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Reactions of an imidoyl halide with manganese carbonyl complexes

Philip L. Motz, John J. Alexander

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172 (U.S.A.)

and Charles F. Campana

Siemens Analytical X-Ray Instruments, Inc. Madison, Wisconsin 53711-0508 (U.S.A.)

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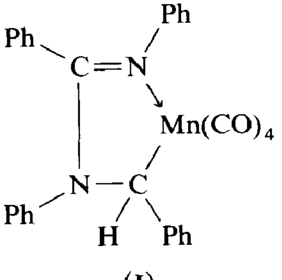
Abstract

PhC(=NPh)Cl has been allowed to react with both $[Mn(CO)_5]^-$ and $Mn_2(CO)_{10}$. The carbonylate anion gave $(CO)_4M\overline{n[C(H)(C_6H_5)N(C_6H_5)C(C_6H_5)=N}(C_6H_5)]$ which results from head-to-tail coupling of two imidoyl groups and reduction of the internal C=N bond. This compound has been characterized by X-ray crystallography. With $Mn_2(CO)_{10}$ the diazabutadiene complex $[(C_6H_5)N=C(C_6H_5)C(C_6H_5)=N(C_6H_5)]Mn_2(CO)_6$ was isolated.

Iminoacyl complexes of the transition metals have recently been an area of considerable research interest and the chemistry of η^2-iminoacyls has recently been reviewed [1]. Such complexes have been synthesized principally by insertion of isocyanides into metal-alkyl bonds [1] and by reaction of carbonylate anions with imidoyl halides [2–4]. We recently had occasion to attempt the preparation of iminoacylmanganese complexes in connection with our investigation [5] of iminoacyl coupling mediated by Mn complexes. We report herein the results of allowing PhC(=NPh)Cl to react with $[Mn(CO)_5]^-$ and with $Mn_2(CO)_{10}$.

We expected to obtain $(CO)_5MnC(=NPh)Ph$ upon treating PhC(=NPh)Cl with an equimolar amount of $Na[Mn(CO)_5]$ in THF at −78°C and allowing the mixture to warm to room temperature. Instead, I was isolated in 3.5% yield along with 2.4% dimanganese decacarbonyl.



(I)

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Table 1

Spectroscopic data for I and II

	IR (cm^{-1})	NMR(δ)
I	2035(s), 1988(s), 1973(s), 1941(s) (C≡O); 1541(w) (C=N) [a]	7.25–6.88 (m, 20H), C_6H_5; 5.24 (s, 1H) CH [c]
II	2060(s), 2021(s), 1980(s), 1951(m) (C≡O); 1520(m) (C=N) [b]	

[a] In hexane. [b] In $CHCl_3$. [c] In $CDCl_3$.

The IR spectrum of I (Table 1) in hexane shows four strong CO stretches at 2035, 1988, 1973 and 1941 cm^{-1}, a pattern typical of *cis*-disubstitution in an octahedral carbonyl complex. A band at 1541 cm^{-1} is in the region expected for C=N stretching. The ^{1}H NMR shows a signal at 5.24 ppm which was not present in the starting imidoyl chloride and integrated for one proton as well as a multiplet in the aromatic region which integrated for twenty protons.

An X-ray structure established the geometry of I, and an ORTEP drawing of the complex is shown in Fig. 1. Table 2 gives atomic coordinates for non-hydrogen atoms, and Table 3 shows pertinent bond distances and bond angles. The complex is viewed as arising from head-to-tail coupling of two imidoyl chloride molecules followed by addition of a H to C(5). The organic moiety chelates to the metal center through an alkyl carbon (C(5)) and through a donor–acceptor bond between Mn and N(8), forming a five-membered manganacyclic ring. This ring is not planar. The best least-squares plane through the four non-metal atoms lies 0.02–0.04 Å from these four atoms while the Mn lies 0.53 Å out of the plane. The plane defined by Mn, C(5) and N(6) misses including C(7) by 0.44 Å and N(8) by 0.64 Å.

