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Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Crystal Structure and Molecular Geometry of μ-Carbonyl-bis(μ-hexafluoroisopropylidenimino)-hexacarbonyldimanganese(*Mn–Mn*), $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$, a Complex with Bridging Alkylidenimino Ligands

MELVYN ROWEN CHURCHILL* and KUO-KUANG G. LIN

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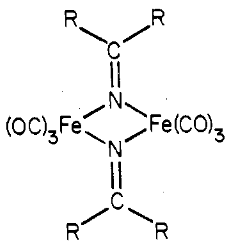
The complex μ-carbonyl-bis(μ-hexafluoroisopropylidenimino)-hexacarbonyldimanganese(*Mn–Mn*), $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with $a = 9.298\ (5)$ Å, $b = 26.614\ (19)$ Å, $c = 9.543\ (8)$ Å, $\beta = 121.00\ (5)^\circ$ and $V = 2024.2$ Å^3; $\rho(\text{obsd}) = 2.06\ (1)$ and $\rho(\text{calcd}) = 2.080$ g cm^{-3} for mol wt 634.0 and $Z = 4$. X-Ray diffraction data complete to $2\theta = 45^\circ$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer and the structure was solved via the use of the Patterson, Fourier, and least-squares refinement techniques. The positions of all atoms have been accurately determined, the resulting discrepancy indices being $R_F = 10.91\%$ and $R_{wF} = 6.23\%$ for all 2630 reflections or $R_F = 5.17\%$ and $R_{wF} = 5.67\%$ for the 1512 data with $I \geq 3\sigma(I)$. The $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$ molecule consists of two $Mn(CO)_3$ groups which are held together by two bridging $[(CF_3)_2C{=}N]$ ligands, one bridging carbonyl ligand, and a Mn–Mn bond 2.518 (2) Å in length. The molecule is thus a member of the series $(OC)_3M(\mu\text{-}X)_3M(CO)_3$, of which the founder member is $Fe_2(CO)_9$. An unexpected feature of the $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$ molecule is the highly asymmetric ("semibridging") nature of the bridging carbonyl ligand, for which Mn(1)–CO = 1.944 (9) Å and Mn(2)–CO = 2.173 (9) Å. This asymmetry is apparently compensated by a small, but significant, contrary asymmetry in Mn–N distances to the two bridging $[(CF_3)_2C{=}N]$ ligands.

Introduction

Transition metal complexes containing alkylidenimino ligands, $R_2C{=}N{-}$, have been known for some time.[1] Crystallographic studies on two such species have been reported previously. Thus, $(p\text{-tol})_2C{=}N{-}N{=}C(p\text{-tol})_2$ reacts with $Fe(CO)_5$, yielding the bridging alkylidenimino complex $[(p\text{-tol})_2C{=}N]_2Fe_2(CO)_6$, which has been shown[2,3] to have the structure I (R = *p*-tol). A species with a terminal alkylidenimino ligand has also been investigated; $(\pi\text{-}C_5H_5)Mo(CO)_2[N{=}C(CMe_3)_2]$, II, has an almost linear Mo–N–C skeleton and a short Mo–N distance of only 1.87 Å.[4]

Alkylidenimino ligands can coordinate to a single central atom in two distinct ways. Thus, in some silicon[5] and titanium[6] complexes, the M–N–C system is bent, with sp^2-hybridized nitrogen (see III) while in some molybdenum[4] (see II) and boron[7-9] species, the M–N–C system is linear, with sp-hybridized nitrogen (see IV). These two cases have been treated in terms of the alkylidenimino ligand behaving as a one- and three-electron donor, respectively. This



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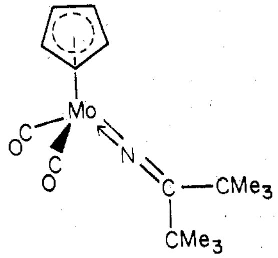


II

Table I. Experimental Data for the X-Ray Diffraction Study of $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$

(A) Crystal Parameters at 20.6°[a]

