Isocyanide Insertion Reactions. The Reaction of Mn(CO)₄CNCH₃ Anion with Iodomethane and the Crystal and Molecular Structure of (CH₃)N=C(CH₃)(CH₃)C=N(CH₃)Mn(CO)₃Mn(CO)₃

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Abstract: The compound (CH₃)N=C(CH₃)(CH₃)C=N(CH₃)Mn(CO)₃Mn(CO)₃ (I) was obtained from the reaction of Mn(CO)₄(CNCH₃)⁻ with CH₃I. The product was analyzed crystallographically. Crystal data: space group $P\bar{1}$, a = 7.352 (2) Å, b = 8.863 (2) Å, c = 12.324 (6) Å, α = 83.44 (4)°, β = 85.66 (3)°, γ = 72.45 (2)°, Z = 2, V = 760.0 (6) Å³, ρ_{calcd} = 1.70 g/cm³. The molecule contains a five-membered metallacyclic ring consisting of one manganese atom and a tetramethyl-α-diimine ligand. The latter is bonded to the manganese atom via the nitrogen atoms. The five-membered ring is bonded via the two imine π bonds and the manganese atom to a manganese tricarbonyl group. The Mn–Mn bonding distance is 2.615 (1) Å. The molecule is formally isoelectronic and isostructural to the RC=C(R)(R)C=C(R)Fe(CO)₃Fe(CO)₃ molecules which have been widely discussed in the development of the theories of semibridging carbonyl ligands. The relationship of I to these molecules is discussed.

Introduction

In the past we have reported the synthesis and reactivity of organometallic anions containing isocyanide ligands.[1-5] These anions readily engage in halide displacement reactions to form neutral products containing isocyanide ligands, eq 1.[1-3]

$$ML(CO)_x(CNR)_y^- + R'X \rightarrow ML(CO)_x(CNR)_yR' \quad (1)$$
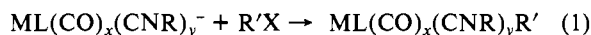
However, when R′ is a simple alkyl group, the reactions are complicated by isocyanide insertion processes.[4,5] We have recently investigated the reaction of Mn(CO)₄(CNCH₃)⁻ with CH₃I and discovered the completely unexpected product (CH₃)N=C(CH₃)(CH₃)C=N(CH₃)Mn(CO)₃Mn(CO)₃ (I). This compound was analyzed by X-ray crystallographic methods and was found to contain the structure I. I is formally isoelectronic and iso-

I   II
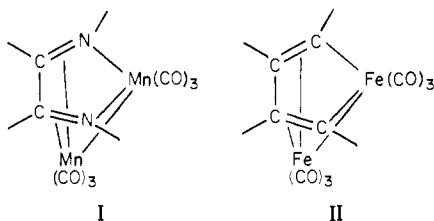
structural to the iron compounds II[6-8] which have attracted considerable attention because they contain a semibridging carbonyl group.[9,10] Here we report the details of the synthesis and structure of I and discuss it in relation to the molecules II.

Experimental Section

Reactions were performed in an inert atmosphere by using solvents (THF and hexane) dried by refluxing over sodium benzophenone and

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Table I. Experimental Data for X-Ray Diffraction Study of (CH₃)N=C(CH₃)(CH₃)C=N(CH₃)Mn(CO)₃Mn(CO)₃ (I)

(A) Crystal Parameters at 20 °C	
space group: P$\bar{1}$, No. 2 [C_i]	
a = 7.352 (2) Å	V = 760.0 (6) Å³
b = 8.863 (2) Å	Z = 2
c = 12.324 (6) Å	mol wt = 390.1
α = 83.44 (4)°	ρ_{calcd} = 1.70 g/cm³
β = 85.66 (3)°	
γ = 72.45 (2)°	

