

The preparation of new manganese(II) isocyanide complexes, $\text{MnI}_2(\text{CNBu}^t)_n$ ($n = 1, 1.5, 2$) and the mixed isocyanide/tertiary-phosphine complex $\text{MnI}_2(\text{PPh}_3)(\text{CNBu}^t)_2$. The isolation and X-ray crystallographic characterisation of the $\text{Mn}^{\text{I}}/\text{Mn}^{\text{II}}$ mixed-valence isomeric complexes $[\text{Mn}(\text{CNBu}^t)_6][\text{MnI}_3(\text{PPh}_3)]$ and $[\text{Mn}(\text{CNBu}^t)_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBu}^t)]$

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Abstract

The complexes $\text{MnI}_2(\text{CNBu}^t)_n$ ($n = 1, 1.5$ and 2) have been prepared by reaction of MnI_2 or MnI_2L_n ($\text{L} = \text{PPh}_3$, THF, $n = 2$; $\text{L} = (4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$, $n = 1.5$) with CNBu^t in toluene. The reaction of $\text{MnI}_2(\text{PPh}_3)_2$ with CNBu^t in *n*-pentane slurry gives the complex of formula $\text{MnI}_2(\text{PPh}_3)(\text{CNBu}^t)_2$. When $\text{MnI}_2(\text{PPh}_3)_2$ reacts with an excess of CNBu^t in toluene, red–orange crystals of $[\text{Mn}(\text{CNBu}^t)_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBu}^t)]$ and yellow crystals of $[\text{Mn}(\text{CNBu}^t)_6][\text{MnI}_3(\text{PPh}_3)]$ are formed. X-ray diffraction studies of the two types of crystal show them to have the ion-pair structures. IR studies suggest that in the $\text{MnI}_2(\text{CNBu}^t)_n$ complexes the Mn–C bond is predominantly of σ -character, whereas in the mixed phosphine/isocyanide derivatives the Mn–C bond is predominantly of π -character.

Introduction

Isocyanides are among the few ligands with an electron lone pair on a carbon atom. The presence of this lone pair on the terminal carbon atom enables isocyanides to act as carbon ligands in coordination compounds and to behave as Lewis bases similar to carbon monoxide and phosphines. A characteristic property of isocyanide ligands is the capacity to function as stronger π -acceptors than phosphines [1]. Moreover, some of the properties of isocyanides can be varied in the same manner as phosphines.

There has been a good deal of recent interest in the spectroscopic and chemical properties of homoleptic isocyanide complexes [2–15], but there are only a very few reports of isocyanide complexes of the Group 7A metals, and it is only recently that complexes with Tc have been reported [16, 17].

Manganese forms isocyanide complexes in the 0, +1, +2, and +3 oxidation states during cyclic voltammetry of $[\text{Mn}(\text{CNR})_6]^{z+}$ ($\text{R} = \text{Me, Ph}$; $z = 1, 2, 3$) [18–21] and manganese(II) isocyanide complexes containing $[\text{Mn}(\text{CNR})_6]^{2+}$ (e.g. $\text{R} = \text{Ph, Et, Bu}^t, \text{CH}=\text{CH}_2$) are

known [19, 22, 23]. The latter are usually prepared via the electrolytic or chemical (e.g. nitric acid) oxidation of the corresponding manganese(I) complex followed by precipitation with the appropriate anion. In the case of manganese(I) complexes $\nu(\text{CN})$ decreases upon coordination indicating $d-\pi^*_{\text{CN}}$ bonding in the complexes, whereas for the corresponding manganese(II) complex $\nu(\text{CN})$ increases [24].

We have previously reported the direct synthesis of manganese(II) complexes of *t*-butyl isocyanide, $\text{MnX}_2(\text{CNBu}^t)$ ($\text{X} = \text{Cl, Br, I, NCS}$) [25], and assigned the halide complexes a structure similar to that found for $\text{MnI}_2(\text{PPhMe}_2)$ by X-ray crystallography, viz. an infinite sheet of $[\text{MnX}_2]_n$ with alternate manganese atoms being coordinated by two phosphine ligands, i.e. the 6,4,6,4 structure of King *et al.* [26]. Since bistertiary-phosphine complexes of manganese(II) are known, e.g. $[\text{Mn}(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_3)_2]$ [27] and $[\text{MnI}_2(\text{PET}_3)_2]$ [28] we attempted to synthesise mixed $\text{CNBu}^t/\text{PBu}^t_3$ complexes, but found that reacting $\text{MnX}_2(\text{CNBu}^t)$ with PBu^t_3 in a 1:1 ratio in toluene led, not to addition, but to substitution to yield $\text{MnX}_2(\text{PBu}^t_3)$ [25].

However, we were subsequently able to synthesise mixed-ligand complexes: the deep blue complex

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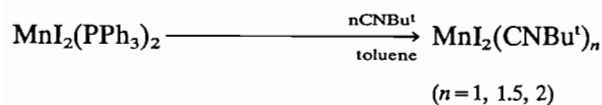
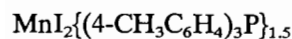
[MnBr₂(CNBu^t)(PPhMe₂)] was isolated from the reaction of MnBr₂(PPhMe₂) with CNBu^t in stoichiometric quantities in toluene [29]. Clearly, the relative stabilities of the species MnX₂(CNR), MnX₂(PR¹₃) and MnX₂(CNR)(PR¹₃) are halide and ligand dependent. Moreover, in ethanol solution rearrangement of [MnBr₂(CNBu^t)(PPhMe₂)] occurs to give [Mn(CNBu^t)₄(PPhMe₂)] [MnBr₄] from which, upon reaction with other phosphines, can be obtained [Mn(CNBu^t)₄(PR₃)₂]²⁺ (PR₃ = PPrⁿ₃, PPhEt₂, PPh₂Me). Air oxidation of an ethanol solution of [Mn(CNBu^t)₄(PPhMe₂)₂]²⁺ produces the red [Mn(CNBu^t)₄(PPhMe₂)₂][MnBr₃(OPPhMe₂)] [29].

