

Coupling of Iminoacyl Groups to Diazabutadienes on Manganese Carbonyl Complexes

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$\text{RC(O)Mn(CO)}_4(\text{CNC}_6\text{H}_4\text{-}p\text{-Me})$ ($\text{R} = p\text{-ClC}_6\text{H}_4\text{CH}_2, \text{C}_6\text{H}_5\text{CH}_2, p\text{-MeOC}_6\text{H}_4\text{CH}_2$) couple in refluxing THF giving diazabutadiene (DAB) complexes $[\text{p-MeC}_6\text{H}_4\text{N}=\text{C(R)C(R)}=\text{NC}_6\text{H}_4\text{-}p\text{-Me}]\text{Mn}_2(\text{CO})_6$. The DAB ligand acts as an eight-electron donor. This behavior contrasts with that of acyl complexes of aliphatic isocyanides that undergo simple thermal decarbonylation in refluxing THF. Trapping studies with isocyanide, triphenylphosphine, and galvinoxyl suggest that decarbonylation is followed by rapid preferential isocyanide insertion and that the coupling involves a free radical process. The DAB dimers are resistant to thermal displacement of DAB by CO and of CO by triphenylphosphine and substituted acetylenes. $[\text{PhN}=\text{C(Ph)C(Ph)}=\text{NPh}]\text{Mn}_2(\text{CO})_6$ (**5e**) was prepared in low yield from the thermal reaction of $\text{PhN}=\text{C(Ph)Cl}$ with $\text{Mn}_2(\text{CO})_{10}$. The crystal structures of the compounds $[\text{p-MeC}_6\text{H}_4\text{N}=\text{C(CH}_2\text{C}_6\text{H}_4\text{-}p\text{-Cl)C(CH}_2\text{C}_6\text{H}_4\text{-}p\text{-Cl)}=\text{NC}_6\text{H}_4\text{-}p\text{-Me}]\text{Mn}_2(\text{CO})_6$ (**5a**) and **5e** were determined. For **5a**, data are as follows: monoclinic, $P2_12_12_1$; $a = 10.540$ (2) Å, $b = 12.775$ (2) Å, $c = 25.510$ (2) Å; $Z = 4$. For **5e**, crystal data are as follows: monoclinic; $P2_1/c$; $a = 12.457$ (2) Å, $b = 11.204$ (2) Å, $c = 22.454$ (4) Å; $\beta = 108.46$ (1)°; $Z = 4$. Both structures display an almost planar manganacyclic ring folded slightly at the N's and a Mn-Mn distance shorter than that in $\text{Mn}_2(\text{CO})_{10}$.

Introduction

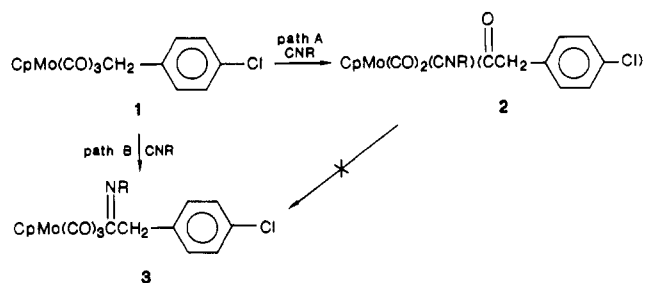
Reactions leading to C-C bond formation are of immense importance in organic chemistry. In recent years, organometallic reagents have been employed in many types of reactions forming C-C bonds,¹ both stoichiometric and catalytic.

One important class of reactions leading to C-C bond formation is insertion reactions.² Prominent among these is the CO insertion or carbonylation reaction which has been studied extensively.³

Isocyanides, RNC, are isoelectronic with CO and, hence, might be expected to display similar chemistry.⁴ Indeed, many such similarities are apparent. For example, isocyanides often replace terminal carbonyl ligands. Isocyanides are known also to insert into metal-carbon bonds to produce complexes containing the iminoacyl ($\text{MC}(\text{=NR})$) group. However, an important difference between the two is that isocyanides are slightly better sigma donors while functioning as comparable π -acceptors to carbon monoxide.⁵

Almost all the carbonylations that have been investigated experimentally are intramolecular; that is, the inserted CO is one already coordinated to the metal. Insertions of RNC into metal-carbon bonds are, in contrast, often so-called direct (intermolecular) insertions in which the incoming ligand is the one inserted. (Of course, it is not always possible to distinguish coordination of isocyanide prior to insertion.) Several recent examples of apparently direct insertions of isocyanides into transition metal-alkyl,^{6a,6-10} Zr-H,¹¹ lanthanide-H,¹² and transition metal- μ -alkylidene¹³ bonds have been reported. In contrast, an intramolecular insertion occurs with $\text{Pd}[\text{o-}$

Scheme I



$\text{C}_6\text{H}_4\text{NMe}_2)(\text{CNR})\text{Cl}$ ($\text{R} = t\text{-Bu}, p\text{-tolyl}$) affording $[\text{Pd}(\text{C}(\text{=NR}))\text{o-C}_6\text{H}_4\text{NMe}_2]\text{Cl}]_2$.¹⁴

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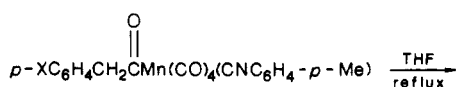
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Some years ago Yamamoto and Yamazaki¹⁵ investigated the reactions of $\text{CpMn}(\text{CO})_3\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-X}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{X} = \text{Cl, H, OCH}_3$) with $\text{C}_6\text{H}_{11}\text{NC}$. Scheme I summarizes their results. Two reaction pathways lead separately to carbonylation by isocyanide functioning as a Lewis base (path A) and to direct insertion forming the iminoacyl product (path B). Migration of the benzyl group from CO to coordinated CNR does not occur since heating 2 does not produce 3. The maximum yield of 3 resulted for $\text{X} = \text{Cl}$.

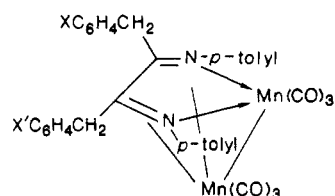
These results prompted us¹⁶ to investigate the reactions of isocyanides with $p\text{-XC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_5$ ($\text{X} = \text{H, Cl}$). In an earlier study, we reported that these Mn complexes react with aliphatic RNC ($\text{R} = n\text{-C}_4\text{H}_9, t\text{-C}_4\text{H}_9, \text{C}_6\text{H}_{11}$) exclusively via carbonylation to give $p\text{-XC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{-Mn}(\text{CO})_4(\text{CNR})$ which, on thermolysis, gave exclusively $p\text{-XC}_6\text{H}_4\text{CH}_2\text{Mn}(\text{CO})_4(\text{CNR})$. We have now attempted similar reactions employing the aromatic isocyanide $p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$ and wish to report that novel and surprisingly different chemistry is observed. This chemistry forms the subject of the present report.

Results and Discussion

Thermolysis of $p\text{-XC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4\text{-}(\text{CNC}_6\text{H}_4\text{-}p\text{-Me})$. Reaction of p -tolyl isocyanide with substituted benzylpentacarbonylmanganese complexes gave the expected acyl products **4a-c**. When these acyls were refluxed in THF, crystals of the dimers **5a-c** were isolated. Lower yields were obtained in refluxing heptane



- 4a:** $\text{X} = \text{Cl}$
b: $\text{X} = \text{H}$
c: $\text{X} = \text{OMe}$



- 5a:** $\text{X} = \text{X}' = \text{Cl}$
b: $\text{X} = \text{X}' = \text{H}$
c: $\text{X} = \text{X}' = \text{OMe}$
d: $\text{X} = \text{H, X}' = \text{OMe}$

and on heating to 94 °C in the solid state under N_2 until gas evolution ceased. **5a-d** contain neutral diazabutadiene ligands that apparently result from oxidative coupling of two formally negative iminoacyl groups accompanied by reduction of Mn(I) to Mn(0). The 1,4-diazabuta-1,3-diene ligand functions as an eight-electron donor. The lone pairs on both N atoms are coordinated to one Mn atom supplying four electrons. The four π -electrons in the C-N double bonds are coordinated to the other Mn. These complexes would be termed $\sigma\text{-N, } \sigma\text{-N}'; \eta^2\text{-CN, } \eta^2\text{-CN}'$, in the notation of van Koten and Vrieze.¹⁷ **5a-d** are iso-electronic with $\text{Mn}_2(\text{CO})_{10}$ and with $\text{CpMn}(\text{CO})_3$.

Spectral data (Table I) and X-ray crystal structures (vide infra) are consistent with the structure depicted for **5a-d**. All display four stretches in the terminal $\text{C}\equiv\text{O}$