(B) Measurement of Intensity Data
radiation: λ(Mo Kα) = 0.710 73 Å
monochromator: graphite
takeoff angle: 2.5°
detector aperture: horizontal, A + B tan θ, A = 3.0, B = 1.0 mm; vertical, 4.0 mm
crystal-detector distance: 330 mm
reflctns measd: +h, ±k, ±l
data range: 2θ$_{min}$, 0.0°; 2θ$_{max}$, 50.0°
scan type: moving crystal-stationary counter
scan speed: variable θ$_{max}$ = 10.0°/min, θ$_{min}$ = 1.33°/min
θ scan width: 0.80 + 0.347 tan θ° on each side of calcd position
bkgd: ¹/₄ additional scan at each end of scan
std reflctns: 3 measd after approx each 90 data reflctns showed only random fluctuation of ±3%
no. reflctns measd: 2649
data used (F^2 > 3.0σ(F^2)): 2242 reflctns
absorptn coeff μ (cm⁻¹): 17.7 (no correctn applied)

distilled just prior to use. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. ¹H NMR spectra were recorded on a Bruker HX-270 operating in FT mode. Mn(CO)₄(CNCH₃)⁻ was prepared as previously reported.[3] Reagent grade CH₃I (Eastman) was used without further purification. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of (CH₃)N=C(CH₃)(CH₃)C=N(CH₃)Mn(CO)₃Mn(CO)₃ (I). A 0.305-g (1.06-mmol) sample of Mn(CO)₄(CNCH₃)Br was reduced with Na(Hg) at 0 °C in THF solvent.[3] The solution of Mn(CO)₄(CNCH₃)⁻ was decanted from the Na(Hg) and filtered. At −78 °C, 0.079 mL (1.27 mmol) of CH₃I was added via syringe. When being stirred, the reaction solution was allowed to warm slowly to about 0 °C, stirred at 0 °C for 30 min, then warmed to room temperature, and stirred an additional 30 min. During this time the reaction solution changed from yellow to orange. The solvent was removed in vacuo. The residue

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Table II. Final Fractional Atomic Coordinates for $(CH_3)N=C(CH_3)(CH_3)C=N(CH_3)Mn(CO)_3Mn(CO)_3$ (I)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Mn(1)	0.21735 (6)	0.25569 (5)	0.24908 (4)	C(11)	0.4725 (4)	0.2609 (3)	0.1554 (3)
Mn(2)	0.23984 (6)	0.54350 (5)	0.25470 (4)	C(12)	0.4322 (5)	0.3188 (4)	0.4492 (3)
O(1)	0.0950 (4)	0.0732 (3)	0.0977 (2)	C(13)	0.6705 (5)	0.0856 (4)	0.3117 (3)
O(2)	0.1982 (4)	−0.0027 (3)	0.4197 (2)	C(14)	0.5790 (5)	0.1588 (4)	0.0672 (3)
O(3)	−0.1858 (4)	0.4361 (4)	0.2967 (3)	C(15)	0.2718 (5)	0.4457 (4)	0.0190 (3)
O(4)	0.4763 (4)	0.7611 (3)	0.2319 (3)	H(121)	0.443 (5)	0.203 (4)	0.479 (3)
O(5)	0.0367 (5)	0.6879 (4)	0.4515 (2)	H(122)	0.325 (6)	0.386 (5)	0.483 (3)
O(6)	−0.0783 (4)	0.7824 (3)	0.1410 (3)	H(123)	0.575 (6)	0.325 (5)	0.462 (4)
N(1)	0.4011 (3)	0.3444 (3)	0.3298 (2)	H(131)	0.779 (8)	0.100 (6)	0.339 (5)
N(2)	0.3297 (3)	0.4030 (3)	0.1340 (2)	H(132)	0.623 (7)	0.020 (5)	0.371 (4)
C(1)	0.1428 (5)	0.1471 (4)	0.1549 (3)	H(133)	0.707 (8)	−0.021 (6)	0.276 (5)
C(2)	0.2050 (5)	0.0995 (4)	0.3543 (3)	H(141)	0.476 (6)	0.147 (5)	0.009 (4)
C(3)	−0.0257 (5)	0.3722 (4)	0.2787 (3)	H(142)	0.628 (6)	0.040 (5)	0.088 (3)
C(4)	0.3842 (5)	0.6755 (4)	0.2412 (3)	H(143)	0.681 (7)	0.179 (6)	0.036 (4)
C(5)	0.1202 (5)	0.6288 (4)	0.3770 (3)	H(151)	0.257 (5)	0.340 (4)	−0.015 (3)
C(6)	0.0499 (5)	0.6889 (4)	0.1821 (3)	H(152)	0.394 (5)	0.462 (5)	−0.034 (3)
C(10)	0.5144 (4)	0.2276 (4)	0.2666 (3)	H(153)	0.165 (5)	0.528 (4)	0.016 (3)

