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Preliminary communication

SYNTHESIS AND X-RAY STRUCTURE OF (2,2,6,6-TETRAMETHYLPIPERIDINYL-1-OXO-*O*,*N*)TRICARBONYLMANGANESE(0); "SIDE-ON" COORDINATION OF THE NITROXYL RADICAL TO MANGANESE*

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Summary

The title compound was prepared by photolysis of $Mn_2(CO)_{10}$ and 2,2,6,6-tetramethylpiperidinyl-1-oxo (TMPO) in pentane. $(TMPO)Mn(CO)_3$, a 16 electron compound with coordination number 5, was characterized by a single X-ray diffraction study. It shows "side-on" bonding of the nitroxyl radical to the manganese atom, resulting a novel three-membered Mn—N—O metallacycle. The photolysis of $Re_2(CO)_{10}$ in presence of TMPO also yields the analogous $(TMPO)Re(CO)_3$.

There has been a lively interest during the past few years in the photoinduced homolytic fission of the metal—metal bonds in dinuclear metal carbonyls and in the radicals produced [1]. Radical scavenging by halogen compounds usually leads to formation of mononuclear metal carbonyl halides [2]. On the other hand manganese carbonyl radicals can be readily trapped to form spin adducts with nitroso compounds [3] or tetracyanoethylene [4]. High resolution ESR spectra of manganese carbonyl radical adducts to *o*-quinones and to α-diketones via chelation of the carbonyl oxygen of the organic compounds have also been well documented [5].

We wish to report the synthesis of $(TMPO)Mn(CO)_3$ a coordinatively unsaturated 16 electron compound prepared by a photochemical route. Combination of

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*Dedicated to Professor E.O. Fischer on the occasion of his 65th birthday.

photogenerated reactive $Mn(CO)_5$ radicals with the nitroxyl radical TMPO by loss of CO affords in good yield (>50%) the new pentacoordinated complex. $(TMPO)Mn(CO)_3$ has been characterized by elemental analysis, infrared and mass spectra. The infrared spectrum exhibits three active carbonyl stretching modes characteristic for a facial $Mn(CO)_3$ group (2031s, 1933s, 1915s cm^{-1} (n-pentane)). Nearly equal intensities of the IR peaks indicate 90° angles between the CO ligands. The molecular ion peak is absent, but all the expected fragment ions, ligands and manganese ions are observed in the mass spectra.

$(TMPO)Re(CO)_3$ is formed by analogous photolysis of $Re_2(CO)_{10}$ in the presence of TMPO (IR ν(CO): 1987s, 1959s, 1915s cm^{-1} (n-pentane)).

The crystal and molecular structures of $(TMPO)Mn(CO)_3$ have been determined by a single crystal X-ray analysis*. The monomeric molecules contain a pentacoordinated manganese atom bound to a facial CO group and a chelating *N*,*O*-bonded TMPO. Views of the molecular structure of the title compound are shown in Figs. 1 and 2. Bond distances and angles are tabulated in Table 1.