Table I. Spectral Data

compd	IR, cm^{-1}	$^1\text{H NMR}^b$	
4c	2171 (m), 2153 (sh) ($\text{C}\equiv\text{N}$)	7.24–7.07 (m) ($\text{C}_6\text{H}_5, \text{C}_6\text{H}_4$) 4.16 (s) (CH_2)	
	2069 (s), 2016 (s), 1990 (s), 1978 (s) ($\text{C}\equiv\text{O}$)	3.87 (s) (OMe) 2.38 (s) (Me)	
	1630 (m) ($\text{C}=\text{O}$) ^a		
	5a	2038 (s), 2006 (s), 1958 (s, br), 1916 (s) ($\text{C}\equiv\text{O}$) ^a	7.24–6.41 (m) ($\text{C}_6\text{H}_5, \text{C}_6\text{H}_4$) 3.74 (dd, $J = 16.6$ Hz) (CH_2) 2.28 (s) (Me)
5b	1550 (m), 1489 (m) ($\text{C}=\text{N}$)		
5b	2038 (s), 2000 (s), 1940 (s, br), 1910 (m, sh) ($\text{C}\equiv\text{O}$) ^a	7.24–6.41 (m) ($\text{C}_6\text{H}_5, \text{C}_6\text{H}_4$) 3.77 (dd, $J = 16.3$ Hz) (CH_2) 2.28 (s) (Me)	
	1500 (m), 1494 (m) ($\text{C}=\text{N}$)		
5c	2034 (s), 2000 (s), 1940 (s, br), 1912 (s) ($\text{C}\equiv\text{O}$) ^a	7.27–6.74 (m) ($\text{C}_6\text{H}_5, \text{C}_6\text{H}_4$) 3.77 (s) (OMe)	
	1510 (m), 1503 (m) ($\text{C}=\text{N}$)	3.72 (dd, $J = 16.5$ Hz) (CH_2) 2.28 (s) (Me)	
	5d	2035 (s), 2001 (s), 1941 (s, br), 1912 (s) ($\text{C}\equiv\text{O}$) ^a	7.23–6.61 (m) ($\text{C}_6\text{H}_5, \text{C}_6\text{H}_4$) 4.05 (m) (CH_2) 3.76 (s) (OMe) 2.28 (s) (Me)
5d	1507 (m), 1499 (m) ($\text{C}=\text{N}$)		
	8a	2082 (m), 1992 (sh), 1988 (s), 1954 (s) ($\text{C}\equiv\text{O}$) ^c	
8a	1568 ($\text{C}=\text{N}$)		
	8c	2062 (m), 1988 (s), 1962 (s), 1944 (s) ($\text{C}\equiv\text{O}$) ^c	7.88–6.87 (m) (C_6H_4) 4.58 (s) (CH_2) 3.82 (s) (OMe) 2.31 (s) (Me)
	1710 (m) ($\text{C}=\text{N}$)		
12a	2064 (s), 1995 (s), 1985 (s), 1954 (s) ($\text{C}\equiv\text{O}$) ^c	7.24–6.78 (m) (C_6H_4) 3.80 (s) (CH_2) 2.37 (s) (Me) 2.35 (s) (Me)	
	1620 (m) ($\text{C}=\text{N}$)		
	12b	2072 (m), 1989 (s), 1980 (s), 1954 (s) ($\text{C}\equiv\text{O}$) ^d	7.22–6.80 (m) (C_6H_4) 3.74 (s, br) (CH_2, OMe) 2.35 (s, br) (Me)
12b	1624 (w), 1615 (w) ($\text{C}=\text{N}$)		
	13a	2004 (s), 1933 (s), 1909 (s) ($\text{C}=\text{O}$) ^a	7.25–6.74 (m) ($\text{C}_6\text{H}_5, \text{C}_6\text{H}_4$) 3.43 (dd, $J = 13.6$ Hz) (CH_2) 2.39 (s) (Me) 2.33 (s) (Me)
13a	1610 (m), 1597 (m) ($\text{C}=\text{N}$)		
	13b	2008 (s), 1933 (s), 1909 (s) ($\text{C}=\text{O}$) ^a	7.41–6.35 (m) ($\text{C}_6\text{H}_5, \text{C}_6\text{H}_4$) 3.72 (s) (OMe) 3.41 (dd, $J = 13.3$ Hz) (CH_2) 2.38 (s) (Me)
	1618 (m), 1612 (m) ($\text{C}=\text{N}$)		

^aIn CHCl_3 . ^bIn CDCl_3 . Shifts reported in ppm downfield from internal TMS standard. Abbreviations: m, multiplet; s, singlet; d, doublet. ^cIn hexane. ^dIn CCl_4 .

stretching region. The absence of bands ca. 2100 cm^{-1} indicates that the terminal isocyanide of the starting $p\text{-XC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CNR})$ compounds is no longer present. Two bands in the 1550–1480 cm^{-1} region are consistent with the presence of $\text{C}=\text{N}$ groups.

All the complexes display $^1\text{H NMR}$ signals in the aromatic region due to the phenyl rings of the benzyl ligands and the p -tolyl groups as well as a methyl singlet at 2.28 ppm due to the p -tolyl groups. The diastereotopic benzylic protons appear as doublets of doublets centered around 3.7 ppm having $J \sim 16\text{--}17$ Hz. Both **5c** and **5d** show a signal at 3.7 ppm for the methoxy protons.

The yields of the dimers vary with the electron-withdrawing ability of X in the order $\text{X} = \text{Cl}$ (49%) > H (35%) > OMe (26%). It may well be that this observation merely reflects increased thermal stability of the starting acyls when X is more electron-withdrawing. Presumably **4b** and **4c** disappear via other thermally available decomposition pathways.

Refluxing equimolar quantities of **4b** and **4c** in THF produced **5b**, **5c**, and **5d** (the dimer having two differently substituted benzyl groups) in a 1:0.7:1 ratio instead of the statistical 1:1:2 ratio. In addition, small amounts of $\text{Mn}_2(\text{CO})_9(\text{CN-}p\text{-tolyl})$ and $\text{Mn}_2(\text{CO})_8(\text{CN-}p\text{-tolyl})_2$ were isolated. (Total yield of DAB dimers was 76%.) This

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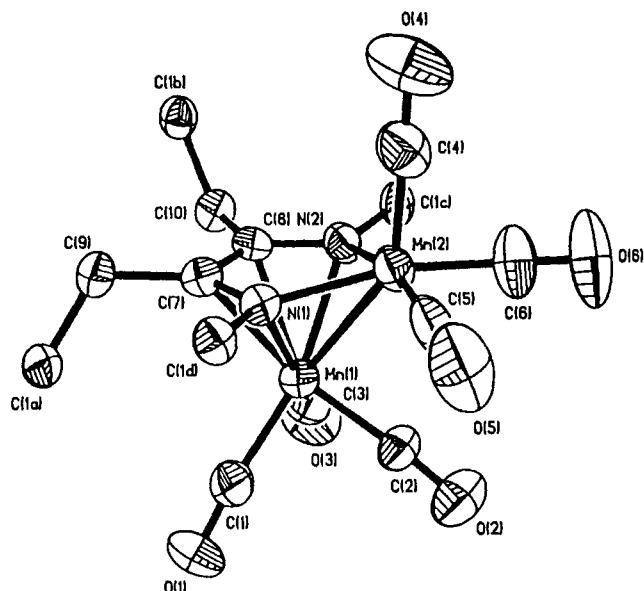


Figure 1. Coordination at manganese in **5a** with phenyl groups omitted for clarity. Ellipsoids drawn to include 50% probability density.

admittedly fragmentary evidence is in accord with the notion that the lower thermal stability of the acyls in the order **4a** > **4b** > **4c** is the reason behind the decreased yields of **5c** and **5d** (which involve **4c** as a reactant) as compared to **5b**.

Adams¹⁸ obtained a similar complex, (1,2,3,4-tetramethyl-1,4-diazabuta-1,3-diene)hexacarbonyldimanganese, in 7% yield by treating $[\text{Mn}(\text{CO})_4(\text{CNMe})]^-$ with MeI at -78°C in THF. The formation of this complex will be discussed further in the section on mechanism. More recently Keijsper, van Koten, Vrieze, Zoutberg, and Stam¹⁹ prepared (1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene)hexacarbonyldimanganese in 10% yield by allowing (1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene)bromotricarbonylmanganese to react with $\text{CpFe}(\text{CO})_2^-$. In their work, the diazabutadiene ligand was not formed via a coupling reaction. Rather the diazabutadiene (DAB) was allowed to react with $\text{Mn}(\text{CO})_5\text{Br}$ to give the starting material. This compound is one of a large number of DAB complexes containing H on the carbons and a variety of R groups on N prepared from the free DAB ligands by van Koten, Vrieze, and co-workers.¹⁷

Structures of [1,4-Di-*p*-tolyl-2,3-bis(*p*-chlorobenzyl)-1,4-diazabuta-1,3-diene] $\text{Mn}_2(\text{CO})_6$ (5a**) and [1,2,3,4-Tetraphenyl-1,4-diazabuta-1,3-diene] $\text{Mn}_2(\text{CO})_6$ (**5e**).** The molecular structures of **5a** and **5e** were determined by single-crystal X-ray diffraction studies. **5e** was prepared via the reaction of $\text{PhC}(\text{=NPh})\text{Cl}$ with $\text{Mn}_2(\text{C}\text{O})_{10}$,²⁰ its structure is presented here for comparison with that of **5a**. Tables II and III list fractional atomic coordinates for the non-hydrogen atoms in **5a** and **5e**, respectively, while Figures 1 and 2 show their molecular structures. Table IV presents selected bond distances and angles.²¹

The mirror symmetry of **5a** is broken only by the phenyl rings of the chlorobenzyl groups. **5e** displays only slight deviation from mirror symmetry on account of the phenyl

Table II. Fractional Atomic Coordinates ($\times 10^4$) for Non-Hydrogen Atoms of [1,4-Di-*p*-tolyl-2,3-bis(*p*-chlorobenzyl)-1,4-diazabuta-1,3-diene]hexacarbonyldimanganese (5a**)**

atom	x	y	z
Mn(1)	2084 (1)	7334 (1)	3090 (1)
Mn(2)	2792 (1)	6633 (1)	4015 (1)
Cl(1)	-4041 (2)	6984 (2)	1732 (1)
Cl(2)	-479 (3)	2397 (2)	5276 (1)
O(1)	544 (6)	6497 (5)	2230 (2)
O(2)	3889 (6)	5670 (5)	2818 (2)
O(3)	3163 (6)	8779 (5)	2315 (2)
O(4)	2628 (8)	6919 (6)	5143 (2)
O(5)	2561 (6)	4346 (4)	4139 (3)
O(6)	5558 (6)	6391 (6)	4121 (3)
N(1)	1067 (5)	6839 (4)	3746 (2)
N(2)	2778 (6)	8077 (4)	3758 (2)
C(1)	1079 (8)	6830 (6)	2577 (3)
C(2)	3220 (7)	6311 (6)	2945 (3)
C(3)	2758 (9)	8227 (6)	2618 (3)
C(4)	2689 (8)	6789 (6)	4695 (3)
C(5)	2649 (8)	5229 (7)	4090 (3)
C(6)	4497 (8)	6507 (6)	4077 (3)
C(7)	658 (7)	7843 (5)	3625 (2)
C(8)	1657 (6)	8561 (5)	3623 (2)
C(9)	-740 (7)	8162 (5)	3561 (3)
C(10)	1546 (7)	9706 (5)	3525 (3)
C(11)	-2547 (9)	3515 (7)	4003 (4)
C(12)	7190 (9)	633 (7)	4107 (5)
C(A1)	-1472 (6)	7817 (5)	3086 (3)
C(A2)	-2282 (7)	6938 (5)	3106 (3)
C(A3)	-3037 (8)	6701 (6)	2689 (3)
C(A4)	-3033 (8)	7293 (6)	2250 (3)
C(A5)	-2248 (9)	8138 (6)	2210 (3)
C(A6)	-1461 (7)	8385 (6)	2628 (3)
C(B1)	1063 (6)	360 (5)	3986 (3)
C(B2)	687 (7)	9935 (5)	4461 (3)
C(B3)	233 (7)	556 (6)	4863 (3)
C(B4)	151 (7)	1618 (5)	4784 (3)
C(B5)	500 (8)	2053 (5)	4321 (3)
C(B6)	973 (8)	1426 (5)	3923 (3)
C(C1)	3919 (6)	8736 (5)	3826 (3)
C(C2)	4026 (7)	9307 (6)	4279 (3)
C(C3)	5103 (8)	9885 (6)	4365 (3)
C(C4)	6060 (7)	9957 (5)	4003 (4)
C(C5)	5934 (7)	9382 (6)	3555 (3)
C(C6)	4881 (7)	8775 (6)	3460 (3)
C(D1)	129 (6)	6023 (5)	3796 (3)
C(D2)	79 (7)	5192 (5)	3450 (2)
C(D3)	-771 (7)	4384 (5)	3514 (3)
C(D4)	-1610 (7)	4382 (6)	3936 (3)
C(D5)	-1542 (7)	5301 (6)	4286 (3)
C(D6)	-675 (7)	5998 (5)	4227 (3)