Our interest in this area of chemistry began with the manganese(II) phosphine complexes of type MnX₂(PR₃) (X = Cl, Br, I, NCS), and our discovery that these complexes can reversibly coordinate small molecules such as dioxygen [25, 30, 31], carbon monoxide [32], ethylene [33] and nitric oxide [34] under very mild conditions and irreversibly coordinate sulfur dioxide. We felt it was of interest to extend the study to manganese(II) complexes of isocyanides and mixed isocyanide/phosphine complexes. We thus wish to report some novel *t*-butyl isocyanide complexes, MnI₂(CNBu^t)_n (*n* = 1, 1.5, 2), the unusual mixed species, MnI₂(PPh₃)(CNBu^t)₂, and the X-ray crystal structures of two mixed-valence species which co-crystallise, [Mn(CNBu^t)₆][MnI₃(PPh₃)] and [Mn(PPh₃)(CNBu^t)₅]-[MnI₃(CNBu^t)].

Results and discussion

MnI₂(CNBu^t)_n (*n* = 1, 1.5, 2)

Although previous workers have synthesised manganese(II) complexes containing isocyanide ligands by oxidation of the appropriate manganese(I) complex, the complexes reported here are obtained by a more straightforward method:



The complexes are listed in Table 1, together with melting points and room temperature magnetic moments. It is clear from these data and the $\nu(\text{CN})$ IR data of Table 2 that these are discrete complexes and not merely mixtures of MnI₂ and CNBu^t. All of the complexes except one exhibit much reduced magnetic moments, presumably because of antiferromagnetic coupling through Mn–I–Mn bridges. The exception is MnI₂(CNBu^t)₂ which has the expected room temperature moment of 5.9 μ_B ; it is undoubtedly a monomeric

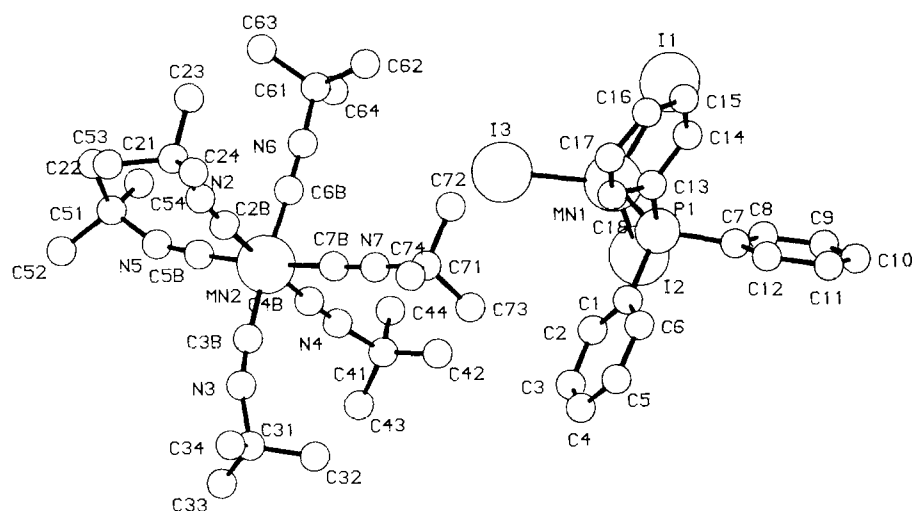
TABLE 1. Physical and analytical data for the manganese complexes

Complex	Colour	Melting point (°C)	μ_{eff} (μ_B)	Analysis: found (calc.) (%)					
				C	H	N	P	X	
MnI ₂ (CNBu ^t)	yellow	154 ^a	5.1	15.6 (15.3)	2.9 (2.3)	4.0 (3.6)	0.0 (0.0)	64.4 (64.8)	
MnI ₂ (CNBu ^t) _{1.5}	yellow/grey	160 ^a	5.2	20.8 (20.7)	3.4 (3.1)	3.6 (4.8)	0.0 (0.0)	58.8 (58.5)	
MnI ₂ (CNBu ^t) ₂	yellow/orange	129	5.9	26.3 (25.3)	4.3 (3.8)	5.9 (5.9)	—	53.2 (53.5)	
MnI ₂ (PPh ₃)(CNBu ^t) ₂	yellow	148	5.2	44.8 (45.6)	4.8 (4.5)	3.9 (3.8)	3.8 (4.2)	34.0 (34.5)	
[MnI ₃ (PPh ₃)] [Mn(CNBu ^t) ₆]	yellow	171	—	45.8 (46.0)	5.4 (5.5)	6.5 (6.7)	2.2 (2.5)	31.2 (30.5)	
[MnI ₃ (CNBu ^t)] [Mn(PPh ₃)(CNBu ^t) ₅]	yellow	174	—	46.3 (46.0)	5.7 (5.5)	6.3 (6.7)	2.4 (2.5)	30.8 (30.5)	

^aDecomposed.

