

CATALYTIC SYNTHESIS OF $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$ COMPLEXES AND THE CRYSTAL AND MOLECULAR STRUCTURE OF $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$

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Summary

The complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$ ($\text{R} = \text{Bu}^t$, $\text{C}_6\text{H}_5\text{CH}_2$, C_6H_{11} , $\text{C}_6\text{H}_3\text{Me}_2$ -2,6, Me) are synthesized by the PdO catalysed thermal reaction between $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and RNC . The crystal and molecular structure of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ has been determined by single crystal X-ray diffraction. In this structure the isonitrile ligand is bent away from the ring with a C–N–C angle of $172(2)^\circ$.

Introduction

Direct replacement of CO in $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ by donor ligands L to give $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$ is extremely difficult to achieve by thermal means [1]. Consequently the only synthetic routes presently available to synthesize $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$ complexes employ photochemical [1] or Me_3NO induced [2] techniques. For instance, irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ in the presence of THF (tetrahydrofuran) or KCN yields $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{THF})$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CN})]\text{K}$ which on reaction with RNC [3] or RX ($\text{X} = \text{I}, \text{Cl}$) [4,5] yields the desired product $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$. To date, isolation of the apparently unstable $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})(\text{CNR})_2$ derivatives have not been achieved [3]. Trisubstituted derivatives, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CNR})_3$, have also been reported and have been synthesized either by irradiation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and RNC in THF [3] or from $[\text{Mn}(\text{CNC}_6\text{H}_5)]\text{I}$ and $\text{Na}[\text{C}_5\text{H}_5]$ [6].

Interestingly the catalytic synthesis of $(\eta^5\text{-C}_5\text{H}_5\text{Me})\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ has recently been achieved by electrochemical techniques [7]. However, this reaction involves the displacement of acetonitrile (and not CO) from $(\eta^5\text{-C}_5\text{H}_5\text{Me})\text{Mn}(\text{CO})_2(\text{NCMe})$ by Bu^tNC and consequently still necessitates the use of photochemical techniques in the synthesis of the acetonitrile derivative. To date no thermal displacement reactions of CO on $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ by isonitriles have been reported.

The success of our method of using PdO as a catalyst for the direct displacement of CO by RNC on a variety of metal carbonyl complexes [8] led us to investigate the possibility of extending our catalytic procedures to the $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ system [8d]. The results of this study are reported herein.

The possibility that $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$ complexes might exist in different conformations was suggested by unexpected features in the IR spectrum (solid, solution state) of the complex with $\text{R} = \text{Bu}^t$. Similar effects have been observed for the related $(\text{C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2(\text{CNBu}^t)$ complex [9]. In an attempt to obtain an understanding of this phenomenon the crystal and molecular structure of the complex $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ was undertaken and the results of this structure determination are also included in this publication.

Experimental

$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ was purchased from Strem Chemicals, PdO from Johnson Matthey Chemicals Ltd, and the isonitriles purchased (Fluka A.G.: Bu^tNC , $\text{C}_6\text{H}_{11}\text{NC}$ and $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$; Aldrich: $\text{C}_6\text{H}_5\text{CH}_2\text{NC}$) or prepared by literature methods [10] MeNC). All reactions were routinely carried out under an argon atmosphere. Toluene was dried by distillation over sodium metal. Merck Kieselgel 60 (60–200 μm) silica gel and 40×2 cm columns were used for column chromatography.

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Pye Unicam SP 300 spectrophotometer and ^1H NMR spectra on a Bruker WP80 FTNMR spectrometer. Microanalysis were performed by the Microanalytical Laboratories, C.S.I.R., Pretoria.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$ ($\text{R} = \text{Bu}^t$, $\text{C}_6\text{H}_5\text{CH}_2$, C_6H_{11} , $2,6\text{-Me}_2\text{C}_6\text{H}_3$, Me)

$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (2 mmol) and PdO (30 mg) were added to toluene (10 ml) and the solution heated to reflux. The appropriate RNC (5 mmol) was then added to the reaction vessel, and the reaction monitored by thin layer chromatography (eluent: hexane, or hexane/ CH_2Cl_2 (10%)). The reaction was allowed to proceed for 6 h (except in the case of $\text{R} = \text{Me}$, where the reaction time was 24 h), after which heating was stopped and the product isolated by column chromatography. Gradient elution, starting with hexane (to remove unreacted starting material) and gradually increasing the proportion of CH_2Cl_2 to 50% in a CH_2Cl_2 /hexane mixture was employed. Recrystallization from CH_2Cl_2 /hexane gave the desired products as yellow solids (Table 1).