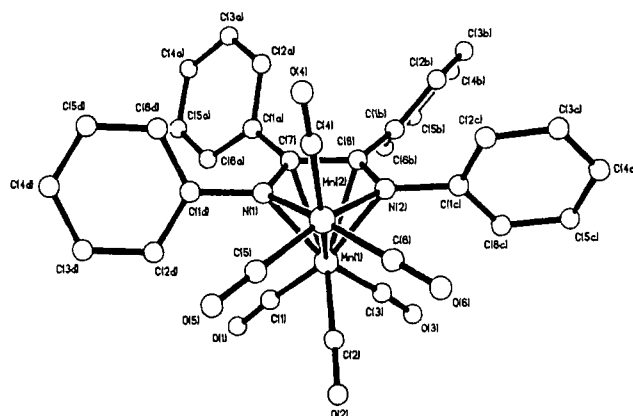


Figure 2. The molecular geometry of **5e**.

rings. Both complexes display five-membered manganese-cyclic rings consisting of the $\text{Mn}(2)\text{-N}(1)\text{-C}(7)\text{-C}(8)\text{-N}(2)$ atoms. Neither ring is precisely coplanar; both exhibit a fold at the N atoms. The dihedral angles between the

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(21) Because of differing numbering conventions used C(9) and C(10) in **5a** are respectively equivalent to C(1a) and C(1d) in **5e**.

Table III. Fractional Atomic Coordinates ($\times 10^4$) for Non-Hydrogen Atoms of [1,2,3,4-Tetraphenyl-1,4-diazabuta-1,3-diene]hexacarbonyldimanganese (5e)

atom	x	y	z
Mn(1)	2312.3 (5)	-46.4 (6)	6285.9 (3)
Mn(2)	3739.1 (5)	250.3 (6)	7412.6 (3)
O(1)	-114 (3)	-601 (4)	5814 (2)
O(2)	2630 (3)	-2493 (4)	6794 (2)
O(3)	2225 (4)	-1038 (4)	5061 (2)
O(4)	5030 (4)	1849 (4)	8412 (2)
O(5)	2969 (3)	-941 (4)	8378 (2)
O(6)	5662 (3)	-1431 (3)	7740 (2)
N(1)	2348 (3)	1168 (3)	7000 (2)
N(2)	3939 (3)	785 (3)	6612 (2)
C(1)	826 (4)	-344 (5)	6005 (2)
C(2)	2563 (4)	-1516 (5)	6630 (3)
C(3)	2304 (5)	-638 (5)	5538 (3)
C(4)	4518 (4)	1228 (5)	8006 (3)
C(5)	3242 (4)	-479 (5)	7992 (3)
C(6)	4905 (5)	-771 (5)	7605 (2)
C(7)	2260 (4)	1837 (4)	6467 (2)
C(8)	3170 (4)	1595 (4)	6232 (2)
C(1)	1398 (4)	2775 (5)	6207 (2)
C(2a)	1752 (5)	3937 (5)	6162 (2)
C(3a)	977 (6)	4832 (5)	5930 (3)
C(4a)	-163 (6)	4591 (6)	5750 (3)
C(5a)	-532 (5)	3465 (7)	5805 (3)
C(6a)	237 (4)	2562 (5)	6035 (3)
C(1b)	3310 (4)	2212 (4)	5677 (2)
C(2b)	4284 (5)	2852 (5)	5728 (3)
C(3b)	4381 (6)	3494 (6)	5225 (3)
C(4b)	3515 (7)	3516 (6)	4671 (3)
C(5b)	2555 (6)	2888 (5)	4613 (3)
C(6b)	2441 (5)	2220 (5)	5105 (3)
C(1c)	4971 (4)	535 (4)	6459 (2)
C(2c)	5940 (4)	1035 (5)	6845 (3)
C(3c)	6958 (5)	882 (6)	6724 (3)
C(4c)	6994 (5)	201 (6)	6231 (3)
C(5c)	6034 (5)	-340 (6)	5858 (3)
C(6c)	5018 (4)	-168 (5)	5977 (3)
C(1d)	1551 (4)	1409 (5)	7338 (2)
C(2d)	807 (4)	548 (5)	7400 (2)
C(3d)	83 (4)	795 (6)	7740 (3)
C(4d)	110 (5)	1890 (6)	8019 (3)
C(5d)	871 (4)	2740 (5)	7962 (2)
C(6d)	1595 (4)	2502 (5)	7628 (2)

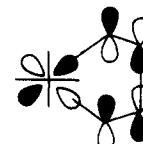
least-squares plane defined by N(1), N(2), and Mn(2) and that defined by N(1), C(7), C(8), and N(2) are 11.0° in **5a** and 8.4° in **5c** as compared to 10.0° in Adams' compound.¹⁸

The coordination around Mn(2) is distorted octahedral. The three carbonyl ligands lie at angles of $88\text{--}90^\circ$ with one another. However, the N(1)–Mn(2)–N(2) angles in both **5a** and **5e** are $\sim 76^\circ$, not far removed from the ideal pentagonal angle. The manganacyclic ring is bent down from the equatorial plane of octahedron. Mn(1) does not lie along the octahedral axis, the "axial" C(4)–Mn(1)–Mn(2) angles being 146° and 149° for **5a** and **5e** instead of the ideal 180° .

The C(7)–N(1) and C(8)–N(2) distances of 1.377 (8) and 1.397 (8) Å in **5a** and of 1.387 (5) and 1.397 (5) Å in **5e** are longer than those in a typical C=N double bond. In free diazabutadienes C–N distances range from ~ 1.26 Å in *c*-C₆H₁₁N=CHCH=N-*c*-C₆H₁₁²² as determined by X-ray analysis to 1.283 (6) Å in *t*-BuN=CHCH=N-*t*-Bu as determined by gas-phase electron diffraction.²³ C(7)–C(8) distances of 1.397 (8) and 1.418 (6) Å were found for **5a** and **5e**, respectively. These are shorter than C–C bond lengths of 1.457 (2) Å in *c*-C₆H₁₁N=CHCH=N-*c*-C₆H₁₁,²² 1.496 (2) Å in *t*-BuN=CHCH=N-*t*-Bu,²³ and 1.48 (1) Å

in isoelectronic CH₂=CHCH=CH₂.²⁴ Adams¹⁸ found similar trends in [MeN=C(Me)C(Me)=NMe]Mn₂(CO)₆. These distortions in bond distances apparently reflect delocalization in the manganacyclic ring.

An interesting question is whether this delocalization arises from interactions of the empty orbitals of the diazabutadiene with filled π -orbitals of Mn(2) within the manganacyclic ring or from the interaction of the π -system with orbitals on Mn(1). The distances between Mn(1) and C(7), C(8), N(1), and N(2) are all in the range 2.08–2.15 Å. π -Back-bonding in the manganacyclic ring should be favored by a low metal oxidation state and the presence of electron-withdrawing groups on the DAB ligand. I shows schematically the interaction of a filled metal π -orbital with the LUMO of a diazabutadiene in C_s local symmetry. Back-bonding should serve to shorten C–C



I

bonds and to lengthen C=N bonds in coordinated as compared to uncoordinated DAB. This is exactly the trend observed. Moreover, Mn–N bond lengths should be shortened by back-bonding in comparison to the case where no back-bonding is possible.

The extent of C–N and C–C bond distortion in **5a** and **5e** can be compared with that in [*c*-C₆H₁₁N=CHCH=N-*c*-C₆H₁₁]Mn(CO)₃Br, in which Mn is in the +I oxidation state and should presumably be a worse π -donor. The average C–N distance of 1.28 Å and the C–C bond distance of 1.48 Å^{25,26} scarcely differ from those of the free ligand. Average C–N distances in **5a** and **5e** are 1.39 Å in both, compared to 1.39 in Adams' dimer.¹⁸ C–C distances are 1.40 and 1.42 Å in Adams' dimer.¹⁸ This increased distortion is consistent with the change from Mn(I) to Mn(0), allowing increased back-bonding in the dimers.

It is also interesting that the presence of potentially electron-withdrawing *p*-tolyl, phenyl, and *p*-chlorobenzyl groups on **5a** and **5e** seems not to lead to any increased distortion of bond lengths in comparison to [1,2,3,4-tetramethyl-1,4-diazabuta-1,3-diene]hexacarbonyldimanganese. In the case of the *p*-tolyl groups attached to the nitrogens, no resonance electron withdrawal is possible since the π -orbitals of the *p*-tolyl rings of **5a** are not in conjugation with the π -system of the manganacycle; ring planes are nearly perpendicular to those of the manganacycles. The phenyl rings on the carbons of **5e** can have only residual conjugation with the DAB π -system. If the best least-squares plane is constructed through (admittedly slightly nonplanar, vide supra) Mn(2)–N(1)–C(7)–C(8)–N(2) in **5e**, the normal to this plane makes angles of 72.9° and 70.2° to the normals to the planes of the phenyl rings bonded to N(1) and N(2), respectively. The normals to the phenyl ring planes on C(7) and C(8) make angles of 58.5° and 52.5° with the "plane" of the manganacycle. Apparently, the inductive effect of the *p*-chlorobenzyl groups on **5a** influences the energies of the π -orbitals relatively little.