The coordination around Mn is approximately octahedral, the major distortion resulting from the small bite of the chelating ligand; angle C(5)–Mn–N(8) 78.9(1)°

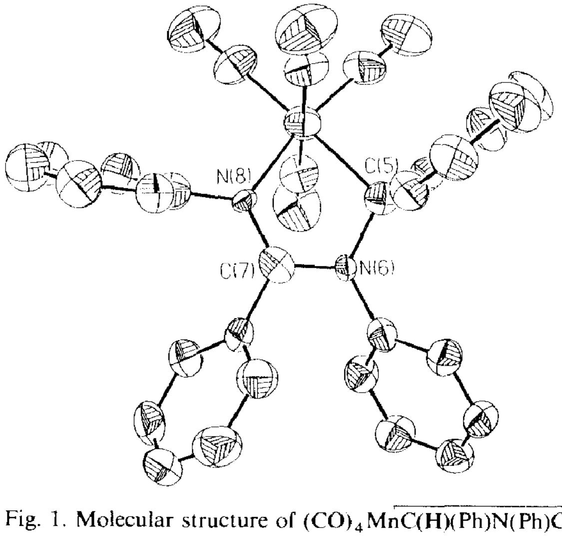


Fig. 1. Molecular structure of $(CO)_4\overline{MnC(H)(Ph)N(Ph)C=N}(Ph)$. (I)

Table 2

Atomic coordinates ($\times 10^4$) for I [a]

Atom	x	y	z
Mn	582(1)	1582(1)	2700(1)
C(1)	−96(4)	2421(3)	1472(3)
O(1)	−481(3)	2966(2)	713(2)
C(2)	1345(4)	769(3)	3961(3)
O(2)	1792(3)	218(2)	4696(2)
C(3)	−1006(4)	1618(3)	3185(3)
O(3)	−2021(3)	1671(3)	3495(2)
C(4)	132(4)	157(3)	1889(3)
O(4)	−212(3)	−741(2)	1394(2)
C(5)	1187(3)	3281(2)	3574(2)
C(5A)	1614(3)	3226(2)	4846(2)
C(5B)	2926(3)	3013(2)	5374(2)
C(5C)	3238(4)	2855(3)	6531(3)
C(5D)	2248(4)	2889(3)	7178(3)
C(5E)	949(4)	3125(3)	6680(3)
C(5F)	638(4)	3300(3)	5527(2)
N(6)	2297(3)	3750(2)	3032(2)
C(6A)	2480(3)	5020(2)	2992(2)
C(6B)	2278(3)	5542(3)	1968(2)
C(6C)	2430(4)	6764(3)	1940(3)
C(6D)	2762(3)	7463(3)	2936(3)
C(6E)	2958(3)	6954(3)	3965(3)
C(6F)	2820(3)	5729(2)	3995(2)
C(7)	2969(3)	2966(3)	2475(2)
C(7A)	4223(3)	3377(2)	2091(2)
C(7B)	4281(4)	3265(3)	938(3)
C(7C)	5439(4)	3645(3)	577(3)
C(7D)	6539(4)	4105(3)	1359(3)
C(7E)	6493(4)	4202(3)	2502(3)
C(7F)	5322(3)	3855(3)	2868(3)
N(8)	2462(3)	1869(2)	2297(2)
C(8A)	3293(3)	954(2)	1967(3)
C(8B)	2894(4)	289(3)	936(3)
C(8C)	3706(5)	−606(3)	642(3)
C(8D)	4885(4)	−828(3)	1360(3)
C(8E)	5264(4)	−186(3)	2376(4)
C(8F)	4473(3)	703(2)	2688(3)

[a] The numbering scheme for the complex is shown in Figure 1.

as opposed to the ideal 90° angle. Other in-plane angles are 85.6(1)° for C(5)–Mn–C(1) and 98.0(1)° for N(8)–Mn–C(4). All four carbonyl ligands are linear with the four Mn–C distances ranging from 1.798(5) to 1.864(4) Å (Mn–C_{avg} 1.828 Å). The four C–O distances span the range 1.137(4) to 1.150(5) Å with C–O_{avg} 1.144 Å.