Crystallographic analysis

Crystals of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ were obtained from a dichloromethane solution as pale yellow needles. Preliminary investigation by standard Weissenberg photography established the space group as either the centrosymmetric $Pnma$ or the non-centrosymmetric $Pna2_1$. Refined cell constants were obtained during data collection on a Phillips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α (λ 0.7107 Å) radiation. Crystal data and details of the data collection are summarized in Table 2. During data collection, the crystal deteriorated on long exposure to the X-ray beam, as was evidenced by the fall-off in intensity of certain standard reflections which were checked at intervals. The data were corrected for

TABLE I
ANALYTICAL AND SPECTROSCOPIC DATA FOR THE $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}(\text{CO})_2$ (CNR) COMPLEXES

Complex	Isolated yield (%) ^a	M.p. (°C)	Elemental analysis (Found (calcd.)) (%)			IR (cm ⁻¹) ^b		¹ H NMR (ppm) ^c		
			C	H	N	$\nu(\text{CN})$	$\nu(\text{CO})$	C ₅ H ₅	C ₆ H ₅	CH ₃
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}(\text{CO})_2(\text{CNBu}^1)$	60	95–96	55.6 (56.0)	5.4 (5.5)	5.4 (5.4)	2114, 2078	1952, 1907 ^d	4.25	–	0.94
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}(\text{CO})_2(\text{CNCH}_2\text{C}_6\text{H}_5)$	70	51–52	61.4 (61.4)	4.2 (4.1)	4.8 (4.8)	2112	1957, 1911	4.23	7.01, 6.99	3.92
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_{11})$	95	68–69	58.7 (58.9)	5.7 (5.7)	4.9 (4.9)	2104, 2070 (sh) ^e	1954, 1907	4.27	1.29, 1.02	–
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_3\text{Me}_2\cdot 2,6)$	15	79–80	61.1 (62.5)	4.6 (4.6)	3.4 (4.6)	2080	1954, 1916	4.27	6.71	2.14
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}(\text{CO})_2(\text{CNMe})$	5 ^f	90–93	49.1 (49.8)	3.9 (3.7)	5.9 (6.5)	2130	1958, 1907	4.22	–	2.12
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{CNBu}^1)$	50	55–56	56.5 (57.1)	5.8 (5.9)	5.4 (5.1)	2107, 2072	1948, 1904	4.18 m ^{g,h}	–	0.96
$(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{CNCH}_2\text{C}_6\text{H}_5)$	50 ⁱ					2123	1946, 1893	4.18m ^{h,j}	7.03	3.97

^a After 6 h. ^b Recorded in hexane. ^c Recorded in C₆D₆ relative to TMS. ^d KBr. ^e $\nu(\text{CN})$ 2118, 2072sh, $\nu(\text{CO})$ 1926, 1971 cm⁻¹. ^f sh = shoulder. ^g After 24 h. ^h C₅H₄CH₃ 1.70. ⁱ m = multiplet. ^j Estimated yield.

TABLE 2
CRYSTAL DATA AND DETAILS OF THE X-RAY DATA COLLECTION

Molecular formula	MnC ₁₂ H ₁₄ NO ₂
M_r	259.18
Space group	<i>Pna</i> 2 ₁
<i>Z</i>	4
<i>a</i>	19.123(9) Å
<i>b</i>	6.020(3) Å
<i>c</i>	10.942(5) Å
<i>V</i>	1259.65 Å ³
D_c	1.37 g cm ⁻³
$F(000)$	536
$\mu(\text{Mo-K}\alpha)$	9.70 cm ⁻¹
Crystal dimensions	600 × 90 × 90 μm
Scan mode	$\omega/2\theta$
Scan width	1.00°
Scan speed	0.033° s ⁻¹
Range of reflections	$3 \leq \theta \leq 25$
Measured intensities	1049
Observed reflection criteria	$F > \sigma(F)$
Unique observed intensities	876
$R = \Sigma F_o - F_c / \Sigma F_o $	0.0996