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Table IV. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for Compounds 5a and 5e

	5a	5e		5a	5e
Bond Distances					
Mn(1)–Mn(2)	2.633 (1)	2.612 (1)	Mn(2)–N(2)	1.958 (5)	1.984 (4)
Mn(1)–C(1)	1.803 (7)	1.788 (5)	C(1)–O(1)	1.131 (8)	1.149 (5)
Mn(1)–C(2)	1.811 (7)	1.804 (6)	C(2)–O(2)	1.129 (8)	1.149 (6)
Mn(1)–C(3)	1.804 (7)	1.802 (6)	C(3)–O(3)	1.131 (8)	1.136 (6)
Mn(2)–C(4)	1.748 (8)	1.760 (6)	C(4)–O(4)	1.157 (9)	1.164 (6)
Mn(2)–C(5)	1.809 (7)	1.804 (6)	C(5)–O(5)	1.139 (8)	1.148 (6)
Mn(2)–C(6)	1.811 (8)	1.791 (6)	C(6)–O(6)	1.133 (9)	1.161 (5)
Mn(1)–N(1)	2.087 (5)	2.092 (4)	C(7)–N(1)	1.387 (8)	1.387 (5)
Mn(1)–C(7)	2.131 (6)	2.153 (4)	C(8)–N(2)	1.377 (8)	1.397 (5)
Mn(1)–N(2)	2.084 (5)	2.137 (3)	C(7)–C(8)	1.397 (8)	1.418 (6)
Mn(1)–C(8)	2.124 (6)	2.149 (4)	C(7)–C(9)	1.535 (9)	1.484 (6)
Mn(2)–N(1)	1.962 (5)	1.975 (3)	C(8)–C(10)	1.489 (9)	1.485 (6)
Bond Angles					
Mn(2)–Mn(1)–N(1)	47.4 (1)	48.1 (1)	Mn(1)–Mn(2)–C(6)	112.9 (3)	113.8 (2)
Mn(2)–Mn(1)–N(2)	47.3 (1)	48.1 (1)	N(1)–Mn(2)–N(2)	75.5 (2)	76.2 (2)
Mn(2)–Mn(1)–C(1)	134.1 (3)	132.6 (2)	N(1)–Mn(2)–C(4)	105.9 (3)	102.9 (2)
Mn(2)–Mn(1)–C(2)	75.5 (2)	74.3 (2)	N(1)–Mn(2)–C(5)	95.3 (3)	97.1 (2)
Mn(2)–Mn(1)–C(3)	134.5 (3)	138.6 (2)	N(1)–Mn(2)–C(6)	164.2 (3)	165.8 (2)
N(1)–Mn(1)–N(2)	70.2 (2)	70.5 (1)	N(2)–Mn(2)–C(4)	103.0 (3)	107.5 (2)
N(1)–Mn(1)–C(1)	99.9 (3)	99.2 (2)	N(2)–Mn(2)–C(5)	165.5 (3)	163.8 (2)
N(1)–Mn(1)–C(2)	106.6 (3)	107.9 (2)	N(2)–Mn(2)–C(6)	96.9 (3)	95.0 (2)
N(1)–Mn(1)–C(3)	158.3 (3)	161.0 (2)	C(4)–Mn(2)–C(5)	90.2 (3)	88.2 (2)
N(1)–Mn(1)–C(7)	38.4 (2)	38.1 (1)	C(4)–Mn(2)–C(6)	89.1 (4)	90.3 (2)
N(2)–Mn(1)–C(1)	164.3 (3)	164.9 (2)	C(5)–Mn(2)–C(6)	89.2 (4)	88.5 (2)
N(2)–Mn(1)–C(2)	103.3 (3)	103.5 (2)	Mn(1)–N(1)–C(7)	72.5 (4)	73.3 (2)
N(2)–Mn(1)–C(3)	96.8 (3)	101.8 (2)	Mn(2)–N(1)–C(7)	119.3 (4)	120.2 (3)
N(2)–Mn(1)–C(8)	38.2 (2)	38.0 (1)	Mn(1)–N(2)–C(8)	72.5 (4)	71.4 (2)
C(1)–Mn(1)–C(2)	89.0 (3)	90.0 (2)	Mn(2)–N(2)–C(8)	120.8 (4)	119.4 (3)
C(1)–Mn(1)–C(3)	88.5 (3)	84.4 (2)	Mn(1)–C(1)–O(1)	173.9 (7)	175.9 (5)
C(1)–Mn(1)–C(7)	99.1 (3)	99.2 (2)	Mn(1)–C(2)–O(2)	174.8 (7)	172.7 (5)
C(1)–Mn(1)–C(8)	127.2 (3)	128.1 (2)	Mn(1)–C(3)–O(3)	178.3 (7)	175.2 (5)
C(2)–Mn(1)–C(3)	93.4 (3)	90.7 (2)	Mn(2)–C(4)–O(4)	178.2 (7)	177.9 (5)
C(2)–Mn(1)–C(7)	144.8 (3)	145.6 (2)	Mn(2)–C(5)–O(5)	179.6 (8)	177.2 (5)
C(2)–Mn(1)–C(8)	143.5 (3)	141.6 (2)	Mn(2)–C(6)–O(6)	177.5 (8)	178.8 (5)
C(3)–Mn(1)–C(7)	120.8 (3)	123.0 (2)	N(1)–C(7)–C(8)	112.0 (6)	111.3 (4)
C(3)–Mn(1)–C(8)	92.5 (3)	96.8 (2)	N(1)–C(7)–C(9)	124.5 (6)	124.8 (4)
C(7)–Mn(1)–C(8)	38.3 (2)	38.5 (2)	C(8)–C(7)–C(9)	123.2 (6)	123.6 (4)
Mn(1)–Mn(2)–N(1)	51.5 (1)	52.0 (1)	N(2)–C(8)–C(7)	110.5 (5)	111.8 (4)
Mn(1)–Mn(2)–N(2)	51.5 (1)	53.3 (1)	N(2)–C(8)–C(10)	123.4 (6)	125.1 (4)
Mn(1)–Mn(2)–C(4)	146.4 (3)	148.8 (2)	C(7)–C(8)–C(10)	126.0 (6)	122.9 (4)
Mn(1)–Mn(2)–C(5)	114.0 (2)	110.9 (2)			

The shortening of the Mn–N distances from ~2.05 Å in $[t\text{-BuN}=\text{CHCH}=\text{N}-t\text{-Bu}]\text{Mn}(\text{CO})_3\text{Br}$ to an average of 1.96 Å in 5a, 1.98 Å in 5e, and 2.00 Å in $[\text{MeN}=\text{C}(\text{Me})\text{-CMe}=\text{NMe}]\text{Mn}_2(\text{CO})_6$ is also consistent with increased back-donation by Mn(0) as depicted in I.

Well known instances of delocalization involving metal back-bonding occur in the tetraazadiene metallacycles.²⁷ The ligands in these complexes are formally related to DAB ligands by the substitution of more electronegative N's for the C(R) groups, thus leading to enhancement of π -back-bonding.

Although the directions of distortions can be accounted for by invoking back-bonding only from Mn(2) within the metallacyclic ring of 5a and 5e, donation from any filled orbital into the LUMO leads to predicted distortions in the same direction. Good model systems for assessing the importance of $\eta^2\text{-C}=\text{N}$ coordination to Mn(1) are not available. We are currently carrying out MO calculations²⁸ on these systems in an effort to shed light on this area.

The observed Mn–Mn bond distances of 2.633 (1) and 2.612 (1) Å for 5a and 5e, respectively, may be compared to the 2.615 (1) Å distance found for $[\text{MeN}=\text{C}(\text{Me})\text{-C}(\text{Me})=\text{NMe}]\text{Mn}_2(\text{CO})_6$ ¹⁸ and the somewhat longer distance of 2.923 (2) Å for $\text{Mn}_2(\text{CO})_{10}$.²⁹

Each molecule contains six approximately linear terminal carbonyl ligands, three on each Mn atom, arranged in a facial geometry. The six Mn–C distances range from 1.748 (8) to 1.811 (8) Å for 5a and 1.760 (6) to 1.804 (6) Å for 5e with $\text{Mn}-\text{C}_{\text{av}}$ of 1.798 and 1.792 Å, respectively. In both molecules the shortest Mn–C distance involves the carbonyl ligand most nearly colinear with the Mn–Mn bond ($\angle\text{Mn}(1)\text{-Mn}(2)\text{-C}(4) \sim 147^\circ$). The six C–O distances range from 1.129 (8) to 1.157 (9) Å in 5a and 1.136 (6) to 1.164 (6) Å in 5a and 5e, respectively, with $\text{C}-\text{O}_{\text{av}}$ of 1.137 and 1.151 Å, respectively. The Mn–C–O angles range from 173.9 (7)° to 179.6 (8)° in 5a and from 172.7 (5)° to 178.8 (5)° in 5e. The smallest angle in 5a corresponds to Mn(1)–C(1)–O(1) (173.9°) while that in 5e is Mn(1)–C(2)–O(2) (172.7°).