The geometry about C(5) is approximately tetrahedral with Mn–C(5)–N(6) 105.0(2)°, Mn–C(5)–C(5A) 113.4(2)° and N(6)–C(5)–C(5A) 112.5(2)°. The C(5)–N(6) bond length of 1.487(4) Å is in agreement with the C–N single bond distance found in diethylamine [6]. The C(7)–N(8) bond length of 1.310(4) Å is significantly shorter than a C–N single bond and is formulated as a double bond.

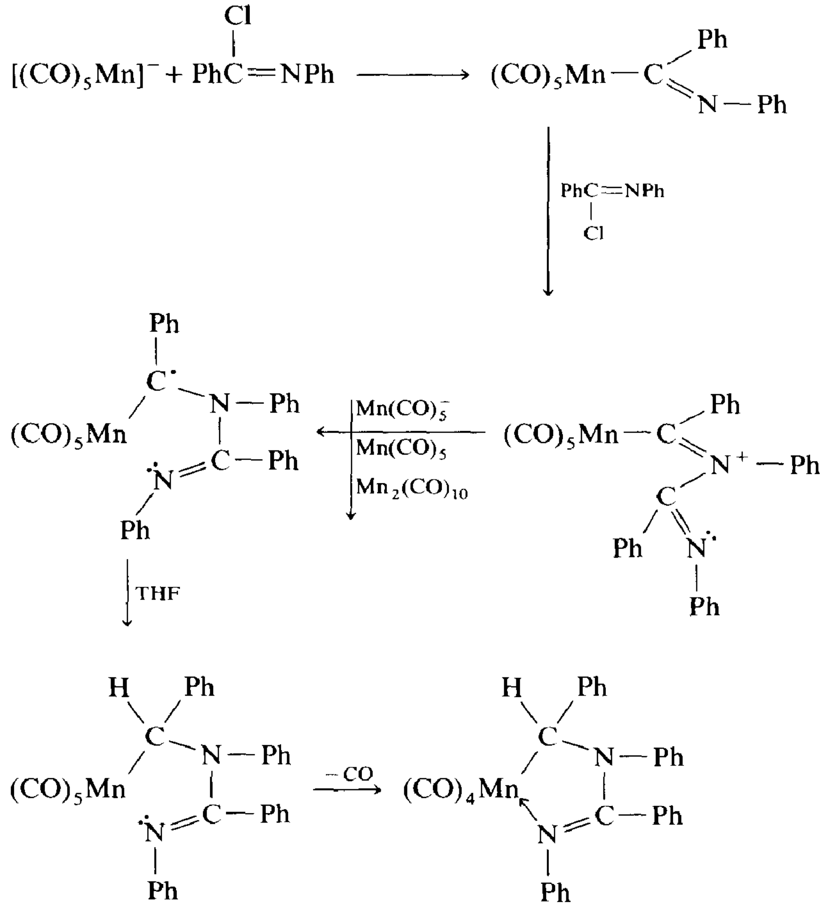
Table 3

Selected bond distances (Å) and bond angles (deg) and their estimated standard deviations for $(CO)_4\overline{Mn[C(H)C_6H_5)N(C_6H_5)C(C_6H_5)=N}\text{-}(C_6H_5)]$ (I)

Bond distances	
Mn–C(1)	1.828(3)
Mn–C(2)	1.864(4)
Mn–C(3)	1.798(5)
Mn–C(4)	1.822(3)
C(1)–O(1)	1.140(4)
C(2)–O(2)	1.137(4)
C(3)–O(3)	1.150(5)
C(4)–O(4)	1.149(4)
Mn–C(5)	2.136(3)
Mn–N(8)	2.053(3)
C(5)–N(6)	1.487(4)
N(6)–C(7)	1.349(4)
C(7)–N(8)	1.310(4)
C(5)–C(5a)	1.503(4)
N(6)–C(6a)	1.441(3)
C(7)–C(7a)	1.487(5)
N(8)–C(8a)	1.433(4)
Bond angles	
C(1)–Mn–C(2)	177.4(2)
C(1)–Mn–C(3)	91.0(2)
C(1)–Mn–C(4)	92.6(1)
C(2)–Mn–C(3)	90.9(2)
C(2)–Mn–C(4)	89.1(1)
C(3)–Mn–C(4)	93.1(2)
C(1)–Mn–C(5)	85.6(1)
C(1)–Mn–N(8)	87.4(1)
C(2)–Mn–C(5)	92.7(1)
C(2)–Mn–N(8)	90.5(1)
C(3)–Mn–C(5)	90.0(1)
C(3)–Mn–N(8)	78.9(1)
C(4)–Mn–C(5)	176.4(2)
C(4)–Mn–N(8)	98.0(1)
C(5)–Mn–N(8)	78.9(1)
Mn–C(5)–N(6)	105.0(2)
Mn–C(5)–C(5a)	113.4(2)
C(5)–N(6)–C(7)	118.1(2)
C(5)–N(6)–C(6a)	118.4(2)
C(6a)–N(6)–C(7)	123.0(3)
N(6)–C(7)–N(8)	117.3(3)
N(6)–C(7)–C(7a)	119.3(2)
C(7a)–C(7)–N(8)	123.4(3)
C(7)–N(8)–Mn	115.8(2)
C(7)–N(8)–C(8a)	118.9(3)
C(8a)–N(8)–Mn	125.0(2)