TABLE 2. IR spectral data for manganese complexes

Complex	$\nu(\text{CN})$	$\nu(\text{Mn-C})$	$\nu(\text{Mn-P})$	$\nu(\text{Mn-I})$
$\text{MnI}_2(\text{CNBu}^t)$	2202(s)	214(s)		120(s, br)
$\text{MnI}_2(\text{CNBu}^t)_{1.5}$	2200(s)	214(s)		124(s)
$\text{MnI}_2(\text{CNBu}^t)_2$	2170(s)	212(s)		192(s)
$\text{MnI}_2(\text{PPh}_3)(\text{CNBu}^t)_2$	2065(s)	212(s)	419(w)	197(s), 153(m, sh)
$[\text{MnI}_3(\text{PPh}_3)][\text{Mn}(\text{CNBu}^t)_6]$	2090(s)	212(s)	420(w)	198(s)
$[\text{MnI}_3(\text{CNBu}^t)][\text{Mn}(\text{PPh}_3)(\text{CNBu}^t)_5]$	2090(s) 2060(s)	212(s)	422(w)	196(s)

Fig. 1. Molecular structure of $[\text{Mn}(\text{CNBu}^t)_6][\text{MnI}_3(\text{PPh}_3)]$ with atom labelling scheme. Hydrogen atoms omitted for clarity.

tetrahedral species similar to the bisphosphine complexes of Wilkinson [27], Kohler [28] and their co-workers.

We have previously reported a complex of stoichiometry $\text{MnI}_2(\text{CNBu}^t)$, obtained by direct reaction of anhydrous MnI_2 and CNBu^t in toluene [25]. That species and the one reported here are clearly isomers, since the $\nu(\text{CN})$ of the former, 2179 cm^{-1} , is different from that of the latter, 2202 cm^{-1} , Table 2. It is important to point out that isomers can exist in the analogous $\text{MnI}_2(\text{phosphine})$ complexes. King *et al.* [26] reported the 6,4,6,4 structure for the complex $\text{MnI}_2(\text{PPhMe}_2)$, but we have recently synthesised the 5,5,5,5 isomer of this complex via a new route [35].

By employing increasing quantities of CNBu^t in the synthesis the complexes $\text{MnI}_2(\text{CNBu}^t)_{1.5}$ and $\text{MnI}_2(\text{CNBu}^t)_2$ can be isolated. The polymeric nature of $\text{MnI}_2(\text{CNBu}^t)_n$ ($n=1, 1.5$) is reflected in their insolubility in organic solvents and by the presence of a $\nu(\text{Mn-I})$ band in their IR spectra at 120 and 124 cm^{-1} , respectively, assignable to the Mn-I-Mn linkage. This band is not present in the $\text{MnI}_2(\text{CNBu}^t)_2$ complex, but there is a band at 192 cm^{-1} , assignable to terminal $\nu(\text{Mn-I})$. The polymeric nature of $\text{MnI}_2(\text{CNBu}^t)_n$ ($n=1, 1.5$) is also revealed in the much reduced room tem-

perature magnetic moments of these species, Table 1, presumably because of antiferromagnetic coupling through the bridging iodines. No such lowering of the magnetic moment is observed for the monomeric $\text{MnI}_2(\text{CNBu}^t)_2$, Table 1. All complexes reported here, however, differ fundamentally from the low-spin hexakis(isocyanide)manganese(II) complexes [1]. The X-band ESR spectra of 1,2-dichloromethane glasses of these complexes at 93 K exhibit bands at $g=6$, suggesting some axial symmetry, and at $g=2$ for $\text{MnI}_2(\text{CNBu}^t)_n$ ($n=1, 1.5$), in keeping with their proposed polymeric structure.

The IR spectra of these $\text{MnI}_2(\text{CNBu}^t)_n$ ($n=1, 1.5, 2$) complexes exhibit a strong band in the 2202–2170 region, Table 2, assignable to $\nu(\text{CN})$ of coordinated CNBu^t . These bands are shifted to higher energy from that of free CNBu^t (2122 cm^{-1}), and suggests that the Mn-C bond is predominantly of σ -character.

The yellow $\text{MnI}_2(\text{PPh}_3)(\text{CNBu}^t)_2$ was prepared from the reaction of $\text{MnI}_2(\text{PPh}_3)$ with two molar equivalents of CNBu^t in *n*-pentane. The IR spectrum exhibits both terminal and bridging $\nu(\text{Mn-I})$ bands, Table 2. In addition, the room temperature magnetic moment, $\mu_{\text{eff}}=5.2\ \mu_B$, is strongly suggestive of iodine bridges, and the complex is probably a hexacoordinate dimer.