Table III. Interatomic Distances (Å) with esds for $(CH_3)N=C(CH_3)(CH_3)C=N(CH_3)Mn(CO)_3Mn(CO)_3$ (I)

Mn(1)-Mn(2)	2.615 (1)	N(2)-C(15)	1.485 (5)
Mn(1)-C(1)	1.801 (4)	C(1)-O(1)	1.154 (5)
Mn(1)-C(2)	1.804 (4)	C(2)-O(2)	1.152 (5)
Mn(1)-C(3)	1.808 (4)	C(3)-O(3)	1.159 (5)
Mn(1)-N(1)	2.111 (3)	C(4)-O(4)	1.151 (5)
Mn(1)-N(2)	2.108 (3)	C(5)-O(5)	1.152 (5)
Mn(1)-C(10)	2.147 (4)	C(6)-O(6)	1.156 (5)
Mn(1)-C(11)	2.137 (4)	C(12)-H(121)	1.03 (5)
Mn(2)···C(3)	2.792 (4)	C(12)-H(122)	0.93 (6)
Mn(2)-C(4)	1.789 (4)	C(12)-H(123)	1.09 (6)
Mn(2)-C(5)	1.810 (4)	C(13)-H(131)	0.94 (8)
Mn(2)-C(6)	1.804 (4)	C(13)-H(132)	0.99 (7)
Mn(2)-N(1)	1.977 (3)	C(13)-H(133)	1.04 (7)
Mn(2)-N(2)	1.995 (3)	C(14)-H(141)	1.11 (6)
N(1)-C(10)	1.392 (5)	C(14)-H(142)	1.02 (6)
N(1)-C(12)	1.488 (5)	C(14)-H(143)	0.87 (7)
C(10)-C(13)	1.509 (5)	C(15)-H(151)	1.11 (5)
C(10)-C(11)	1.407 (5)	C(15)-H(152)	1.11 (5)
C(11)-C(14)	1.510 (5)	C(15)-H(153)	0.90 (5)
N(2)-C(11)	1.388 (4)	C-H$_{av}$	1.01 (6)

Figure 1. A perspective ORTEP diagram of $(CH_3)N=C(CH_3)(CH_3)C=N(CH_3)Mn(CO)_3Mn(CO)_3$ (I) showing 50% probability ellipsoids.

was taken up in benzene and chromatographed over $Al_2O_3 \cdot 3\% \ H_2O$ with hexane/benzene (1/1) solvent. An orange band was eluted and collected. The solvent was removed, and the residue was recrystallized from hexane solvent at −20 °C yielding 0.041 g (7% yield) of I as orange crystals, mp 167–168 °C. IR (hexanes) $\nu(CO)$: 2035 (m), 1998 (s), 1940 (s), 1935 (s), 1926 (m), 1917 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.42 (1), 3.02 (1). Other bands were subsequently eluted from the chromatography column using C_6H_6/THF solvents. These compounds are currently undergoing analysis.

Crystallographic Analysis. Crystals of I suitable for diffraction measurements were obtained as described above. A thick platelet of approximate dimensions 0.20 × 0.40 × 0.35 mm bounded by the faces 010, 0$\bar{1}$0, 111, $\bar{1}\bar{1}\bar{1}$, 101, $\bar{1}0\bar{1}$, 10$\bar{1}$, and $\bar{1}$01 was sealed in a thin-walled glass capillary. All diffraction measurements were made on an Enraf-Nonius CAD-4 four-circle automatic diffractometer. Lattice constants were obtained by using the CAD-4 search, center, index and least-squares routines, and 25 randomly selected reflections. A triclinic lattice was selected. The space group, P$\bar{1}$, was assumed and confirmed by the successful solution and refinement of the structure. ω-scan peak widths at half-height were in the range 0.10–0.15°. The crystal was mounted such that normal to the 10$\bar{2}$ lattice planes was oriented 9.1° from the diffractometer ϕ axis. Crystal data and data collection parameters are listed in Table I. 2649 reflections were collected in the scan range $0 \le 2\theta \le 50°$ from which 2242 ($F^2 \ge 3.0\sigma(F^2)$) were used.