The N(6)–C(7) distance of 1.349(4) Å is comparable to that found in organic amides (1.35 Å) and is attributed to p_π–p_π N–C overlap [7].

A likely mechanism for the formation of I is depicted in Scheme 1. The first step involves the nucleophilic displacement of chloride by $[Mn(CO)_5]^-$ to give an



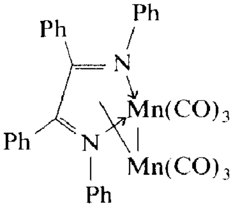
η^1-iminoacyl. The N atom lone pair on the iminoacyl then attacks the C on a second imidoyl chloride displacing chloride and giving a cationic complex. This step is analogous to the self-condensation reaction which is known [8] for C-alkyl imidoyl halides. Furthermore, Brunner, Kerkien and Wachter [9] have isolated the iron complex $[\eta^5\text{-}C_5H_5(CO)_2Fe\{C(C_6H_5)N(CH_3)C(C_6H_5){=}N(CH_3)\}]PF_6$ which has a similar unchelated bis(imino) ligand and Brunner and Wachter [3] have prepared as the analogous molybdenum complex $[\eta^5\text{-}C_5H_5(CO)_2Mo\{C(C_6H_5)N(CH_3)C\text{-}(C_6H_5){=}N(CH_3)\}]PF_6$ in which the imino N has displaced a CO on Mo, thus closing the chelate ring. Both of these complexes were obtained from treatment of $PhC({=}NMe)Cl$ with the appropriate carbonylate anion.

We propose that electron transfer from excess $[Mn(CO)_5]^-$ reduces the internal C–N double bond to yield an imino radical which presumably abstracts H from THF. Dimerization of the $[Mn(CO)_5]^{\cdot}$ radicals leads to the formation of $Mn_2(CO)_{10}$ which also was isolated. Finally, the N atom of the external imino group displaces a CO and coordinates to Mn. An alternative would be a source of hydride which adds to the cation.

In addition to the cationic product mentioned above, Brunner and Wachter [3] obtained a small yield of the Mo analogue of I along with the dimer $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$. Although, these workers consider that the analogue of I is the result of a H^- addition to the cationic complex, it seems likely that a radical mechanism such as that in Scheme 1 can account for their observations as well. None of the proposed ionic substance $[(CO)_5Mn\{C(C_6H_5)=N(C_6H_5)C(C_6H_5)=N(C_6H_5)]Cl$ was isolated from our reaction mixture.

An interesting comparison with these results is provided by the work of Alper [1] and of Adams [2] and their coworkers. Alper and Tanaka found that treatment of imidoyl chlorides with $[Co(CO)_3PPh_3]^-$ at 0–25° in THF afforded η^1-iminoacyls $R^1C(=NR^2)Co(CO)_3PPh_3$. On the other hand Adams, Chodosh and Golembeski isolated $Co_2(CO)_5(PMe_2Ph)\{(C_6H_5)CN(C_6H_5)\}_2$ by allowing PhC(=NPh)Cl to react with $[Co(CO)_4]^-$ for two days in the presence of the phosphine in an unspecified solvent. This dinuclear product was proposed to arise from attack of excess $[Co(CO)_4]^-$ on the cationic species $[(CO)_4CoCPh(=NPh)CPh(=NPh)]^+$. Even though $[Mn(CO)_5]^-$ is about 200 times more nucleophilic toward CH_3I than $[Co(CO)_4]^-$ [10], we obtained no evidence of a dinuclear Mn product.