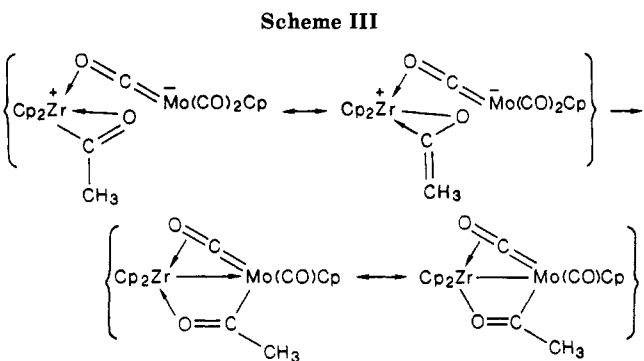
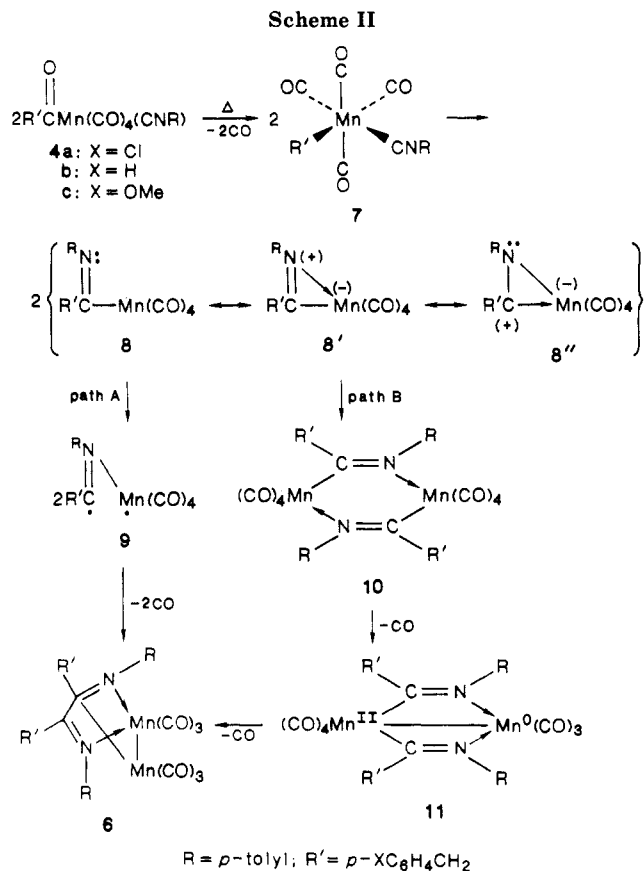
The shortest nonbonded Mn–C distance in both complexes is between Mn(2) and C(2) and is 2.8 Å in 5a and 2.4 Å in 5e. Even though these distances may well indicate some interaction between Mn(2) and the C(2)–O(2) ligand, the differences between the distances and bond angles involving this carbonyl and other carbonyls are not large enough to describe C(2)–O(2) as a semibridging carbonyl according to Cotton's criteria.³⁰ Adams¹⁸ also concluded that a similarly situated carbonyl in (1,2,3,4-tetra-methyldiazabutadiene) $\text{Mn}_2(\text{CO})_6$ was not to be described as semibridging.

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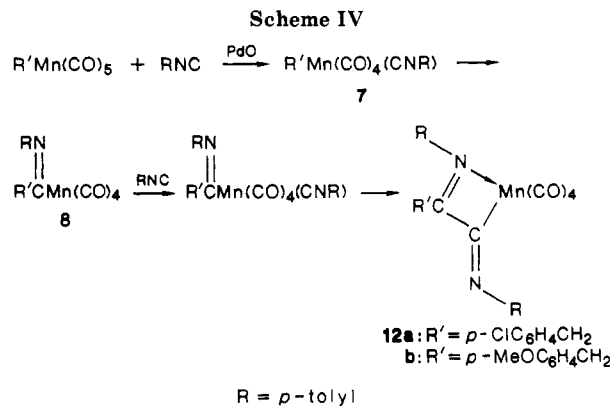
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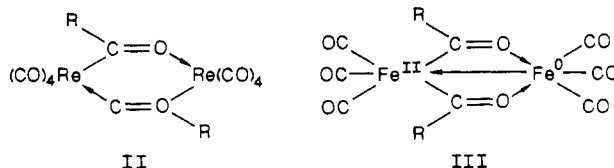
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Mechanism of Dimer Formation. Two important aspects of the reactions presented here are: what the mechanism of dimerization may be and why it occurs only with an aromatic and not with aliphatic isocyanides. Our results are not yet complete enough to address the second issue. Scheme II depicts possible pathways for the dimerization. It seems likely that thermal decarbonylation produces 7 which undergoes rapid and preferential insertion of isocyanide into the Mn-C bond producing the iminoacyl 8. 8 might then undergo dimerization via a free radical route (path A) involving a species such as 9. Alternatively, a dimer such as 10 might form in which an 18-electron configuration is attained by coordination of the iminoacyl N of one molecule to the Mn of another. Rearrangement of 10 could lead to a species such as 11, in which two iminoacyl carbons are coordinated to one Mn and two iminoacyl nitrogens to the other. This process would involve an oxidation state of +II for the C-coordinated Mn and 0 for the N-coordinated Mn. A Mn-Mn bond would permit attainment of the 18-electron configuration for both Mn atoms. Reductive elimination and CO loss converts 11 to 6. Some precedent exists for the chemistry proposed in path B for the 10 to 11 conversion.



Norton and co-workers³¹ have observed the transfer of an acyl group from Zr(IV) to Mo(I) as shown in Scheme III. The mechanism of Norton's transformation was demonstrated to be nucleophilic attack on acetyl C by low-valent Mo. Breaking of a Mn-N bond in 10 (or initial formation of a species with only one Mn-N bond) could lead to attack by Mn on iminoacyl C. Also worth noting is the existence of II which is isoelectronic with 10³² and III which is isoelectronic with 11³³ as well as a Rh analogue of 10.³⁴



Whatever might be one's views of the feasibility of the free-radical path (A) or the concerted path (B), it seems likely that species such as 7 and 8 are involved in the dimerization. Hence, we set out to prepare and to thermalize 7 and/or 8.

Recently, Coville^{35,36} and co-workers have demonstrated that PdO catalyzes CO substitution in very inert $M_2(CO)_{10}$ ($M = Mn, Re$). In the hope of achieving direct replacement of CO by RNC to afford 7, we allowed the $R'Mn(CO)_5$ and CN-*p*-tolyl to react in the presence of a catalytic amount of PdO. Whether the reactants were mixed in a 1:1 or 1:2 ratio, the major product formed was 12, presumably via the mechanism depicted in Scheme IV.

7 is probably formed initially, but very rapid isocyanide insertion leads immediately to 8. A second isocyanide coordinates and is rapidly inserted. The reaction stops when the iminoacyl lone pair coordinates forming a four-membered manganacyclic ring and an 18-electron complex, 12.

Spectral data for 12a,b are consistent with the proposed structure. An X-ray structure of 12b confirms the geometry and will be discussed in a separate publication.³⁷

A small quantity of a compound whose spectroscopic properties (see Table I) matched those expected for 8c ($R = p\text{-tolyl}$, $R' = CH_2C_6H_4\text{-}p\text{-OMe}$) was isolated from the reaction of $p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{Mn(CO)}_5$ with (*p*-tolyl)NC

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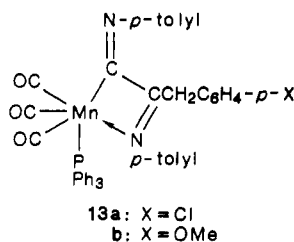
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used to prepare **4c**. A band of medium intensity at 1710 cm^{-1} in the IR is attributed to the C=N stretch of an η^2 -iminoacyl.³⁸ The mass spectrum of **8c** exhibits a molecular ion peak (m/e 411), and also peaks for the stepwise loss of CO, culminating in the carbon monoxide-free ion $[\text{M} - 4\text{CO}]^+$ (m/e 293, relative intensity 100). This ion then loses manganese to give the metal-free ion $[\text{M} - 4\text{CO} - \text{Mn}]^+$ (m/e 238, relative intensity 23). Unfortunately, the sample decomposed when we attempted to grow crystals and could not be prepared again. Also isolated was a trace of **12b**.

Our inability to prepare pure samples of **7** or **8** led us to carry out trapping experiments. Refluxing a THF solution of *cis-p*- $\text{ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN-}p\text{-tolyl})$ (**4a**) in the presence of an equimolar amount of *p*-tolyl isocyanide led to the formation of the bis(imino) complex **12a** as the major product. No evidence of dimerization to form **5a** was observed. This suggests that the formations of **5** and **12** proceed through a common intermediate, **8**, which can be trapped by RNC, giving **12**, or dimerizes, giving **5**.

Refluxing equimolar quantities of *cis-p*- $\text{ClC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN-}p\text{-tolyl})$ (**4a**) and triphenylphosphine in THF gave a single manganese-containing product which decomposed on attempted chromatography.

In contrast, *cis-p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN-}p\text{-tolyl})$ (**4c**) and triphenylphosphine in refluxing THF gave **13b** in 29% yield. There is no obvious explanation for these different results.



Refluxing a THF solution of **4a** with galvinoxyl gave traces of $\text{Mn}_2(\text{CO})_{10-n}(\text{CN-}p\text{-tolyl})_n$ ($n = 1, 2$) as the only recovered manganese-containing products. No evidence of dimerization was detected by either thin-layer or column chromatography. This suggests the possibility of a free-radical mechanism such as that proposed as path A in Scheme II. In sum, our studies are consistent with the proposals of Scheme II involving **7** and **8**, followed by steps involving radicals such as those of path A. We plan further mechanistic studies employing other isocyanides, radical initiators, and ESR spectroscopy.

Directly related to the coupling reaction reported here is the work of Rothwell and co-workers,³⁹ who have investigated the intramolecular coupling of η^2 -iminoacyl ligands on $\text{M}(\text{OAr})_2(\eta^2\text{-C}(\text{=NR}')\text{R})_2$ ($\text{M} = \text{Ti, Zr, Hf}$) which gives complexes $\text{M}(\text{OAr})_2[\text{R}'\text{NC}(\text{R})\text{=C}(\text{R})\text{NR}']$ formulated as enediamides. Intramolecular coupling of acyl with iminoacyl ligands leading to enamidolates was also observed.⁴⁰ Coupled products have been structurally characterized.⁴¹ Formulation of the ligands resulting from iminoacyl coupling as diazabutadienes (neutral) or endiamides (dianions) reflects increasing electron delocalization which increases along a continuum from, for example, $\text{Mn}[\text{N}(t\text{-Bu})\text{CHCHN}(t\text{-Bu})]_2$ ¹⁷ to our complexes to those

of Rothwell and co-workers.

Other chemistry relevant to this work includes inter- and intramolecular coupling of (usually η^2) acyl and formyl ligands on early transition metals,⁴²⁻⁴⁵ lanthanides,⁴⁶ and actinides⁴⁷ to afford enediolate ligands and the coupling of isocyanides effected by $[(\text{MeC}_5\text{H}_4)\text{ZrH}(\mu\text{-H})]_2$ to afford enediamide-type ligands,⁴⁸ presumably via a formimino-type intermediate. Curtis and Reo have recently observed¹⁰ the coupling of an η^2 -iminoacyl to a coordinated alkyne on a Ta center. The oxophilicity of these metals has been thought to be important for the acyl coupling through contribution of an oxycarbene resonance structure.⁴⁹

These coupling reactions can be considered as part of the more general phenomenon of reductive coupling of CO^{50-56} and isocyanide⁵⁷⁻⁶³ ligands mediated by metals.