TABLE 3. Fractional atomic coordinates and vibrational parameters (\AA^2) for non-hydrogen atoms of the complex $[\text{Mn}(\text{CNBu}^t)_6][\text{MnI}_3(\text{PPh}_3)]$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
I(1)	0.2013(1)	0.15758(7)	0.41958(6)	0.0751(3)
I(2)	0.3026(1)	0.32856(7)	0.17753(6)	0.0855(3)
I(3)	-0.0494(2)	0.42958(8)	0.32020(8)	0.1440(6)
Mn(1)	0.1101(3)	0.2950(1)	0.2908(1)	0.0649(7)
P(1)	-0.0589(4)	0.2429(2)	0.2341(2)	0.055(1)
C(1)	-0.1519(16)	0.3212(9)	0.1471(8)	0.055(4)
C(2)	-0.1106(17)	0.3966(9)	0.1047(9)	0.070(5)
C(3)	-0.1745(20)	0.4572(10)	0.0356(10)	0.079(6)
C(4)	-0.2775(21)	0.4450(10)	0.0103(9)	0.076(6)
C(5)	-0.3221(18)	0.3701(11)	0.0505(9)	0.081(5)
C(6)	-0.2582(17)	0.3082(10)	0.1195(9)	0.063(5)
C(7)	0.0227(16)	0.1485(9)	0.2084(8)	0.049(4)
C(8)	0.1599(17)	0.1195(10)	0.2078(9)	0.066(5)
C(9)	0.2228(19)	0.0450(12)	0.1892(10)	0.089(6)
C(10)	0.1525(21)	0.0002(11)	0.1743(9)	0.072(5)
C(11)	0.0159(22)	0.0280(11)	0.1743(10)	0.093(6)
C(12)	-0.0503(20)	0.1036(10)	0.1940(9)	0.084(5)
C(13)	-0.1882(16)	0.2061(9)	0.3060(8)	0.050(4)
C(14)	-0.1517(17)	0.1261(9)	0.3694(8)	0.065(5)
C(15)	-0.2493(19)	0.0951(10)	0.4260(8)	0.068(6)
C(16)	-0.3798(19)	0.1425(12)	0.4178(9)	0.070(5)
C(17)	-0.4140(18)	0.2219(11)	0.3595(10)	0.086(5)
C(18)	-0.3206(18)	0.2541(10)	0.3023(8)	0.063(5)
Mn(2)	-0.4728(2)	0.7804(1)	0.2324(1)	0.0475(6)
C(2B)	-0.6300(17)	0.7955(9)	0.2981(8)	0.060(5)
C(3B)	-0.5597(17)	0.8451(9)	0.1369(9)	0.062(5)
C(4B)	-0.3159(17)	0.7609(9)	0.1696(9)	0.069(5)
C(5B)	-0.4414(15)	0.8738(9)	0.2464(8)	0.050(4)
C(6B)	-0.3810(17)	0.7085(10)	0.3264(9)	0.061(5)
C(7B)	-0.5070(17)	0.6793(10)	0.2290(8)	0.059(5)
N(2)	-0.7181(13)	0.8021(8)	0.3414(7)	0.061(4)
N(3)	-0.6083(13)	0.8803(8)	0.0767(7)	0.063(4)
N(4)	-0.2213(14)	0.7457(8)	0.1319(7)	0.074(4)
N(5)	-0.4223(12)	0.9298(7)	0.2603(6)	0.048(3)
N(6)	-0.3261(13)	0.6643(8)	0.3858(7)	0.061(4)
N(7)	-0.5263(14)	0.6182(8)	0.2274(7)	0.079(4)
C(21)	-0.8206(18)	0.8031(11)	0.4032(10)	0.077(5)
C(22)	-0.8760(16)	0.8934(10)	0.4015(9)	0.074(5)
C(23)	-0.7572(21)	0.7463(11)	0.4816(9)	0.122(8)
C(24)	-0.9270(20)	0.7691(14)	0.3910(13)	0.169(9)
C(31)	-0.6511(21)	0.9023(13)	-0.0039(11)	0.079(6)
C(32)	-0.6071(52)	0.8212(30)	-0.0240(26)	0.064(18)
C(33)	-0.6128(61)	0.9726(35)	-0.0567(30)	0.075(19)
C(34)	-0.8185(68)	0.9107(42)	0.0090(36)	0.122(28)
C(32B)	-0.5031(47)	0.8820(30)	-0.0487(26)	0.147(21)
C(33B)	-0.7052(38)	0.9993(21)	-0.0468(18)	0.078(12)
C(34B)	-0.7182(43)	0.8457(26)	-0.0073(21)	0.105(15)
C(41)	-0.1103(20)	0.7124(12)	0.0824(11)	0.070(5)
C(42)	-0.1290(40)	0.6326(24)	0.0799(23)	0.085(14)
C(43)	-0.0907(39)	0.7848(23)	0.0105(22)	0.072(13)
C(44)	0.0140(43)	0.6896(27)	0.1310(24)	0.106(17)
C(42B)	-0.0503(37)	0.6189(22)	0.1264(21)	0.049(13)
C(43B)	-0.1804(47)	0.7194(30)	0.0072(27)	0.096(20)
C(44B)	-0.0143(49)	0.7728(28)	0.0474(27)	0.083(17)
C(51)	-0.3999(18)	0.9754(9)	0.3070(8)	0.069(5)
C(52)	-0.4275(19)	1.0705(10)	0.2554(9)	0.100(6)
C(53)	-0.4988(19)	0.9593(12)	0.3777(9)	0.124(7)
C(54)	-0.2555(20)	0.9342(12)	0.3335(10)	0.117(7)

(continued)

TABLE 3. (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(61)	-0.2605(18)	0.6155(9)	0.4583(8)	0.068(5)
C(62)	-0.2859(19)	0.5260(10)	0.4901(8)	0.099(7)
C(63)	-0.3203(20)	0.6618(10)	0.5167(9)	0.113(7)
C(64)	-0.1098(18)	0.6098(12)	0.4429(11)	0.119(7)
C(71)	-0.5461(22)	0.5406(11)	0.2292(11)	0.100(6)
C(72)	-0.5003(28)	0.4723(12)	0.3051(11)	0.190(12)
C(73)	-0.4627(20)	0.5155(11)	0.1643(10)	0.128(7)
C(74)	-0.6897(25)	0.5540(18)	0.2252(20)	0.306(18)

TABLE 4. Selected bond lengths (\AA) for $[\text{MnI}_3(\text{PPh}_3)]\text{-}[\text{Mn}(\text{CNBu}^t)_6]$