In another attempt to prepare $(CO)_5MnC(=NPh)Ph$ we refluxed PhC(=NPh)Cl and $Mn_2(CO)_{10}$ in a 2/1 molar ratio in toluene for 17 h. The only product isolated from this reaction was II in 2% yield. The X-ray crystal structure of II has been reported elsewhere [5]. One can only speculate about the route which transforms the imidoyl chloride into a coordinated diazabutadiene. However, we have argued [5]



(II)

that η^1-PhC(=NPh)Mn(CO)$_5$ and/or η^2-PhC(=NPh)Mn(CO)$_4$ are likely intermediates in the process of conversion of $(CO)_4(RNC)MnC(O)CH_2C_6H_4p$-X to $[RN=C(CH_2C_6H_4p\text{-}X)C(CH_2C_6H_4p\text{-}X)=NR]Mn_2(CO)_6$, and either or both of these iminoacyl complexes may be produced in this reaction. Production of $[Mn(CO)_5]^{\cdot}$ at the elevated temperature seems likely. This radical has been implicated in a variety of thermal and photochemical substitution reactions on $Mn_2(CO)_{10}$ [11]. The Mn radical could displace $Cl^{\cdot}$ from the imidoyl chloride giving η^1-PhC(=NPh)Mn(CO)$_5$ which could then form η^2-PhC(=NPh)Mn(CO)$_4$. The $Cl^{\cdot}$ could suffer a number of fates including chlorination of solvent, formation of $ClMn(CO)_5$ or formation of Cl_2. We saw no evidence of the production of $ClMn(CO)_5$, however.

Experimental

IR spectra were recorded with a Perkin–Elmer Model 599 spectrophotometer using 0.1 mm sodium chloride cells. Band positions were determined relative to the 1601 cm^{-1} peak of polystyrene. Proton NMR spectra were obtained on an IBM NR-80 instrument in the Fourier transform mode. Positive chemical shifts are given in ppm downfield from tetramethylsilane.

Preparative chromatographic separations were conducted with columns 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. High-resolution mass spectra were obtained on a Kratos MS801-DS55 spectrometer.

Dimanganese decacarbonyl was purchased from the Pressure Chemical Company. Tetrahydrofuran (THF) was dried by distillation from benzophenone ketyl. Toluene was dried with sodium ribbon. Reagent grade dichloromethane, chloroform and hexane were freshly distilled before use. PhC(=NPh)Cl was prepared by literature methods [12]. All other chemicals were reagent grade and were used as received.

Preparation of $(CO)_4\overline{Mn[C(H)(C_6H_5)N(C_6H_5)C(C_6H_5)=N}(C_6H_5)]$ *(I).* A THF (20 ml) solution of $C_6H_5(Cl)=N(C_6H_5)$ (5.467 g, 25.35 mmol) was treated with an equimolar THF (40 ml) solution of $Na[Mn(CO)_5]$ at −78° C. The reaction mixture was stirred under argon for 30 min, allowed to warm to room temperature, and stirred for an additional 30 min. The solvent was removed at reduced pressure and the resulting yellow residue was loaded onto a grade III acidic alumina column with the aid of a minimum amount of hexane. Elution with hexane removed, in order, $Mn_2(CO)_{10}$ (0.240 g, 0.615 mmole 2.4%) and I. Other yellow bands could not be eluted. Complex I was further purified by recrystallization from diethyl ether/hexane at −24° C to give yellow crystals suitable for X-ray analysis (yield: 0.234 g, 3.49%); m.p. 112–114° C.

High-resolution mass spectrum: m/e (relative intensity) 528 (M^+, not observed), 444 (17), 416 (85), 362 (22), 313 (25), 235 (11), 180 (100), 132(20), 77 (82), 55 (18).