It is of particular interest that the reductive coupling of RNC observed by us occurs with nonoxophilic Mn and requires no added reagents. Generally, the later transition metals require the use of anionic reagents and/or strongly donating ligands.⁶⁴

An interesting exception to this generalization was recently found by Kubiak and co-workers.⁶⁵

Our results make it seem likely that Adams' isolation¹⁸ of $[\text{MeNC}(\text{Me})\text{C}(\text{Me})\text{NMe}]\text{Mn}_2(\text{CO})_6$ from the reaction of $\text{Mn}(\text{CO})_4(\text{CNMe})^-$ and MeI proceeds with formation of $\text{MeMn}(\text{CO})_4(\text{CNMe})$ and via Scheme II. However, we were not able to isolate any coupling product from refluxing $\text{CH}_3\text{C}(\text{O})\text{Mn}(\text{CO})_4(\text{CN-}p\text{-tolyl})$ in THF.

Reactivity of the Dimers. The ultimate reducing agent in these iminoacyl couplings is the Na employed to reduce $\text{Mn}_2(\text{CO})_{10}$ to $\text{Mn}(\text{CO})_5^-$. If the DAB ligand could be displaced from the product dimer to re-form $\text{Mn}_2(\text{CO})_{10}$, the process might conceivably be made catalytic.

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5a proved to be remarkably unreactive to ligand displacement. No reaction was observed on refluxing for 14 h in isooctane under N₂ nor on stirring at ambient temperature for 6 h in THF under 1 atm of CO. Overnight reflux in THF or CH₂Cl₂ in the presence of equimolar PPh₃ did not result in any reaction.

The distortions in bond lengths of the DAB ligand in 5a as compared to free DAB (vide supra) suggest that coordination might activate DAB toward reaction with other unsaturated molecules. Our attempts to induce reaction between 5a and alkynes also resulted in failure. Refluxing 5a in toluene with MeO₂CC≡CCO₂Me for 24 h gave no reaction. In the presence of MeO₂CC≡CCO₂Me, irradiation of 5a in benzene for 2 h gave 48% recovered starting material and a trace of the diazabutadiene (*p*-tolyl)NC(CH₂C₆H₄-*p*-Cl)N(*p*-tolyl). Refluxing 5a in benzene for various time periods with PhC≡CPh, PhC≡CH and Me₃NO or HC≡CCO₂Me and Me₃NO gave no evidence of reaction by TLC.

By way of contrast, Ru₂(CO)₆(DAB) complexes in which the DAB ligand functions as a six-electron donor react with a number of small molecules,^{17,66} inserting them into the Ru-C bond of the η²-C=N group. However, Fe₂(CO)₆(DAB) complexes were found⁶⁷ not always to react in this way. (DAB)Fe(CO)₃ was found to react with alkynes affording 1,5-dihydropyrrol-2-ones.⁶⁸ Other complexes having DAB ligands which are eight-electron donors were also found to react with small molecules. For example, Ru₂(CO)₅(DAB) has been found to react with a number of different reagents affording products of C-C, C-H, and N-H coupling on the DAB ligand.⁶⁹⁻⁷² Ru₃(CO)₈(DAB) adds a methylene fragment on reaction with CH₂N₂, rupturing a Ru-Ru bond.⁷³ Recent MO calculations suggest that the Ru-Ru bonding character of the LUMO coupled with its antibonding character between the μ-CO and DAB ligands is responsible for its reactivity with CO and other small molecules.⁷⁴

The Ru complexes that undergo coupling reactions are those having a vacant coordination site on Ru or having only one η²-C=N.⁶⁹ The unreactivity of our Mn dimers may be connected to the coordinative saturation at all metal centers. We are attempting to prepare dimers analogous to 5a having CO's substituted by easily replaceable Lewis base ligands⁷⁵ in order to generate coordinative unsaturation more easily. We also plan further investigation of the photochemistry of 5. Re complexes will also be prepared and studied.

Experimental Section

Infrared solution spectra were recorded with a Perkin-Elmer Model 599 spectrophotometer, using either potassium bromide (0.1 mm) or sodium chloride (0.1 mm) cells. Band positions were

determined relative to the 1601 cm⁻¹ peak in polystyrene.

¹H NMR spectra were obtained on an IBM NR-80 instrument in Fourier transform mode.

Analytical thin-layer chromatography was conducted by using E. Merck silica gel 60-PF254 precoated plates. Compounds were made visible by UV light (254 nm) and by I₂ vapor. Preparative chromatographic separations were conducted by column chromatography using neutral or acidic alumina, 80-200 mesh, or using E. Merck silica gel, finer than 220 mesh.

Melting points were determined on a Mel-Temp apparatus, using open-end capillaries, and are uncorrected. Low-resolution mass spectra were obtained on a Hewlett-Packard 5995A quadrupole GC/MS system by means of direct inlet. High-resolution mass spectra (HRMS) were obtained on a Kratos MS802-DS55 spectrometer. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

Methylmanganese pentacarbonyl,⁷⁶ benzylmanganese pentacarbonyl,⁷⁶ (*p*-methoxybenzyl)pentacarbonylmanganese,⁷⁶ (*p*-chlorobenzyl)pentacarbonylmanganese,⁷⁶ cyclohexyl isocyanide,⁷⁷ and *p*-tolyl isocyanide⁷⁸ were prepared by standard literature methods. Dimanganese decacarbonyl was purchased from the Pressure Chemical Co., and *tert*-butyl isocyanide and galvinoxyl were purchased from Aldrich. All other laboratory chemicals were reagent grade and were used as received.

Tetrahydrofuran, THF, was dried by distillation from sodium benzophenone ketyl. Toluene and benzene were dried with sodium ribbon. Reagent grade dichloromethane, chloroform, hexane, and petroleum ether (bp 60-80 °C) were freshly distilled before use. All other solvents were reagent grade and were used as received.

Preparation of Tetracarbonyl(*p*-tolyl isocyanide)(*p*-chlorophenyl)acetyl]manganese (4a) and Tetracarbonyl[η²-(*p*-chlorobenzyl)(*p*-tolylimino)methyl]manganese (8a). A solution of (*p*-chlorobenzyl)pentacarbonylmanganese (4.00 g, 12.5 mmol), *p*-tolyl isocyanide (1.461 g, 1.50 mL, 12.5 mmol), and 60 mL of freshly distilled THF was stirred under argon at ambient temperature for approximately 18 h. After removal of THF by rotary evaporation, the resulting brown residue was dissolved in a minimum amount of chloroform and eluted through a grade II acid alumina column (35 cm by 2.5 cm). Elution with 1:9 diethyl ether/hexane removed small amounts of Mn₂(CO)₉(CNR) and Mn₂(CO)₈(CNR)₂ (R = *p*-tolyl). Elution with 1:4 diethyl ether/hexane removed a yellow band, 8a (0.135 g, 2.6% yield), a red band, 12a (0.15 g, 2.3% yield), and the desired product 4a as a yellow-orange band. Reduction in volume by rotary evaporation, enriching in hexane and cooling to 0 °C gave 4a as a colorless solid that was collected on a glass frit and air-dried; yield 2.16 g (39.5%).

4a: mp 86.5-88.0 °C. High-resolution mass spectrum: *m/e* (relative intensity) 437 (M⁺, not observed), 339 (19), 311 (20), 284 (41), 243 (87), 172 (100), 118 (60), 91 (13). Anal. Calcd for C₂₀H₁₃ClMnNO₅: C, 54.88; H, 2.99; N, 3.20. Found: C, 55.07; H, 2.90; N, 3.18.

8a: mp 140-142 °C.

Preparation of Tetracarbonyl(phenylacetyl)(*p*-tolyl isocyanide)manganese (4b). This compound was prepared by using the same procedure as for 4a except that the reaction time was 15 h and that precipitation of the product required cooling in hexane to -78 °C: mp 53-55 °C; yield 31.3%. High-resolution mass spectrum: *m/e* (relative intensity) 403 (M⁺, not observed), 339 (18), 311 (15), 284 (32), 209 (100), 172 (96), 118 (42), 91 (17).

Preparation of Tetracarbonyl[*p*-methoxyphenyl]acetyl](*p*-tolyl isocyanide)manganese (4c). This compound was prepared by using the same procedure as for 4a except that the reaction time was 10 h, and the chromatography was done on a grade II neutral alumina column (37 cm by 3 cm). Elution with 1:9 diethyl ether/hexane removed small amounts of Mn₂(CO)₉(CN-*p*-tolyl) and Mn₂(CO)₈(CN-*p*-tolyl)₂. Elution with 1:4 diethyl ether/hexane removed unreacted *p*-CH₃OC₆H₄CH₂Mn(CO)₅, a yellow band, 8c, a red band, 12b, the desired acyl 4c,

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as an orange band, and an unidentified yellow band. Removal of solvent from **4c** gave a brown oil which was taken up in 50 mL of carbon tetrachloride. Removal of solvent gave a pale brown solid that was recrystallized from carbon tetrachloride/hexane as a colorless solid in 25.5% yield.

4c: mp 64–66 °C. Low-resolution mass spectrum: m/e (relative intensity) 435 (M^+ , not observed), 367 (4), 339 (12), 311 (16), 284 (19), 172 (54), 121 (41), 118 (29), 55 (100).

8c: low-resolution mass spectrum, m/e (relative intensity) 405 (M^+ , 23), 377 (16), 349 (2), 321 (23), 293 (100), 238 (23), 121 (8), 55 (22).