Lorentz-polarization effects, but absorption corrections were not made. Structure analysis and refinement were carried out using the program SHELX 82 [11a]. Initial coordinates for the manganese atom were derived from a Patterson synthesis, the other fifteen non-hydrogen atoms being located from difference Fourier syntheses. The basic structure was solved using the centrosymmetric *Pnma*, but refinement was only possible after transforming to the noncentrosymmetric *Pna*2₁. The fourteen hydrogen atoms were placed from subsequent difference Fourier syntheses. Posi-

TABLE 3
FRACTIONAL ATOMIC COORDINATES FOR THE NON-HYDROGEN ATOMS

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mn	0.4744(1)	0.6579(5)	0.7500(0)
N	0.341(1)	0.393(3)	0.745(4)
O(1)	0.423(1)	0.948(6)	0.553(2)
O(2)	0.416(2)	0.956(5)	0.935(3)
C(1)	0.569(3)	0.625(6)	0.845(4)
C(2)	0.580(1)	0.707(5)	0.712(2)
C(3)	0.562(2)	0.550(7)	0.648(4)
C(4)	0.534(1)	0.363(4)	0.706(3)
C(5)	0.548(2)	0.425(5)	0.835(3)
C(6)	0.394(1)	0.491(4)	0.748(5)
C(7)	0.270(1)	0.299(3)	0.737(3)
C(8)	0.235(2)	0.411(9)	0.655(3)
C(9)	0.235(3)	0.377(5)	0.885(4)
C(10)	0.275(1)	0.059(4)	0.728(3)
C(11)	0.439(2)	0.841(5)	0.633(3)
C(12)	0.443(2)	0.830(9)	0.864(2)

TABLE 4
BOND LENGTHS (Å)

Mn–C(1)	2.10(3)	C(1)–C(2)	1.55(5)
Mn–C(2)	2.09(2)	C(2)–C(3)	1.23(4)
Mn–C(3)	2.12(4)	C(3)–C(4)	1.39(5)
Mn–C(4)	2.17(2)	C(4)–C(5)	1.49(4)
Mn–C(5)	2.20(3)	C(5)–C(1)	1.27(5)
Mn–C(11)	1.82(3)	C(11)–O(1)	1.13(4)
Mn–C(12)	1.72(4)	C(12)–O(2)	1.20(5)
Mn–C(6)	1.85(2)	C(6)–N	1.17(2)
N–C(7)	1.48(2)	C(7)–C(9)	1.82(4)
C(7)–C(8)	1.30(5)	C(7)–C(10)	1.45(3)

TABLE 5
BOND ANGLES (°)

O(1)–C(11)–Mn	173(3)	C(11)–Mn–C(6)	91(2)
O(2)–C(12)–Mn	173(3)	C(12)–Mn–C(6)	93(2)
N–C(6)–Mn	177(2)	C(12)–Mn–C(11)	91(1)
C(7)–N–C(6)	172(2)		

tional parameters and anisotropic temperature factors for the non-hydrogen atoms were refined by full-matrix least squares analysis. The methyl hydrogens were assigned a common temperature factor. The cyclopentadienyl ring showed disorder, and in the initial stages was refined as a rigid pentagon. All restraints were removed in the final cycles. Least-squares refinement was considered complete when all positional shifts were less than 0.5σ . At this stage, the conventional $R = 0.0996$. Unit weights were used. Scattering factors for Mn were taken from International Tables [11b], and anomalous dispersion corrections for Mn were made [11c]. Final atomic

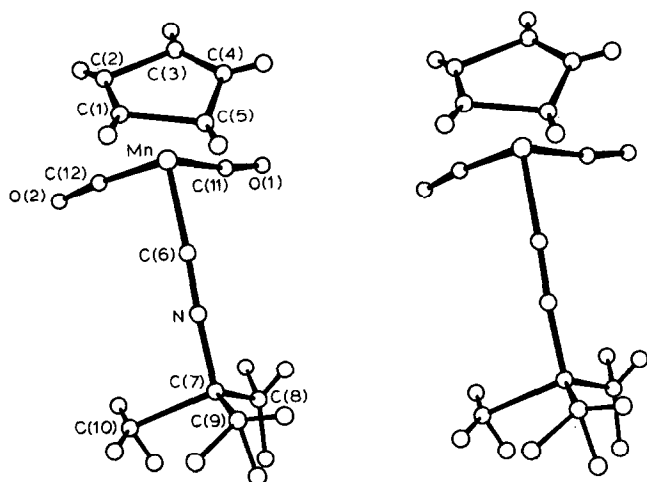


Fig. 1. ORTEP [12] view of the molecule, showing the numbering scheme used.