Preparation of (1,2,3,4-tetraphenyldiazabutadiene)hexacarbonyldimanganese (II). A toluene (25 ml) solution of $Mn_2(CO)_{10}$ (0.453 g, 1.159 mmol) and $C_6H_5C(Cl)=N(C_6H_5)$ (0.500 g, 2.38 mmol) was refluxed under argon for 17 h. After cooling 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 minimum volume of chloroform and loaded onto a silica gel column. Elution with chloroform removed, in order, unreacted $Mn_2(CO)_{10}$ and II. Three other orange bands could not be separated well enough for characterization. Complex II 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%); m.p. 192–195° C.

Spectral data: 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).

Structure determination [13].* X-ray data for $(CO)_4\overline{Mn[C(H)(C_6H_5)N(C_6H_5)C(C_6H_5)=N}(C_6H_5)]$ were collected with a Nicolet P3/F diffractometer, equipped with a highly oriented graphite crystal, and molybdenum target tube (Mo-K_α, λ 0.71073 Å), at 20° C. Computer calculations were performed on an Eclipse S/140 system, located at the University of Wisconsin at Madison, Wisconsin. Table 4 gives information pertinent to the data collection and analysis.

A yellow prismatic crystal was isolated, mounted on the tip of a glass fiber, and optically centered on a Nicolet P3/F diffractometer. Least-squares analysis of 15 intense reflections measured at both their $+2\theta$ and -2θ values yielded the cell

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* Reference number with asterisk indicates a note in the list of references.

Table 4

Crystallographic data

Empirical formula	$MnC_{30}H_{21}N_2O_4$
Mol. wt. g/mol	528.45
Crystal size, mm	0.20 × 0.20 × 0.20
Cell constants a, Å	10.050(2)
b, Å	11.270(3)
c, Å	11.927(3)
α, deg	93.38(2)
β, deg	100.73(2)
γ, deg	92.11(2)
Cell volume, $Å^3$	1323.4(4)
Z	2
d(calc'd), g/cm^3	1.33
Abs. coeff, cm^{-1}	5.1
Data collection range	$1.7° \leq \theta \leq 27.5°$
Total reflections	3727
Reflections with $I > 3\sigma(I)$	2100
Total variables	334
$R = \Sigma \| F_o \| - \| F_c \|\| / \Sigma F_o \|$	0.0354
$R_w = [\Sigma w(\| F_o \| - \| F_c \|)^2 / \Sigma w(\| F_o \|^2]^{1/2}$	0.0271

constants. Axial photographs and a limited search through an octet of reciprocal space revealed symmetry consistent with the triclinic space group $P\bar{1}$ (No. 2) [14].

θ–2θ scans were collected with variable scan speeds ranging from 3.91 to 29.30 deg. $min.^{-1}$, depending on the intensity of the reflection. Intensities were measured for 3727 reflections of the type $+h$, + and $-k$, + and $-l$ in the region $3° < 2\theta < 45°$; maximum h, 11, extreme k, + and −13, extreme l, + and −13. From these, 2100 unique reflections ($I > 3\sigma(I)$) were obtained by averaging. Empirical absorption corrections, based on ψ-scan data for 5 azimuthal reflections, were applied. Three intense reflections were used as standards and measured after every 97 reflections to monitor crystal stability and long-term drift. The minimum and maximum drift corrections were 0.9909 and 1.0078, respectively, and the minimum and maximum transmission factors were 0.466 and 0.481.

The structure was successfully solved and refined by full-matrix least squares. A combination of direct methods (SHELXTL 5.1 with the SOLV 1.2 option) and Fourier techniques were used to locate the positions of the 37 non-hydrogen atoms. Isotropic refinement of this non-hydrogen model converged to $R = 0.071$. Hydrogen atoms were placed at 0.96 Å from their respective carbon atom and were assigned an isotropic thermal parameter of 0.0600. These values were held constant in subsequent refinement. Subsequent refinement included anisotropic temperature parameters for manganese, carbon, nitrogen, and oxygen. This (a total of 334 variables) led to a final convergence of $R = 0.0354$ and $R_w = 0.0271$ with the goodness-of-fit being 1.435. The largest shift/esd in the final cycle was 0.029, and the largest peak on the final difference map was 0.2 $e^-/Å^3$.

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