Mn(1)–I(1)	2.677(2)
Mn(1)–I(2)	2.701(3)
Mn(1)–I(3)	2.650(3)
Mn(1)–P(1)	2.696(6)
P(1)–C(7)	1.83(2)
P(1)–C(1)	1.83(1)
P(1)–C(13)	1.82(2)
Mn(2)–C(2B)	1.91(2)
Mn(2)–C(3B)	1.88(2)
Mn(2)–C(4B)	1.89(2)
C(2B)–N(2)	1.14(2)
N(2)–C(21)	1.45(2)

TABLE 5. Selected bond angles ($^\circ$) for $[\text{MnI}_3(\text{PPh}_3)]\text{-}[\text{Mn}(\text{CNBu}^t)_6]$

I(2)–Mn(1)–I(1)	113.0(1)
I(3)–Mn(1)–I(1)	114.1(1)
I(3)–Mn(1)–I(2)	116.2(1)
P(1)–Mn(1)–I(2)	105.8(1)
C(7)–P(1)–Mn(1)	113.4(6)
C(8)–C(7)–P(1)	120.0(2)
N(6)–C(6B)–Mn(2)	179.0(1)
C(61)–N(6)–C(6B)	177.0(2)
C(7B)–Mn(2)–C(3B)	88.5(7)
C(4B)–Mn(2)–C(2B)	177.9(6)

The phosphine-containing complexes, in contrast to the others, exhibit $\nu(\text{CN})$ in the 2060–2090 cm^{-1} range, suggesting that in these complexes the Mn–C bond is primarily of π -character.

Treatment of $\text{MnI}_2(\text{PPh}_3)_2$ with an excess of CNBu^t (c. 1:10) affords two most interesting examples of manganese(I) and manganese(II) occurring in the same complex, viz. reaction in toluene affords both yellow crystals, $[\text{Mn}(\text{CNBu}^t)_6][\text{MnI}_3(\text{PPh}_3)]$, and red–orange crystals, $[\text{Mn}(\text{CNBu}^t)_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBu}^t)]$, separable by fractional crystallisation.

Structure of $[\text{Mn}(\text{CNBu}^t)_6][\text{MnI}_3(\text{PPh}_3)]$

The structure of the yellow crystals is made up of a manganese(I) complex cation, $[\text{Mn}(\text{CNBu}^t)_6]^+$, and

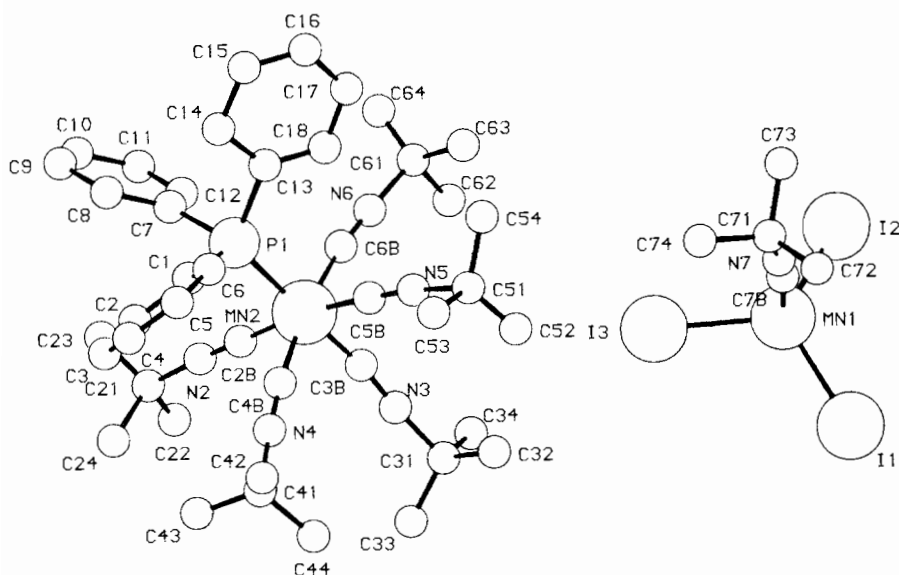


Fig. 2. Molecular structure of $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBU}')]$ with atom labelling scheme. Hydrogen atoms omitted for clarity.

a manganese(II) anion, $[\text{MnI}_3(\text{PPh}_3)]^-$, as can be seen from Fig. 1. Atomic coordinates are given in Table 3 and bond lengths and angles in Tables 4 and 5, respectively. The cation contains manganese(II) octahedrally coordinated by six isocyanide ligands. The mean Mn–C distance is 1.897 Å and the mean C–N and N–C distances are 1.161 and 1.458 Å, respectively. The Mn–C–N and C–N–C linkages are almost linear (mean Mn–C–N 177.1(3)°, mean C–N–C 170.1(7)°).

The geometry of the tertiary butyl group is normal and the bond lengths and angles agree well with the $[\text{Mn}(\text{CNC}_2\text{H}_5)_6]^+$ cation postulated by Ljungstrom and co-workers [36]. The short Mn–C bond and the relatively long C–N bond indicate an increase in the metal $\rightarrow \pi^*$ (ligand) transfer with decreasing effective nuclear charge on the metal atom, as predicted by molecular orbital calculation on $[\text{Mn}(\text{CNCH}_3)_6]^+$ with a Mn–C bond distance of 1.97 Å [37].

The manganese(II) complex anion, $[\text{MnI}_3(\text{PPh}_3)]^-$, has a monomeric pseudotetrahedral structure, with the manganese atom coordinated to three terminal iodide atoms and the phosphorus atom of the triphenylphosphine moiety. The bond angles at the manganese atom are nearer the idealised tetrahedral angle (109.5°), with the mean I–Mn–I bond angles slightly greater than this angle while the mean I–Mn–P bond angles are slightly less. This behaviour is presumably due to the fact that I–I steric repulsion is greater than that for I–P. The Mn–I distances are close to that found in other pseudotetrahedral manganese(II) complexes. However, the Mn–P bond length is significantly longer (2.697 Å) than the mean length (2.573 Å) for manganese(II) complexes [38]. This difference in bond length may be due to the electronic and steric effects in the ion.