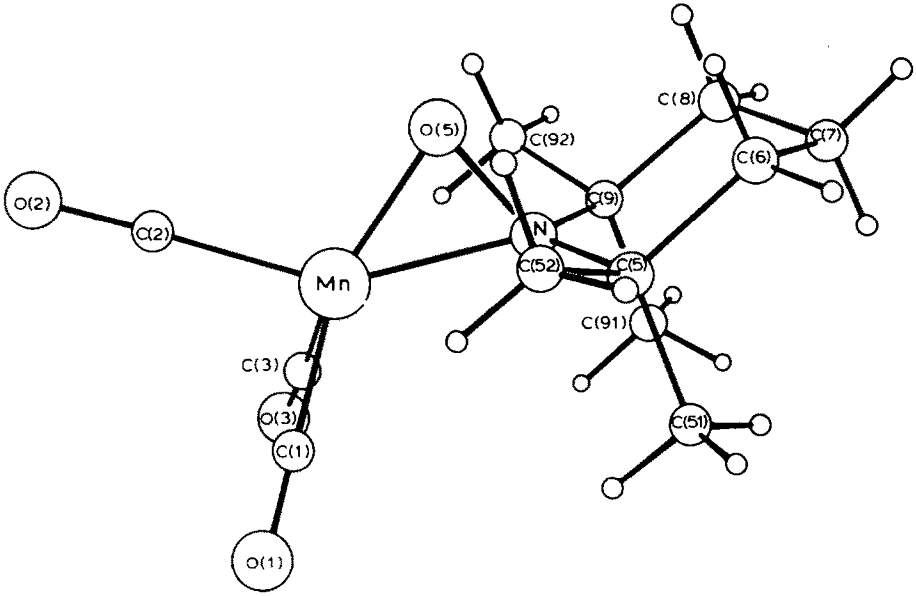

Fig. 1. Molecular structure of $(TMPO)Mn(CO)_3$.

The existence of three membered M—N—O metallacycles has only recently been documented, although a number of examples are now known. Doedens reported the structure of $PdCl(PPh_3)$(TMPO-*O*,*N*), a metal complex of a reduced nitroxyl radical [6]. The synthesis and structural studies of *O*,*N*-bonded

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* Crystal data: $C_{12}H_{18}MnNO_4$, M = 295.22, monoclinic, space group $P2_1/c$, a 6.285(2), b 14.806(7), c 14.840(6) Å, β 90.029(31)°, U 1381 Å^3, Z = 4, D_c 1.42 g cm^{-3}, μ(Mo-K_α) 10.1 cm^{-3}, $\Delta\omega$ 1.2°. Intensity data were recorded at −55°C on a Syntex P3 diffractometer (graphite monochromated Mo-K_α X-radiation, λ 0.71069 Å) using a ω-scan with $2.5 < \dot{\omega} < 29.3$ min^{-1} and $2 < 2\theta < 45°$. Of the 2093 reflections collected 1675 with $I > 2\sigma$ were used in the structure determination. The structure was solved by direct methods using the SHELXTL program system and refined by least-squares. The final refinement converged to R_1 = 0.032 and R_2 = 0.044. To our knowledge this is the first X-ray structural determination of a pentacoordinated 16 electron complex of manganese.

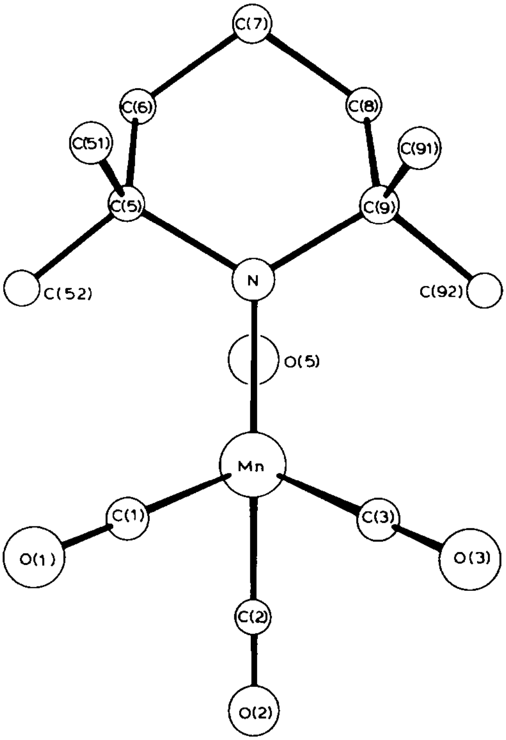

Fig. 2. Molecular structure of (TMPO)Mn(CO)$_3$, with hydrogen atoms omitted for clarity; view in the plane Mn—N—O(5)—C(7)—C(2)—O(2).