coordinates (Table 3), bond lengths (Table 4) and bond angles (Table 5) are listed. Tables of anisotropic temperature factors for the non-hydrogen atoms and bond lengths and angles involving hydrogen atoms, and lists of structure factors are available from the authors. Figure 1 shows an ORTEP [12] view of the molecule, with the numbering system used.

Discussion

The PdO catalysed reaction between $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and RNC has allowed for the synthesis of a series of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$ substituted complexes. Product yields varied from poor (MeNC) to excellent (Bu^tNC) (Table 1). By contrast, the thermal uncatalysed reaction did not proceed under the identical experiment conditions. In a preliminary communication [8d] we reported that the catalyst mixture $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2/\text{PdO}$ also catalysed the substitution reaction. Further studies have now shown the rate observed either for the use of a catalyst mixture (iron dimer/PdO) or for PdO alone (equal amounts of Pd in both reactions) are the same.

Attempts to extend the catalysed reaction to the substrate $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_3$ has met with moderate success. Catalysed reactions to produce $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{CNR})$ ($\text{R} = {}^t\text{Bu}$, $\text{C}_6\text{H}_5\text{CH}_2$) do occur but as predicted [9] reactions are slower.

Attempts to extend the reaction to the use of phosphines has failed e.g. $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3 + \text{PPhMe}_2 \xrightarrow{\text{PdO}}$ no reaction in refluxing toluene (6 h).

The isonitrile complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$ have been fully characterized by NMR and IR spectroscopy (Table 1). The IR spectra are expected to show 2 $\nu(\text{CO})$ and 1 $\nu(\text{NC})$ stretching vibration. This has been observed previously for $\text{RNC} = \text{C}_6\text{H}_5\text{CONC}$ [4] and MeNC [3] and was also observed for the complexes with $\text{RNC} = \text{C}_6\text{H}_5\text{CH}_2\text{NC}$ and 2,6- $\text{C}_6\text{H}_3\text{Me}_2\text{NC}$ prepared in this study. However, for $\text{RNC} = \text{Bu}^t\text{NC}$ and $\text{C}_6\text{H}_{11}\text{NC}$ two $\nu(\text{NC})$ (and two $\nu(\text{CO})$) vibrations were observed in both the solid and solution states. This phenomenon of observing more IR active $\nu(\text{NC})$ bands than expected has also been detected in a series of (arene) $\text{Cr}(\text{CO})_2(\text{CNBu}^t)$ complexes [9].

An IR study of the complex $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ in solvents of different

TABLE 6

IR SPECTRAL STUDY OF $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ IN DIFFERENT SOLVENTS

Solvent	$\nu(\text{CO})$ (cm^{-1})	$\nu(\text{CN})$ (cm^{-1})		Ratio A/B ^a
		A	B	
THF	1941, 1888	2106, 2074sh		2.9/1
CHCl_3	1942, 1882	2114, 2082sh		2.2/1
CH_2Cl_2	1940, 1881	2116, 2082sh		2.0/1
$\text{C}_6\text{H}_5\text{CH}_3$	1943, 1883	2110, 2080		1.7/1
C_6H_6	1944, 1893	2108, 2074		1.6/1
CCl_4	1948, 1897	2104, 2073		1.4/1
C_6H_{12}	1952, 1905	2102, 2070		1.2/1

^a Estimated from peak areas ($\pm 15\%$).