Preparation of [1,4-Di-*p*-tolyl-2,3-bis(*p*-chlorobenzyl)-1,4-diazabuta-1,3-diene]hexacarbonyldimanganese (5a**). **4a** (0.400 g, 0.914 mmol) was refluxed for 1 h in dry THF (15 mL). The solvent was removed under reduced pressure. The resulting red residue was dissolved in a minimum amount of dichloromethane (10 mL) and diluted with hexane (40 mL). The volume was reduced by rotary evaporation to the first appearance of a red precipitate, followed by cooling at 0 °C for 20 h. The resulting red crystals were collected on a glass frit, washed with 2 × 5 mL portions of cold hexane, and air-dried: mp 192–193 °C; yield 0.171 g (49%). Low-resolution mass spectrum: m/e (relative intensity) 763 (M^+ , not observed), 707 (10), 678 (20), 650 (4), 594 (64), 539 (32), 297 (84), 242 (55), 179 (97), 125 (100), 55 (62). Anal. Calcd for $C_{36}H_{26}C_{12}Mn_2N_2O_6$: C, 56.64; H, 3.43; N, 3.67. Found: C, 55.68; H, 3.26; N, 3.40.**

Preparation of [1,4-Di-*p*-tolyl-2,3-dibenzyl-1,4-diazabuta-1,3-diene]hexacarbonyldimanganese (5b**). **4b** (0.500 g, 1.24 mmol) was refluxed for 1 h in dry THF (20 mL). The resulting red solution was worked up in a manner similar to that of **5a** to give **5b** as red crystals: mp 192–193 °C; yield 0.217 g (35%). High-resolution mass spectrum: m/e (relative intensity) 694 (M^+ , 10), 638 (11), 610 (8), 526 (100), 471 (72), 416 (16), 263 (72), 208 (56). Anal. Calcd for $C_{36}H_{28}Mn_2N_2O_6$: C, 62.26; H, 4.06; N, 4.03. Found: C, 61.84; H, 4.07; N, 3.95.**

Preparation of [1,4-Di-*p*-tolyl-2,3-bis(*p*-methoxybenzyl)-1,4-diazabuta-1,3-diene]hexacarbonyldimanganese (5c**). **4c** (0.450 g, 1.03 mmol) was refluxed for 25 min in dry THF (20 mL). Workup as described above for **5a** gave red crystals: mp 212–214 °C; yield 0.102 g (26.1%). High-resolution mass spectrum: m/e (relative intensity) 754 (M^+ , not observed), 586 (100), 531 (53), 476 (17), 238 (9), 121 (12). Anal. Calcd for $C_{38}H_{32}Mn_2N_2O_8$: C, 60.49; H, 4.27; N, 3.71. Found: C, 60.28; H, 4.39; N, 3.58.**

Preparation of [1,4-Di-*p*-tolyl-2-(*p*-methoxybenzyl)-3-benzyl-1,4-diazabuta-1,3-diene]hexacarbonyldimanganese (5d**). A THF (15 mL) solution of **4b** (0.300 g, 0.744 mmol) and **4c** (0.330 g, 0.761 mmol) was refluxed for 90 minutes. The solvent was removed at reduced pressure. The resulting red solid was dissolved in 20 mL of 1:1 dichloromethane/hexane and passed through 4 in. of grade I acidic alumina. The alumina was washed with an additional 20 mL of 1:1 dichloromethane/hexane; the fractions were combined and taken to dryness by rotary evaporation. The resulting red solid was chromatographed on 40 g of silica gel (21 cm by 3 cm). Elution with 1:1 chloroform/hexane gave, in order $Mn_2(CO)_9(CN-p-tolyl)$ (0.021 g, 12%), $Mn_2(CO)_8(p-tolyl)_2$ (0.019 g, 9.1%), **5b** (0.073 g, 28%), **5d** (0.155 g, 28.8%), and **5c** (0.057 g, 19.9%). Total product yield: 97.7%. High-resolution mass spectrum: m/e (relative intensity) 724 (M^+ , 1), 668 (9), 640 (21), 556 (79), 501 (43), 446 (100), 238 (28), 208 (94), 121 (27).**

Preparation of Tetracarbonyl[1,2-bis(*p*-tolylimino)-3-(*p*-chlorophenyl)propyl]manganese (12a**). A toluene (20 mL) solution of (*p*-chlorobenzyl)pentacarbonylmanganese (1.40 g, 4.37 mmol), *p*-tolyl isocyanide (0.974 g, 1.00 mL, 8.31 mmol), and anhydrous PdO (0.023 g, 0.19 mmol) was stirred under nitrogen for 18 h at room temperature. After the solvent was reduced at reduced pressure, the remaining residue was taken up in a minimum amount of chloroform and eluted through a silica gel (200 g) column (33 cm by 4 cm). Elution with 1:9 ethyl acetate/hexane removed, in order, small amounts of $Mn_2(CO)_{10}$, unreacted $p-C_6H_4CH_2Mn(CO)_5$, an unidentified red oil (0.023 g), an unidentified yellow oil (0.060 g), and **12a** (1.226 g, 53.3%). Elution with 1:4 ethyl acetate/hexane removed an unidentified colorless organic solid (0.200 g). **12a**: low-resolution mass spectrum, m/e (relative intensity) 526 (M^+ , 2), 414 (20), 359 (16), 297 (33), 242**

(19), 180 (50), 125 (70), 92 (38), 55 (100). Anal. Calcd for $C_{27}H_{20}ClMnN_2O_4$: C, 61.65; H, 3.83; N, 5.33. Found: C, 61.55; H, 3.83; N, 5.32.

Preparation of Tetracarbonyl[1,2-bis(*p*-tolylimino)-3-(*p*-methoxyphenyl)propyl]manganese (12b**). The procedure was the same as that for **12a** except that reflux time was 20 min. After the solvent was removed at reduced pressure, the remaining residue was taken up in a minimum amount of chloroform and eluted through a silica gel (200 g) column (33 cm by 4 cm). Elution with 3:17 ethyl acetate/hexane removed **12b** as a red band. Crystals suitable for X-ray analysis were grown from slow evaporation of a dichloromethane/hexane solution at 0 °C. (0.200 g, 18.3%). High-resolution mass spectrum, m/e (relative intensity) 522 (M^+ , not observed), 410 (22), 356 (40), 239 (64), 292 (23), 176 (15), 121 (32), 117 (100), 91 (32), 55 (10). Anal. Calcd for $C_{28}H_{23}MnN_2O_5$: C, 64.37; H, 4.44; N, 5.36. Found: C, 64.38; H, 4.47; N, 5.22.**

Preparation of *fac*-Tricarbonyl[1,2-bis(*p*-tolylimino)-3-(*p*-chlorophenyl)propyl](triphenylphosphine)manganese (13a**). Triphenylphosphine (0.160 g, 0.611 mmol), **12a** (0.250 g, 0.475 mmol), and trimethylamine *N*-oxide dihydrate (0.060 g, 0.540 mmol) were stirred under nitrogen in dichloromethane (20 mL) for 5 h. The solvent was removed and the resulting red oil chromatographed on grade I acidic alumina. Elution with 1:1 dichloromethane/hexane resulted in separation of two red bands. After removal of the solvent, the first was determined to be unreacted **12a** and the second **13a**: mp 148–149 °C; yield 0.217 g (60.0%). Anal. Calcd for $C_{44}H_{35}ClMnN_2O_3P$: C, 69.43; H, 4.64; N, 3.68. Found: C, 69.48; H, 4.51; N, 3.51.**

Trapping Experiments. (i) **4c** (0.500 g, 1.14 mmol), triphenylphosphine (0.300 g, 1.14 mmol), and THF (20 mL) were refluxed under nitrogen for 2 h. The solvent was removed at reduced pressure, and the resulting red residue was chromatographed on grade II neutral alumina (12 cm by 2.5 cm). Elution with 100 mL of 1:3 diethyl ether/pentane removed unreacted triphenylphosphine. Elution with diethyl ether (160 mL) removed a red solution. The ether was removed by rotary evaporation, and the resulting red residue was chromatographed on silica gel (25 cm by 2.5 cm). Elution with 3:17 ethyl acetate/hexane removed an unidentified red band (0.008 g), an unidentified orange band (0.008 g), an unidentified yellow band (0.056 g), and a red band, identified spectroscopically as **13b** (28.7% yield, 0.125 g).

(ii) **4a** (0.250 g, 0.571 mmol), triphenylphosphine (0.150 g, 0.572 mmol), and THF (10 mL) were refluxed under argon for 1 h, during which time the color of the reaction changed from pale yellow to orange. Analysis by thin-layer chromatography (3:17 ethyl acetate/hexane) revealed only triphenylphosphine and one yellow product. The solvent was removed at reduced pressure. Analysis of the resulting yellow solid by IR ($CHCl_3$) gave the following bands and assignments: $C=O$ 2000 (s), 1920 (s), 1890 (s) cm^{-1} ; $C=N$ 1676 (m) cm^{-1} . Attempts at isolation of this one product by column chromatography on silica gel or alumina lead to decomposition of the one manganese complex and formation of four other products, as determined by thin-layer chromatography.

(iii) **4a** (0.250 g, 0.571 mmol), *p*-tolyl isocyanide (0.069 mL, 0.067 g, 0.57 mmol) and THF (20 mL) were refluxed under argon for 2 h, during which time the color of the solution changed from pale yellow to dark red. The solvent was removed at reduced pressure and the resulting residue taken up in hexane and loaded onto a silica gel column (10 cm by 2.5 cm). Elution with hexane removed small amounts of $Mn_2(CO)_9(CN-p-tolyl)$ and $Mn_2(CO)_8(CN-p-tolyl)_2$. Elution with 1:4 diethyl ether/hexane removed a red band, identified spectroscopically as the bis(imino) complex **12a** (0.184 g, 61.2%).