All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Neutral atom scattering factors were calculated by standard procedures.[11a] Anomalous dispersion
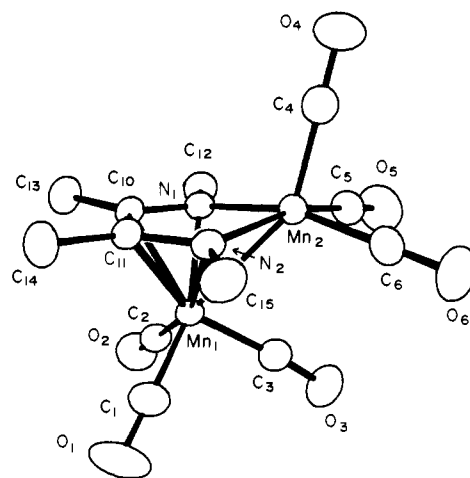
(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975, Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

corrections were made for all nonhydrogen atoms.[11b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}(|F_o| - |F_c|)^2$ employing unit weights for all reflections.

Structure Solution. The structure was solved by a combination of Patterson and difference Fourier techniques. A three-dimensional Patterson function provided the coordinates of the manganese atoms. All remaining atoms including hydrogens were located in subsequent difference Fourier syntheses. All nonhydrogen atoms were refined by using anisotropic thermal parameters. All hydrogen atoms were refined by using isotropic thermal parameters. The linear absorption coefficient for I is 17.7 cm^{-1}. No absorption correction was applied. The final values of the residuals were $R = 0.027$ and $R_w = 0.032$. The esd in an observation of unit weight was 0.76. The largest value of shift/error on the final cycle was 0.09 among the nonhydrogen atoms and 0.29 among the hydrogen atoms. The largest peaks in a final difference Fourier synthesis were 0.44, 0.43, and 0.35 e/Å^3 and were clustered about the manganese atoms. They are believed to be structurally insignificant. Final fractional atomic coordinates are listed in Table II. Final interatomic distances and angles with errors calculated from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV. Tables of final thermal parameters and structure factor amplitudes are available.[12]

Results and Discussion

The molecular structure of I is shown in Figure 1. The molecule contains a metallacyclic ring consisting of the atoms Mn(2)-N(1)-C(10)-C(11)-N(2). This ring could be viewed as consisting of an α-diimine ligand coordinated to a manganese tricarbonyl group through its nitrogen atoms. The ring is not

(12) See supplementary material.

Table IV.   Interatomic Angles (Deg) with Esds for (CH₃)N=C(CH₃)(CH₃)C=N(CH₃)Mn(CO)₃Mn(CO)₃ (I)