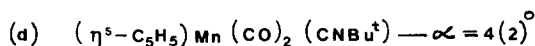
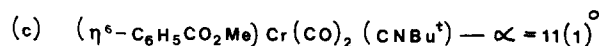
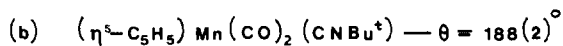
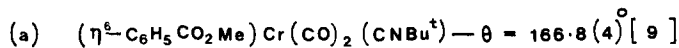
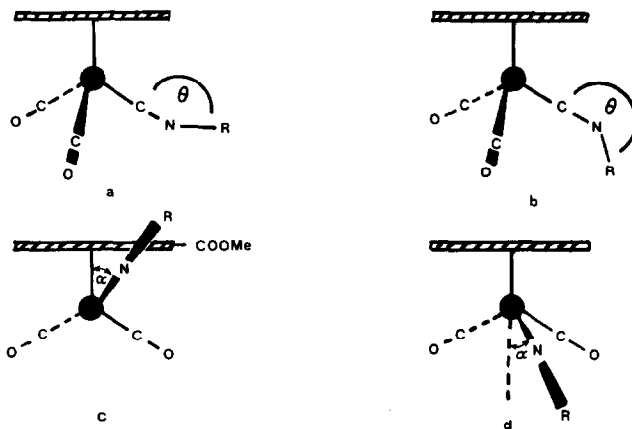


Fig. 2. Diagrams of $(\eta^5\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2(\text{CNBu}^t)$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$.

polarity (Table 6) revealed that the relative intensity of the lower frequency $\nu(\text{NC})$ band increases with decreasing solvent polarity. This suggests the existence of conformers with different dipole moments (Fig. 2) (cf. ref. [9]).

A crystal structure determination of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ was thus undertaken to obtain structural information which might assist in explaining the observed phenomenon. The structure of the molecule is illustrated in Fig. 1. A notable feature is the non-linear isonitrile ligand ($\text{C}(6)\text{-N-C}(7)$ angle, $172(2)^\circ$) in which the isonitrile ligand bends away from the ring (Fig. 2b). This is to be compared to the crystal structure of $(\eta^5\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2(\text{CNBu}^t)$ [9], in which a non-linear isonitrile ligand was also observed (C-N-C angle $166.8(4)^\circ$), but the isonitrile was bent towards the ring (Fig. 2a). In both isonitrile structures the C-N-C plane of the isonitrile ligand is close to perpendicular to the mean plane of the respective carbocycle rings (11° for Cr, 4° for Mn) (Figs. 2c, 2d). It is thus possible that the observation of a non-linear RNC group could give rise to different conformers, two of which correspond to the structures shown in Figs. 2a and 2b. This could provide an explanation of the solution IR data. It is to be noted, however, that the space group used in the structure determination of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ only allows for the existence of one conformer, of the manganese complex. Consequently an alternative explanation is required to explain the solid state (KBr) IR data.

Comparison of the structural data for $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNBu}^t)$ with those of related compounds, e.g. $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (I) [13] $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]$ (II) [14] and $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]$ (III) [15] shows that bond lengths and angles are normal. The average Mn-CO bond distance is $1.77(4)$ Å, compared with values of $1.780(2)$, $1.75(1)$ and $1.77(1)$ Å for I, II and III respectively.

The angles within the $\text{Mn}(\text{CO})_2\text{L}$ 'tripod' are normal $91(2)$, $93(2)$ and $91(1)^\circ$ for $\text{C}(6)-\text{Mn}-\text{C}(11)$, $\text{C}(6)-\text{Mn}-\text{C}(12)$ and $\text{C}(11)-\text{Mn}-\text{C}(12)$ respectively). The average $\text{M}-\text{C}$ ring distance of $2.14(3)$ Å correlates with that of $2.124(2)$ for I, and of $2.15(1)$ Å for II. The $\text{Mn}-(\text{C}_5\text{H}_5)$ distance is 1.78 Å, close to the 1.766 Å reported for I.

Unfortunately, some degree of disorder in the cyclopentadienyl ring (as evidenced by the irregular C–C bond lengths) prevented a detailed analysis of the conformation of the $\text{Mn}(\text{CO})_2\text{L}$ 'tripod' relative to the C_5H_5 ring, as has been done for the $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ precursor [13].

In summary, an extension of our catalytic procedures to the reaction between $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and isonitriles resulted in the successful synthesis of several $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CNR})$ complexes, and further demonstrates the utility and versatility of Pd catalysts for the substitution of isonitriles on metal carbonyl compounds.

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