(iv) (*p*-Chlorobenzyl)pentacarbonylmanganese (0.500 g, 1.56 mmol), *p*-tolyl isocyanide (0.200 mL, 0.195 g, 1.66 mmol), and THF (20 mL) were stirred under argon for 2 h at ambient temperature. The temperature of the reaction was slowly raised to 73 °C over a 2-h period and maintained between 70 and 75 °C for an additional hour. During the heating the color of the reaction mixture changed from pale orange to dark red. The reaction mixture was cooled to room temperature and the solvent removed at reduced pressure. The resulting residue was taken up in hexane and loaded onto a silica gel column (10 cm by 2.5 cm). Elution with hexane gave one yellow band that was identified as unreacted *p*-

Table V. Crystal and Diffraction Data for 5a and 5e

	5a	5e
Crystal Data		
formula	C ₃₆ H ₂₈ Mn ₂ Cl ₂ N ₂ O ₆	C ₃₂ H ₂₀ Mn ₂ N ₂ O ₆
color habit	orange-red octahedra	orange prisms
size, mm	0.40 × 0.30 × 0.25	0.12 × 0.25 × 0.38
space group	P2 ₁ 2 ₁ 2 ₁ (No. 19)	P2 ₁ /c (No. 14)
unit cell dimens		
a, Å	10.540 (2)	12.457 (2)
b, Å	12.775 (2)	11.204 (2)
c, Å	25.510 (2)	22.454 (4)
β, deg		108.46 (1)
V, Å ³	3435.0 (4)	2972.5 (8)
Z	4	4
mol wt	763.13	638.39
d(calcd), g cm ⁻³	1.48	1.43
d(measd), g cm ⁻³	1.48 (1)	
F(000), e	1552	1296
Data Collection		
diffractometer	Enraf-Nonius CAD-4	Nicolet R3m/V
radiatn	Mo (0.71073)	Mo (0.71073)
monochromator	highly ordered graphite crystal	highly ordered graphite crystal
temp, K	298	294
hkl limits	+14, +17, +34	±15, +14, +25
2θ range, deg	3–60	3–45
scan type	2θ/θ	2θ/θ
scan speed, deg/min	variable	variable; 2.0–29.3
scan range	Δ(2θ) = 0.70 + 0.35 tan θ	0.7° below Kα ₁ to 0.7° above Kα ₂
bkgd measurement	first and last 1/6 of scan	stationary crystal and counter at beginning and end of scan; total background time to scan time ratio of 0.5
std reflctns	3 measured every 2 h	3 measured every 37
reflctns collected	6565 total (5545 independent)	4683 total (3899 independent)
reflctns obsd	2966; F ² > 3σ(F ²)	2321; F > 6σ(F)
absorptn coeff, cm ⁻¹	9.1	8.31
no. of psi scan reflctns		5
min/max transmissn	0.726/0.837	0.843/0.932
Refinement		
system used	block diagonal, least squares	Nicolet SHELXS/SHELXTL PLUS
solution	Patterson map	direct methods (TREF)
final residuals ^{a-c}	w = 0.053, wR = 0.052	w = 0.0352, wR = 0.0341
goodness-of-fit ^d	S = 1.38	S = 1.21
largest shift/esd	0.4	0.001
no. of variables	433	380
data-to-parameter ratio	6.7:1	6.1:1
largest different peak, e Å ⁻³	0.73	0.24

^aR = Σ(|F_o| - |F_c|) / Σ(|F_o|). ^bwR = [(Σw|F_o| - |F_c||²) / Σw|F_o|²]^{1/2}. ^cw = [σ²(F) + gF²]⁻¹. ^dS = [(Σw|F_o| - |F_c||²) / (M - N)]^{1/2} where M is the number of observed reflections and N is the number of parameters refined.

ClC₆H₄CH₂Mn(CO)₅ (0.172 g, 34.4%). Elution with 1:4 diethyl ether/hexane removed a red band, identified spectroscopically as the bis(imino) complex 12a (0.149 g, 34.7%).

(v) A THF (20 mL) solution of 4a (0.500 g, 1.14 mmol) and galvinoxyl (0.481 g, 1.14 mmol) was refluxed under argon for 1 h, during which time the color of the solution changed from purple to red. The reaction mixture was cooled to room temperature and the solvent removed at reduced pressure. The resulting red solid was dissolved into a minimum amount of 1:3 chloroform/hexane and chromatographed on silica gel (25 cm by 4 cm). Elution with 1:3 chloroform/hexane removed, in order, small amounts of Mn₂(CO)₉(CN-*p*-tolyl) and Mn₂(CO)₈(CN-*p*-tolyl)₂, an unidentified orange solid, an unidentified red solid, and a yellow solid (0.145 g). Analysis (infrared and mass spectra) of these three products revealed that they did not contain any manganese carbonyl fragments.

Preparation of (1,2,3,4-Tetraphenyl-1,4-diazabuta-1,3-diene)hexacarbonyldimanganese (5e). A toluene (25 mL) solution of Mn₂(CO)₁₀ (0.453 g, 1.159 mmol) and C₆H₅C(Cl)=N(C₆H₅) (0.500 g, 2.38 mmol) was refluxed under argon for 17 h. After being cooled to room temperature, the solution was filtered through a plug of grade III neutral alumina and the solvent removed at reduced pressure. The resulting orange residue (0.450 g) was dissolved in a minimal volume of chloroform and loaded onto a silica gel column. Elution with chloroform removed in order unreacted Mn₂(CO)₁₀ and 5e. Three other orange bands could not be separated well enough for characterization. Complex 5e

was further purified by recrystallization from slow evaporation of dichloromethane/hexane at 0 °C to give red crystals suitable for X-ray analysis (yield 0.014 g, 2%); mp 192–195 °C. High-resolution mass spectrum: *m/e* (relative intensity) 638 (M⁺, 1), 582 (11), 554 (33), 526 (11), 470 (83), 415 (100), 360 (33), 312 (36), 235 (34), 180 (100).

X-ray Data Collection and Structure Solution for 5a. Precession photographs of the (*h*0*l*), (*h**k*0), and (0*k**l*) nets showed systematic absences (*h*00), (0*k*0), and (00*l*) for *h*, *k*, and *l* odd, respectively, implying space group P2₁2₁2₁ (No. 19) with Z = 4. Cell dimensions were determined by a least-squares fit of the observed 2θ angles for 24 reflections centered automatically.

The orange-red air-stable crystal of octahedral habit was glued to a glass fiber and oriented along *c**. Three-dimensional intensity data were measured at 298 K on a computer-controlled Enraf-Nonius CAD-4 diffractometer at Brookhaven National Laboratory using Mo Kα radiation monochromatized by reflection from a highly ordered graphite monochromator. Data were collected by θ–2θ scans to 2θ = 60°. Absorption corrections were applied to 6986 observations using BNLABS, a local version of ORABS.⁷⁹ The minimum and maximum corrections to F_o² were 0.7259 and 0.8369, respectively, with an agreement between symmetry-equivalent intensities of R = 0.063. These intensities were averaged to give 2966 independent structure amplitudes with F_o²

(79) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* 1957, 10, 180.

$> 3\sigma_{\text{count}}(F_o^2)$, where $\sigma(F_o^2)$ is based on Poisson counting statistics.

The intensities of three monitor reflections were measured periodically; no crystal decomposition was discerned. Background was measured on one-sixth of the total scan width, and normal scans that did not result in sufficiently high precision or net intensity measurements were repeated at slower scan speed. The takeoff angle was 6.2° , and the diffracted beam was automatically corrected for coincidence losses.

Structure factors were derived in the usual way, and an unsharpened, three-dimensional Patterson function was interpreted to give the coordinates of the two manganese and two chlorine atoms. The remaining non-hydrogen atoms were readily located by a combination of differential synthesis refinement⁸⁰ and Fourier methods. Eighteen of the 26 hydrogen atom positions were also located by difference Fourier synthesis. The remaining hydrogens were placed in idealized positions. All hydrogen atoms were given isotropic thermal parameters of 5.5 \AA^2 and were added in a fixed manner to subsequent structure factor calculations. Atomic scattering factors were taken from a standard source,⁸¹ while that for hydrogen was the best spherically averaged value of Stewart et al.⁸² The anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ were taken from the calculations of Cromer⁸³ and were included in F_c ⁸⁴ for the manganese and chlorine atoms. In the final least-squares calculations the function minimized was $\sum \omega \Delta^2$, where $\Delta = |F_o| - |F_c|$ with weights $\omega = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma^2_{\text{count}}(I) + (0.03F^2)^2$. Because of the large number of variables (433) involved when allowance for anisotropic thermal vibration of the non-hydrogen atom was made, each complete cycle of refinement consisted of two parts, each of which included refinement of the manganese and chlorine atoms and half of the remaining non-hydrogen atoms. The light atoms to be refined were chosen on a rotating basis. Three such complete cycles of refinement gave final values for R and of wR of 0.053 and 0.052, respectively, and the error in an observation of unit weight was 1.38. The maximum density in a final difference electron density synthesis was 0.73 e \AA^{-3} .

X-ray Data Collection and Structure Solution for 5e.

From a sample consisting of air-stable orange prisms, a suitable crystal with dimensions of $0.12 \times 0.25 \times 0.38 \text{ mm}$ was isolated, mounted on the tip of a glass fiber with epoxy cement, and

transferred to a Nicolet R3m/V four-circle diffractometer for characterization and data collection (ambient temperature, 294 K).

Unit cell parameters were determined from the angular settings of 15 well centered reflections ($15^\circ < 2\theta < 23^\circ$): $a = 12.457 (2) \text{ \AA}$, $b = 11.204 (2) \text{ \AA}$, $c = 22.454 (4) \text{ \AA}$, $\beta = 108.46 (1)^\circ$, and $V = 2972.5 (8) \text{ \AA}^3$. Axial photographs and a limited search through an octant of reciprocal space revealed systematic absences and symmetry consistent with the monoclinic space group $P2_1/c$ (No. 14).

The $2\theta/\theta$ scans were collected with variable scan speeds ranging from 2.0 to 29.3 deg/min. A quarter-sphere of data ($+h, +k, +l$) was collected with 2θ restricted to $3\text{--}45^\circ$. A total of 4683 reflections were measured and corrected for Lorentz-polarization and absorption effects (empirical absorptions correction based on psi scan data for five azimuthal reflections). The minimum and maximum drift corrections were 0.9702 and 1.0083, respectively, and the minimum and maximum transmission factors were 0.843 and 0.932, respectively. Data averaging yielded 3899 unique reflections of which 2321 had $F > 6\sigma(F)$ with $R(\text{int}) = 0.0199$.

The structure was successfully solved and refined by full-matrix least squares. A combination of direct methods (SHELXS with the TREF option) and Fourier techniques was used to locate the positions of the non-hydrogen atoms. Isotropic refinement of this non-hydrogen model with unit weights converged to $R = 0.0719$ with uncorrected data. Anisotropic refinement of this model lowered the residuals to $R = 0.0483$. Subsequent cycles of least squares included absorption-corrected data, a weighting scheme based on $\sigma(F)$, anisotropic temperature parameters for Mn, C, N, and O atoms, and hydrogens riding on their respective carbon atoms with $\text{C-H} = 0.96 \text{ \AA}$. A single common hydrogen isotropic temperature parameter $U(\text{H})$ for the aromatic hydrogens was also included and allowed to vary. The structure refined smoothly to the final residuals $R = 0.0352$ and $wR = 0.0341$ with the goodness-of-fit being 1.21. The refined hydrogen isotropic parameter was $U(\text{H}) = 0.073 (4)$, the largest |shift/esd| in the final cycle was 0.001, and the largest peak on the final difference map was 0.24 e/\AA^3 .

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates for **5a** and **5e** (15 pages); listings of observed and calculated structure factors for **5a** and **5e** (20 pages). Ordering information is given on any current masthead page.

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