Structure of $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBU}')]$

The structure of the red–orange crystals, $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBU}')]$, is composed of a pseudotetrahedral monomer with the manganese atom coordinated to three terminal iodide atoms and a carbon atom of tertiary-butyl isocyanide, and a pseudo-octahedral monomer with the manganese atom coordinated to a triphenylphosphine and five tertiary-butyl isocyanide moieties, as illustrated in Fig. 2. Atomic coordinates are listed in Table 6, and bond lengths and angles in Tables 7 and 8, respectively. The isocyanide groups are linearly coordinated to the manganese atoms. The average Mn–C–N and C–N–C angles in $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)]^+$ are 173(1) and 173(4)°, respectively. The Mn–P–C angles are in the range 114(1)–120(9)° (mean Mn–P–C 117(1)°).

The short Mn–C and Mn–P distances in $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)]^+$ are consistent with the observation for the short Mn–C distance in $[\text{Mn}(\text{CNBU}')_6]^+$, indicating metal–ligand backbonding. The Mn–C distance in $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)]^+$ is slightly shorter than that in $[\text{Mn}(\text{CNBU}')_6]^+$, indicating, moreover, that the π contribution to the Mn–C bond is enhanced by the presence of triphenylphosphine ligand. Presumably the lower energy $\nu(\text{CN})$ band in the IR spectrum of $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBU}')]$, Table 2, arises from the CNBU' ligands in the cation.

If the bond parameters of the above two cations are compared with those found in other isocyanide manganese species, Table 9, it is found that the Mn–C bond lengths increase with increasing formal oxidation state of manganese, from 1.878 Å in $[\text{Mn}(\text{CNBU}')_5(\text{PPh}_3)]^+$ to 1.935 Å in $[\text{Mn}(\text{CNBU}')_4(\text{PPhMe}_2)_2]^{2+}$. This indicates an increase in the d– π^* contribution to

TABLE 6. Fractional atomic coordinates and vibrational parameters (\AA^2) for non-hydrogen atoms of the complex $[\text{Mn}(\text{CNBu}^t)_5(\text{PPh}_3)][\text{MnI}_3(\text{CNBu}^t)]$

	x	y	z	U_{eq}
I(1)	0.0622(2)	0.1155(2)	0.1338(2)	0.0923(9)
I(2)	0.0311(2)	0.3743(2)	0.1691(2)	0.100(1)
I(3)	0.2099(2)	0.2326(2)	0.3558(2)	0.119(1)
Mn(1)	0.1269(3)	0.2485(4)	0.2079(3)	0.066(2)
N(7)	0.2724(17)	0.2974(18)	0.1715(14)	0.048(9)
C(7B)	0.2225(21)	0.2837(23)	0.1807(18)	0.048(11)
C(71)	0.3407(21)	0.3169(23)	0.1644(19)	0.050(11)
C(72)	0.3428(21)	0.2708(24)	0.0988(20)	0.078(14)
C(73)	0.3431(21)	0.4066(22)	0.1507(20)	0.072(13)
C(74)	0.4121(20)	0.3059(23)	0.2360(19)	0.066(13)
Mn(2)	0.5548(3)	0.2286(3)	0.7187(3)	0.044(1)
P(1)	0.6604(5)	0.3057(6)	0.7827(5)	0.040(2)
C(2B)	0.5434(16)	0.1999(19)	0.8066(17)	0.023(9)
C(3B)	0.4702(21)	0.1701(24)	0.6660(20)	0.051(12)
C(4B)	0.6096(19)	0.1318(24)	0.7323(18)	0.042(11)
C(5B)	0.5614(18)	0.2398(21)	0.6298(18)	0.039(10)
C(6B)	0.4884(21)	0.3199(24)	0.6917(20)	0.051(12)
N(2)	0.5419(14)	0.1814(17)	0.8605(15)	0.039(8)
N(3)	0.4206(19)	0.1220(22)	0.6341(17)	0.067(10)
N(4)	0.6343(14)	0.0696(18)	0.7375(14)	0.033(8)
N(5)	0.5595(16)	0.2459(19)	0.5721(16)	0.052(9)
N(6)	0.4464(17)	0.3697(20)	0.6671(15)	0.054(9)
C(21)	0.5435(20)	0.1519(23)	0.9281(20)	0.049(11)
C(22)	0.4683(22)	0.1195(26)	0.9147(22)	0.085(14)
C(23)	0.5686(23)	0.2140(25)	0.9852(21)	0.084(15)
C(24)	0.6002(22)	0.0767(25)	0.9552(22)	0.084(15)
C(31)	0.3633(24)	0.0636(27)	0.5852(23)	0.072(13)
C(32)	0.3689(28)	0.0655(32)	0.5162(25)	0.134(21)
C(33)	0.3711(23)	-0.0156(25)	0.6245(21)	0.079(14)
C(34)	0.2856(21)	0.1050(26)	0.5730(22)	0.082(15)
C(41)	0.6681(19)	-0.0117(22)	0.7377(18)	0.036(10)
C(42)	0.7323(22)	-0.0063(28)	0.7161(22)	0.095(16)
C(43)	0.6994(24)	-0.0401(28)	0.8120(23)	0.100(17)
C(44)	0.6061(25)	-0.0647(28)	0.6830(24)	0.112(18)
C(51)	0.5641(31)	0.2429(35)	0.4970(29)	0.110(18)
C(52)	0.5150(38)	0.1945(41)	0.4477(35)	0.229(37)
C(53)	0.6422(35)	0.2014(42)	0.5194(36)	0.240(38)
C(54)	0.5699(30)	0.3302(29)	0.4796(27)	0.130(21)
C(61)	0.3946(26)	0.4377(30)	0.6264(25)	0.092(16)
C(62)	0.3131(25)	0.3971(31)	0.6017(26)	0.130(20)
C(63)	0.4053(26)	0.4498(30)	0.5567(23)	0.117(19)
C(64)	0.4046(30)	0.5013(32)	0.6713(27)	0.149(23)
C(1)	0.7502(19)	0.2504(23)	0.8153(18)	0.050(11)
C(2)	0.7727(24)	0.1977(25)	0.8785(22)	0.074(14)
C(3)	0.8371(23)	0.1479(27)	0.8982(24)	0.080(15)
C(4)	0.8754(25)	0.1588(27)	0.8549(23)	0.083(15)
C(5)	0.8591(22)	0.2023(24)	0.7965(21)	0.065(13)
C(6)	0.7929(21)	0.2525(24)	0.7748(20)	0.058(12)
C(7)	0.6668(19)	0.3562(21)	0.8674(17)	0.038(10)
C(8)	0.7348(22)	0.3689(24)	0.9317(20)	0.064(12)
C(9)	0.7374(21)	0.4094(22)	0.9937(20)	0.051(11)
C(10)	0.6737(22)	0.4313(25)	0.9906(22)	0.068(13)
C(11)	0.5992(18)	0.4213(20)	0.9307(17)	0.035(10)
C(12)	0.6024(19)	0.3825(22)	0.8715(18)	0.043(10)
C(13)	0.6802(19)	0.3971(22)	0.7377(18)	0.044(11)
C(14)	0.7532(20)	0.4350(24)	0.7790(19)	0.051(11)
C(15)	0.7609(21)	0.5088(24)	0.7440(19)	0.054(12)
C(16)	0.7066(21)	0.5346(25)	0.6797(20)	0.056(12)
C(17)	0.6365(23)	0.4934(26)	0.6444(22)	0.071(13)
C(18)	0.6254(20)	0.4233(23)	0.6754(18)	0.044(11)