(a) Not Involving Hydrogen Atoms

Mn(2)-Mn(1)-C(1)	137.3 (1)	C(5)-Mn(2)-C(6)	85.8 (2)
Mn(2)-Mn(1)-C(2)	132.9 (1)	C(5)-Mn(2)-N(1)	96.4 (2)
Mn(2)-Mn(1)-C(3)	75.9 (1)	C(5)-Mn(2)-N(2)	163.0 (2)
Mn(2)-Mn(1)-N(1)	48.01 (8)	C(6)-Mn(2)-N(1)	163.4 (2)
Mn(2)-Mn(1)-C(10)	74.7 (1)	C(6)-Mn(2)-N(2)	96.3 (2)
Mn(2)-Mn(1)-C(11)	75.0 (1)	N(1)-Mn(2)-N(2)	76.9 (1)
Mn(2)-Mn(1)-N(2)	48.51 (8)	Mn(1)-N(1)-Mn(2)	79.5 (1)
C(1)-Mn(1)-C(2)	87.8 (2)	Mn(1)-N(1)-C(12)	125.6 (3)
C(1)-Mn(1)-C(3)	92.2 (2)	Mn(1)-N(1)-C(10)	72.3 (2)
C(1)-Mn(1)-N(1)	158.9 (2)	Mn(2)-N(1)-C(12)	124.3 (3)
C(1)-Mn(1)-C(10)	121.0 (2)	Mn(2)-N(1)-C(10)	118.6 (2)
C(1)-Mn(1)-C(11)	94.2 (2)	C(12)-N(1)-C(10)	116.4 (3)
C(1)-Mn(1)-N(2)	98.3 (2)	Mn(1)-C(10)-N(1)	69.5 (2)
C(2)-Mn(1)-C(3)	92.8 (2)	Mn(1)-C(10)-C(13)	130.2 (3)
C(2)-Mn(1)-N(1)	96.4 (2)	Mn(1)-C(10)-C(11)	70.4 (2)
C(2)-Mn(1)-C(10)	95.0 (2)	N(1)-C(10)-C(13)	123.7 (4)
C(2)-Mn(1)-C(11)	123.6 (2)	N(1)-C(10)-C(11)	112.3 (3)
C(2)-Mn(1)-N(2)	160.8 (2)	C(13)-C(10)-C(11)	123.9 (4)
C(3)-Mn(1)-N(1)	108.1 (2)	Mn(1)-C(11)-C(10)	71.2 (2)
C(3)-Mn(1)-C(10)	146.1 (2)	Mn(1)-C(11)-C(14)	129.9 (3)
C(3)-Mn(1)-C(11)	143.2 (2)	Mn(1)-C(11)-N(2)	69.8 (2)
C(3)-Mn(1)-N(2)	105.1 (2)	C(10)-C(11)-C(14)	129.9 (4)
N(1)-Mn(1)-C(10)	38.2 (1)	C(10)-C(11)-N(2)	112.7 (3)
N(1)-Mn(1)-C(11)	66.3 (1)	C(14)-C(11)-N(2)	123.3 (4)
N(1)-Mn(1)-N(2)	71.7 (1)	Mn(1)-N(2)-C(11)	72.0 (2)
C(10)-Mn(1)-C(11)	38.3 (1)	Mn(1)-N(2)-C(15)	124.3 (2)
C(10)-Mn(1)-N(2)	66.3 (1)	Mn(1)-N(2)-Mn(2)	79.1 (1)
C(11)-Mn(1)-N(2)	38.6 (1)	C(11)-N(2)-C(15)	116.5 (3)
Mn(1)-Mn(2)-C(4)	148.5 (1)	C(11)-N(2)-Mn(2)	118.0 (2)
Mn(1)-Mn(2)-C(5)	111.2 (1)	C(15)-N(2)-Mn(2)	125.1 (3)
Mn(1)-Mn(2)-C(6)	111.4 (1)	Mn(1)-C(1)-O(1)	177.4 (4)
Mn(1)-Mn(2)-N(1)	52.53 (9)	Mn(1)-C(2)-O(2)	178.4 (4)
Mn(1)-Mn(2)-N(2)	52.37 (8)	Mn(1)-C(3)-O(3)	174.5 (4)
C(4)-Mn(2)-C(5)	90.0 (2)	Mn(2)-C(4)-O(4)	179.5 (4)
C(4)-Mn(2)-C(6)	91.8 (2)	Mn(2)-C(5)-O(5)	176.5 (4)
C(4)-Mn(2)-N(1)	104.6 (2)	Mn(2)-C(6)-O(6)	176.0 (4)
C(4)-Mn(2)-N(2)	105.9 (2)		

(b) Involving Hydrogen Atoms

N(1)-C(12)-H(121)	110 (3)	C(11)-C(14)-H(141)	110 (3)
N(1)-C(12)-H(122)	107 (3)	C(11)-C(14)-H(142)	117 (3)
N(1)-C(12)-H(123)	109 (3)	C(11)-C(14)-H(143)	118 (4)
H(121)-C(12)-H(122)	109 (4)	H(141)-C(14)-H(142)	93 (4)
H(121)-C(12)-H(123)	101 (4)	H(141)-C(14)-H(143)	114 (5)
H(122)-C(12)-H(123)	120 (4)	H(142)-C(14)-H(143)	102 (5)
C(10)-C(13)-H(131)	120 (4)	N(2)-C(15)-H(151)	110 (2)
C(10)-C(13)-H(132)	112 (3)	N(2)-C(15)-H(152)	110 (2)
C(10)-C(13)-H(133)	120 (4)	N(2)-C(15)-H(153)	109 (3)
H(131)-C(13)-H(132)	105 (5)	H(151)-C(15)-H(152)	98 (3)
H(131)-C(13)-H(133)	110 (5)	H(151)-C(15)-H(153)	113 (4)
H(132)-C(13)-H(133)	81 (5)	H(152)-C(15)-H(153)	116 (4)