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°)

Distances		Angles	
Mn—N	1.981(3)	C(1)—Mn—N	112.2(2)
Mn—O(5)	1.839(3)	C(2)—Mn—N	148.3(2)
N—O(5)	1.413(3)	C(3)—Mn—N	112.0(1)
Mn—C(1)	1.786(4)	N—Mn—O(5)	43.2(1)
Mn—C(2)	1.815(4)	Mn—N—O(5)	63.0(1)
Mn—C(3)	1.775(4)	Mn—O(5)—N	73.7(1)
N—C(5)	1.535(4)	C(1)—Mn—O(5)	135.2(2)
N—C(9)	1.529(4)	C(2)—Mn—O(5)	105.1(1)
		C(3)—Mn—O(5)	135.5(2)

CO angles: C(1)—Mn—C(2): 90.9(2); C(2)—Mn—C(3): 91.0(2); C(1)—Mn—C(3): 84.3(2)

hydroxylamine and its *N*-substituted analogues have been described by Wieghardt [7].

Structural parameters of the Mn—N—O ring include Mn—N 1.981(3) Å, Mn—O(5) 1.839(3) Å and N—O(5) 1.413(3) Å. Of all documented M—N—O metallacycles, (TMPO)Mn(CO)$_3$ exhibits the shortest M—N and M—O bonds. The N—O bond distance of the coordinated TMPO in (TMPO)Mn(CO)$_3$ is 0.13 Å longer than the value found in free TMPO [8], consistent with the formula-

TABLE 2

POSITIONAL PARAMETERS OF THE ATOMS

Atom	*x/a*	*y/b*	*z/c*
Mn	0.58153(8)	0.36270(4)	0.35369(3)
C(1)	0.71977(66)	0.39311(28)	0.45442(26)
O(1)	0.80499(58)	0.41444(26)	0.51839(19)
C(2)	0.35755(64)	0.32152(29)	0.41895(27)
O(2)	0.22053(50)	0.29358(24)	0.46205(22)
C(3)	0.71538(60)	0.25789(26)	0.36657(26)
O(3)	0.79742(50)	0.18903(20)	0.37352(23)
O(5)	0.46222(35)	0.42505(17)	0.25912(16)
N	0.68497(42)	0.43072(18)	0.24745(18)
C(5)	0.76089(56)	0.52872(23)	0.25772(24)
C(51)	0.99569(60)	0.52931(27)	0.28311(26)
C(52)	0.63557(74)	0.57394(28)	0.33208(32)
C(6)	0.71874(69)	0.58091(27)	0.17188(29)
C(7)	0.80680(76)	0.53519(30)	0.08704(28)
C(8)	0.70855(74)	0.44185(30)	0.07902(26)
C(9)	0.75026(58)	0.38124(25)	0.16136(23)
C(91)	0.98228(62)	0.35127(30)	0.16912(30)
C(92)	0.61422(67)	0.29591(28)	0.15061(28)

tion as monoanion ($TMPO^-$). The coplanarity of the Mn—N—O ring system and the Mn—C(2)—O(2) group is noteworthy (see Fig. 2).

Three membered metallacycles of the sort found here are strained and potentially active moieties. Photoinduced reactions with other metal carbonyls as well as studies concerning chemical reactivity and cyclic voltammetry are under investigations.

Experimental

A solution of 390 mg (1.0 mmol) $Mn_2(CO)_{10}$ and 468 mg (3.0 mmol) 2,2,6,6-tetramethylpiperidinyl-1-oxo in n-pentane (20 ml) was irradiated for 30 minutes at 0°C. During photoreaction the initially yellow solution turned deep red. Vacuum sublimation (10^{-2} mmHg, 40°C) gave unreacted TMPO, then sublimation of the residue at 10^{-2} mmHg at 50°C for 2—3 days gave suitable single crystals of the required complex. The elemental analyses (C, H, N) agreed with the calculated values. All manipulations were carried out under dry argon. Solvents were distilled from sodium wire under N_2. Ultraviolet irradiations were performed with a high pressure mercury lamp (Hanau 150W) in a Schlenk tube equipped with a pressure valve.

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