the phenyl rings of the *trans* phosphine ligands have adjusted to accommodate the bridging isocyanide ligand. The orientation of the four phenyl rings on the left side of Fig. 1 is typical of what has been observed in a number of binuclear complexes bridged by two bis(diphenylphosphino)-methane ligands [2,10,21]. On the right side of Fig. 1, the phenyl ring of the isocyanide ligand is interleaved between two phenyl rings (defined by C(37) and C(13)) of the phosphine ligands. These two phenyl rings have rotated from their more normal positions in which they would lie nearly parallel to the Mn—P vectors as do the rings of C(49) and C(19) on the left side of Fig. 1. The closest contacts between the three phenyl rings are in the range 3.25—3.4 Å. Based on the shifts observed for the phenyl resonances in the proton magnetic resonance spectrum of III, we had previously suggested [9] that such close contacts between the isocyanide phenyl ring and the phosphine phenyl rings existed.

Acknowledgement

We thank the National Science Foundation and National Institutes of Health for support and Professor H. Hope for making the crystallographic facilities available.

References

1 R. Colton and C.J. Commons, Aust. J. Chem., 28 (1975) 1673.
2 C.J. Commons and B.F. Hoskins, Aust. J. Chem., 28 (1975) 1663.
3 H.A. Patel, R.G. Fischer, A.J. Carty, P.V. Naik and G.J. Palenik, J. Organometal. Chem., 60 (1973) C49.
4 M.H. Chisholm, F.A. Cotton, M.W. Extine and L.A. Rankel, J. Amer. Chem. Soc., 100 (1978) 807.
5 K. Krogman and R. Mattes, Angew. Chem. Int. Ed. Engl., 5 (1966) 1046.
6 H. Bock and H. tom Diek, Chem. Ber., 99 (1966) 213.
7 M.R. Churchill and B.G. De Boer, Inorg. Chem., 14 (1975) 2630.
8 O.M. Abu Salah, M.I. Bruce, M.R. Churchill and B.G. De Boer, Chem. Commun., (1974) 688.
9 A.L. Balch and L.S. Benner, J. Organometal. Chem., 135 (1977) 339.
10 M. Olmstead, H. Hope, L.S. Benner and A.L. Balch, J. Amer. Chem. Soc. 99 (1977) 5502.
11 C.K. Johnson, ORTEP-2, Oak Ridge National Laboratory, Oak Ridge, TN.
12 "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp. 99—101; (b) pp. 149—150.
13 L.F. Dahl and R.E. Rundle, Acta Crystallogr., 16 (1963) 419.
14 E.L. Muetterties, Bull. Soc. Chim. Belg., 85 (1976) 451.
15 P.W.R. Corfield and H.M.N. Shearer, Acta Crystallogr., 20 (1966) 502.
16 M.I. Bruce, R. Clark, J. Howard and P. Woodward, J. Organometal. Chem., 42 (1972) C107.
17 M.R. Churchill and S.A. Bezman, Inorg. Chem., 13 (1974) 1418.
18 O.M. Abu Salah, M.I. Bruce, R.E. Davis and N.V. Raghavan, J. Organometal. Chem., 64 (1972) C48.
19 W.F. Smith, J. Yule, N.J. Taylor, H.N. Paik and A.J. Carty, Inorg. Chem., 16 (1977) 1593.
20 J. Chatt, A.J.L. Pombeiro, R.L. Richards, G.H.D. Royston, K.W. Muir and R. Walker, Chem. Commun., (1975) 708.
21 L.S. Benner, M.M. Olmstead, H. Hope and A.L. Balch, submitted for publication.