strictly planar but has a slight envelope fold at the nitrogen atoms and an angle of 10.0° between the planes N(1), C(10), C(11), N(2) and N(1), Mn(2), N(2). The C(10)-N(1) and C(11)-N(2) distances at 1.392 (5) and 1.388 (5) Å, respectively, are longer than typical C-N double bonds, while the C(10)-C(11) distance at 1.407 (5) Å is considerably shorter than a typical carbon-carbon single bond. The implication is that there is considerable electron delocalization between the formal C-N double bonds and the C-C single bond in this α-diimine ligand. This delocalization may be augmented by π coordination of the entire five-membered ring to a second manganese tricarbonyl group. This includes a manganese-manganese bond and coordination of the two π bonds of the α-diimine ligand. The Mn-Mn distance at 2.615 (1) Å is considerably shorter than the Mn-Mn single bond distance found in Mn₂(CO)₁₀ (2.923 (3) Å)[13] but is similar to the Mn-Mn bond distance of 2.518 (2) Å found in the molecule (μ-CO)[μ-(CF₃)₂C=N]₂Mn₂(CO₆) which contains two bridging alkylidenimino groups and one bridging carbonyl ligand.[14] The co-
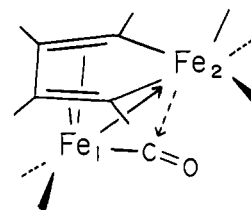

Figure 2.

ordination behavior of α-diimine ligands in metal carbonyl compounds has not been thoroughly investigated. Otsuka et al.[15] synthesized the complexes RN=C(CH₃)(CH₃)C=NRFe(CO₃), R = C₆H₅ and t-C₄H₉, and concluded on the basis of spectroscopic evidence that the diimine was coordinated through the nitrogen atoms only.

To a first approximation all carbonyl ligands are linear. The

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Table V. Structural Parameters for the Semibridging Carbonyl Ligand in the Molecules II and Related Parameters for C(3)–O(3) in I

compd	M–M′, Å	M–C–O, deg	M–C, Å	M′–C, Å	ref
[C(OH)CCH₃]₂Fe₂(CO)₆	2.493 (2)	168.0 (7)	1.736 (8)	2.484 (8)	6
[C₁₂H₁₆]Fe₂(CO)₆	2.462 (3)	161.9 (28)	1.753 (21)	2.321 (19)	7
[(C₆H₅)C₂]Fe₂(CO)₆	2.520 (3)	164.8 (11)	1.727 (13)	2.472 (13)	8
I	2.615 (1)	174.5 (4)	1.808 (4)	2.792 (4)	this work

Scheme I
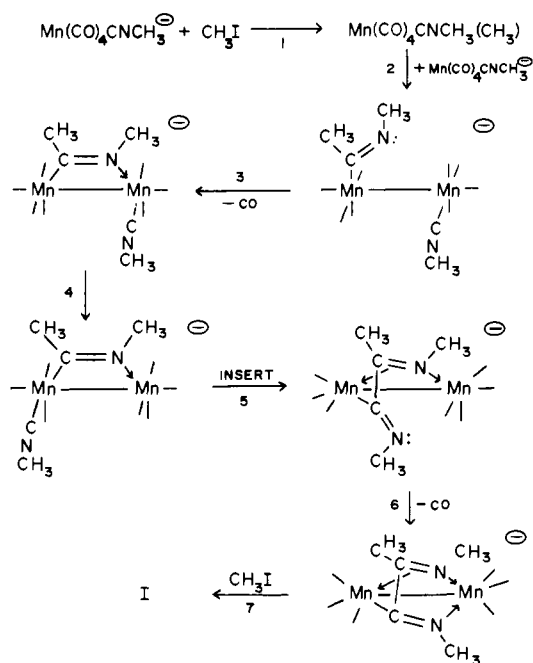
maximum deviation from linearity occurs for the ligand C(3)–O(3) for which the Mn(1)–C(3)–O(3) angle is 174.5 (4)°. The six Mn–C distances span the range 1.789–1.810 Å, Mn–C$_{av}$ = 1.803 (4) Å, and the six C–O distances range from 1.151 to 1.159°, C–O$_{av}$ = 1.154 (4) Å.