TABLE 7. Selected bond lengths (\AA) for $[\text{MnI}_3(\text{CNBu}^t)]\text{-}[\text{Mn}(\text{PPh}_3)(\text{CNBu}^t)_5]$

Mn(1)–I(1)	2.649(6)
Mn(1)–I(2)	2.678(6)
Mn(1)–I(3)	2.704(6)
Mn(1)–C(7B)	2.23(5)
C(7B)–N(7)	1.09(6)
Mn(2)–P(1)	2.29(1)
P(1)–C(1)	1.83(4)
P(1)–C(7)	1.85(4)
Mn(2)–C(2B)	1.92(4)
C(2B)–N(2)	1.13(5)

TABLE 8. Selected bond angles ($^\circ$) for $[\text{MnI}_3(\text{CNBu}^t)]\text{-}[\text{Mn}(\text{PPh}_3)(\text{CNBu}^t)_5]$

I(1)–Mn(1)–I(2)	112.3(2)
I(1)–Mn(1)–I(3)	116.5(2)
I(2)–Mn(1)–I(3)	113.9(3)
C(7B)–Mn(1)–I(1)	109.0(1)
C(7B)–N(7)–C(71)	176.0(3)
N(7)–C(7B)–Mn(1)	175.0(3)
C(2B)–Mn(2)–P(1)	93.2(9)
C(3B)–Mn(2)–C(2B)	88.0(2)
C(1)–P(1)–Mn(2)	114.0(1)
N(2)–C(2B)–Mn(2)	175.0(1)
C(3B)–Mn(2)–P(1)	178.0(1)

the metal–carbon bond with decreasing effective nuclear charge on the metal atom. An opposite trend in Mn–C distances would be expected for bonds of a purely σ -character. In the presence of a poorer π -acceptor than isocyanide, such as PPh_3 , the transfer to the isocyanide ligands is increased, as is apparent from the Mn–C distance of 1.878 \AA in $[\text{Mn}(\text{CNBu}^t)_5(\text{PPh}_3)]^+$ ion.

Finally, it should be mentioned that the isolation of these two isomers from the same reaction is surely a reflection of the room temperature lability of soft ligands when bound to manganese(II).

Experimental

All operations were carried out under dry argon by Schlenk techniques. The solvents and manganese(II) salts were dried by published procedures and MnI_2L_n ($\text{L} = \text{PPh}_3$, THF, $n = 1$; $\text{L} = (4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$, $n = 1.5$) synthesised by published methods [39, 40]. Tertiary butyl isocyanide was purchased from the Fluka Chemical Co. and was used without further purification.