All hydrogen atoms were located and refined, and although the distances show some scatter (range 0.87–1.11 Å), the average value 1.01 Å is similar to the 0.95 Å usually found by crystallographic methods.[16] In the crystal there are no usually short intermolecular contacts. The shortest contacts were between pairs of hydrogen atoms in the range 2.1–2.6 Å.

The gross molecular geometry of I is very similar to the ferracyclopentadienyl complexes (II),[6-8] which contain semibridging carbonyl ligands. As described by Cotton,[9] electron-counting procedures lead to the conclusion that the Fe–Fe bond in these molecules if of a donor–acceptor type (i.e., Fe(1) donates two electrons to Fe(2) (see Figure 2)). This donation to Fe(2) causes a buildup of electron density on Fe(2) producing a dipolar distribution Fe(1)$^{δ+}$ → Fe(2)$^{δ-}$. A carbonyl ligand on Fe(1) then forms a weak bonding interaction to Fe(2) which relieves the charge buildup and produces the semibridging carbonyl ligand.

By the same counting procedures we find that in the absence of a metal–metal interaction each manganese atom in I was a seventeen-electron outer-shell configuration. Eighteen-electron configurations are achieved through the formation of a metal–metal bond consisting of one electron donated by each manganese atom. Thus I does not contain a donor–acceptor metal–metal bond and is not dipolar, at least in the sense that the molecules II are. In this sense, then, there is no need to form a semibridging carbonyl ligand. As observed, to a first approximation I does not contain a semibridging carbonyl ligand. However, closer inspection shows that the carbonyl ligand C(3)–O(3) does occupy the general vicinity of the semibridging carbonyl ligands in the molecules II.

Table V lists examples of molecules of the type II and the structural parameters which characterize the semibridging carbonyl ligand and compares them with the ligand C(3)–O(3) in I. While we would hesitate to call C(3)–O(3) a semibridging ligand, it would also be an oversimplification to say that there is no interaction of C(3)–O(3) with Mn(2). Clearly the truth lies somewhere in between, but we feel these results are in full accord with the theory advanced by Cotton: that the formation of semibridging carbonyl ligands in the molecules II is due in a large part to or is greatly augmented by the presence of the donor–acceptor metal–metal bond.

The mechanism of the formation of I is not known explicitly at this time, but for the reasons indicated below the steps shown in Scheme I are now offered. Analogous to eq 1 the most likely first step in the reaction of Mn(CO)₄CNCH₃⁻ with CH₃I is methylation at the metal atom. Nucleophilic attack of a Mn(CO)₄CNCH₃ anion on the methylated product would be expected to cause methyl migration to the isocyanide ligand and also establish a manganese–manganese bond (step 2). It has been shown previously that isocyanide ligands insert preferentially to carbonyl ligands,[4,5] and Casey[17] has shown that the reaction of CH₃Mn(CO)₅ with Mn(CO)₅⁻ produces a dimanganese complex containing an acyl ligand. Nucleophilic attack of the iminoacyl nitrogen atom on the adjacent manganese atom would lead to loss of one carbonyl ligand and formation of a bridging iminoacyl ligand. Bridging iminoacyl ligands have been observed previously.[18] An exchange of a carbonyl and isocyanide ligand between the metal atoms (step 4) would produce a species having the iminoacyl carbon and isocyanide ligand on the same metal atom. Such facile ligand exchange processes have been observed in isocyanide derivatives of Mn₂(CO)₁₀.[19] Insertion of the isocyanide ligand into the iminoacyl M–C bond would produce the carbon–carbon bond (step 5). "Multiple insertion" of isocyanide ligands has been observed on numerous occasions.[4,5,20] In order for an eighteen-electron configuration on the manganese atom to be maintained, the π bond of the "outer" iminyl group might become coordinated at this time. Attack of the "inner" iminyl group on the adjacent manganese atom could induce a decarbonylation and lead to a chelating diiminyl ligand (step 6). Finally, methylation (step 7) at the carbon atom of the "inner" iminyl group or at the manganese atom followed by reductive elimination would lead to the product I.

Supplementary Material Available: Tables of final thermal parameters and structure factor amplitudes (18 pages) are available. Ordering information is given on any current masthead page.

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