Preparation of $\text{MnI}_2(\text{CNBu}^t)_n$ ($n = 1, 1.5$ and 2)

These complexes can be prepared by two methods. *Method 1.* Anhydrous MnI_2 (1.24 g, 4 mmol) was placed in a predried 250 cm^3 round bottom flask equipped with side arm and tap. The flask was evacuated and heated gently using a Bunsen flame. On cooling,

TABLE 9. Comparison of bond lengths in some isocyanide complexes of manganese

Compound	Formal oxidation state	Formal ground state configuration	Mean Mn-C (Å)	Mean C-N (Å)	Mean N-C(R) (Å)	Reference
[Mn(CNBU ^t) ₅ (PPh ₃) ⁺	I	d ⁶	1.878	1.147	1.493	present work
[Mn(CNBU ^t) ₆] ⁺	I	d ⁶	1.897	1.161	1.458	present work
[Mn(CNC ₆ H ₅) ₆] ⁺	I	d ⁶	1.901	1.162	1.411	7
MnBr(CO) ₃ (CNC ₆ H ₅) ₂	I	d ⁶	1.925	1.124	1.394	9
[Mn(CNBU ^t) ₄ (PPhMe ₂) ₂] ²⁺	II	d ⁵	1.935	1.141	1.461	20

50 cm³ of dry toluene was added using a predried syringe. The flask was again flushed several times with argon. The required quantities of CNBU^t (1, 1.5 or 2 equiv.) was then added and the mixture stirred at room temperature for *c.* 72 h. The product was filtered off and dried *in vacuo*.

Method II. (a) MnI₂(CNBU^t). The complex MnI₂(PPh₃)₂ (1.24 g, 1.49 mmol) was added to 30 cm³ dry toluene in a 250 cm³ side arm flask. Tertiary-butyl isocyanide (0.17 cm³, 14.49 mmol) was then added and the mixture stirred for 48 h. The resulting complex was filtered using a Schlenk apparatus, washed with dry toluene (2 × 30 cm³), and dried *in vacuo*.

(b) MnI₂(CNBU^t)_{1.5}. To a suspension solution of [MnI₂(4-CH₃C₆H₄)₃P]_{1.5} (1.02 g, 1.33 mmol) in toluene (30 cm³) was added CNBU^t (0.23 cm³, 2.0 mmol). The resulting mixture was stirred at room temperature for 48 h with work-up as in (a).

(c) MnI₂(CNBU^t)₂. The reaction of MnI₂(PPh₃)₂ or MnI₂(THF)₂ with 2 equiv. of CNBU^t in toluene at room temperature for 48 h yielded, after work-up as in (a), the complex in essentially quantitative yield.

Preparation of MnI₂(PPh₃)(CNBU^t)₂

To n-pentane (30 cm³), in a flame-dried 250 cm³ side arm flask, was added MnI₂(PPh₃)₂ (0.95 g, 1.14 mmol). Tertiary-butyl isocyanide (0.26 cm³, 2.28 mmol) was then added and the mixture stirred for 72 h. The yellow microcrystals were collected, washed with dry n-pentane (3 × 50 cm³) and dried *in vacuo*.

Preparation of [Mn(CNBU^t)₆][MnI₃(PPh₃)] and [Mn(CNBU^t)₅(PPh₃)][MnI₃(CNBU^t)]

To a suspension of MnI₂(PPh₃)₂ (1.62 g, 1.95 mmol) in toluene (30 cm³) was added an excess of t-butyl isocyanide (2.3 cm³, 20 mmol). As the mixture was stirred, the solid began to dissolve, and after 48 h, a light yellow solution was passed through a glass sinter and the filtrate was allowed to slowly evaporate, producing the two types of crystals which were found to be suitable for X-ray analysis.

Crystal structure determination

Crystal data for [Mn(CNBU^t)₆][MnI₃(PPh₃)]: C₄₈H₆₉Mn₂I₃N₆P, *M* = 1251.7, triclinic, space group *P*1, *a* = 10.447(8), *b* = 17.439(9), *c* = 18.514(9) Å, α = 66.92(5), β = 81.72(5), γ = 72.90(5)°, *V* = 2964.2 Å³, *X* = 2, *D*_c = 1.40 mg m⁻³, *F*(000) = 1246, μ = 37.357 mm⁻¹, (Mo Kα) = 0.71073 Å, *T* = 293 K. A suitable crystal of 0.40 × 0.40 × 0.40 mm dimensions was sealed in a Lindemann tube under argon. After photographic examination, one crystal was transferred to the Nicolet R3m/V diffractometer. The unit cell constants were determined from the setting angles of 25 accurately centred reflections (8.3 ≤ θ ≤ 16.0°). A total of 9085 reflections was collected, corrected for Lorentz-polarization and absorption effects, and averaged to give 7843 unique reflections of which 4789 had *F* ≤ 5σ(*F*) with *R*_{int} = 0.001 for the merging of equivalent reflections. The structure was solved using standard heavy atom procedures and refined by full matrix least-squares methods with all non-hydrogen atoms refined anisotropically and all hydrogen atoms constrained to chemically reasonable positions with shared isotropic parameters, common to each molecule, to give a final *R* = 0.081, *R*_w = 0.081. Structure calculation was performed on the Amdahl 5890 system of the University of Manchester Regional Computing Centre.

Crystal data for Mn(CNBU^t)₅(PPh₃)[MnI₃(CNBU^t)]: C₄₈H₆₉Mn₂I₃N₆P, *M* = 1251.7, monoclinic, space group *P*2₁/*a*, *a* = 19.482(6), *b* = 16.550(6), *c* = 19.997(8) Å, β = 115.53(3)°, *V* = 5818.1 Å³, *Z* = 4, *D*_c = 1.43 mg m⁻³, *F*(000) = 2492, μ = 38.066 mm⁻¹, (Mo Kα) = 0.71073 Å, *T* = 293 K. The X-ray diffraction data and processing was done in the same manner as described for [Mn(CNBU^t)₆][MnI₃(PPh₃)]. A total of 6211 unique reflections was collected and 2581 with *F* ≥ 3σ(*F*) were used in the refinement. The structure was solved using normal heavy atom procedures and full matrix least-squares refinement converged with *R* = 0.120, *R*_w = 0.132.

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