$a = 9.298\ (5)$ Å
$b = 26.614\ (19)$ Å
$c = 9.543\ (8)$ Å

Space group: $P2_1/c$ [C_{2h}^5; No. 14]
$Z = 4$
Mol wt 634.0

$\cos\beta = -0.5151\ (7)$
$\beta = 121.00\ (5)°$
$V = 2024.2$ Å^3

ρ(calcd) = 2.080 g cm^{-3}
ρ(obsd) = 2.06 (1) g cm^{-3} by neutral buoyancy in aqueous BaI_2

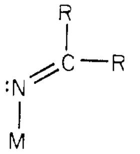
(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: used for $I > 8500$ counts/sec
Takeoff angle: 3.0°
Detector aperture: 4 mm × 4 mm
Crystal-detector distance: 330 mm
Crystal orientation: mounted on [001]
Reflections measured: $\pm h, +k, +l$
Maximum 2θ: 45°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (1.60 + 0.692 \tan\theta)°$, starting 0.80° below the Mo Kα_1 peak
Background measurement: stationary crystal, stationary counter; 20 sec each at beginning and end of 2θ scan
Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an anisotropic linear decay correction)[b] were 2.66% for 002, 1.26% for $\bar{4}02$, and 2.13% for 060
Reflections collected: 2630 independent measurements and 81 systematic absences

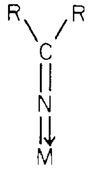
(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 14, using an "ignorance factor" of $p = 0.04$
Absorption coefficient: $\mu = 14.67$ cm^{-1}; maximum and minimum transmission factors were 0.845 and 0.617[c]

[a] Based on λ(Mo Kα_1) 0.709300 Å—see J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967). [b] Data reduction was performed using the Fortran IV program RDUS, by B. G. DeBoer. [c] Absorption corrections were carried out using the Fortran IV program DRAB, by B. G. DeBoer.



III



IV

"ampheroteric" behavior is reminiscent both of the ligand nitric oxide (NO) and of aryldiazo (RN=N–) ligands.

We have previously reported the results of an X-ray crystallographic investigation of the aryldiazo complex $(OC)_4Mn(\mu\text{-}N_2Ph)_2Mn(CO)_4$[10,11] which was synthesized[11] via the reaction

$$2Mn(CO)_5Br + 2Me_3SiN{=}NPh \rightarrow (OC)_4Mn(\mu\text{-}N_2Ph)_2Mn(CO)_4 + 2Me_3SiBr + 2CO$$

Abel and coworkers have carried out a similar reaction using $Mn(CO)_5Br$ and $Me_3SnN{=}C(CF_3)_2$ and have isolated a binuclear manganese complex. This was initially believed to be $(OC)_4Mn(\mu\text{-}NC(CF_3)_2)_2Mn(CO)_4$—i.e., completely analogous to the phenyldiazo derivative.[12] However, the current X-ray diffraction study shows the true stoichiometry to be $(OC)_3Mn[(\mu\text{-}CO)(\mu\text{-}NC(CF_3)_2)_2]Mn(CO)_3$. A preliminary report of this work has appeared previously;[13] a complete account is given below.

Collection of X-Ray Diffraction Data

Dark red crystals of $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$ were provided by Professor E. W. Abel of the University of Exeter, Exeter, England.

Table II. Atomic Positions, with Esd's, for $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$[a]

Atom	*x*	*y*	*z*
Mn(1)	0.54172 (14)	0.131273 (49)	0.21342 (15)
Mn(2)	0.23854 (14)	0.105393 (47)	0.04347 (14)
F(11)	0.54248 (71)	0.11260 (22)	0.68593 (62)
F(12)	0.55569 (74)	0.03485 (22)	0.64458 (64)
F(13)	0.68534 (65)	0.08722 (27)	0.58376 (62)
F(14)	0.24641 (69)	0.05732 (25)	0.54180 (70)
F(15)	0.12346 (67)	0.11004 (23)	0.35098 (73)
F(16)	0.14799 (67)	0.03514 (23)	0.29821 (74)
F(21)	0.36820 (71)	0.29531 (21)	0.22726 (76)
F(22)	0.55609 (67)	0.25439 (20)	0.21489 (72)
F(23)	0.36693 (71)	0.29194 (21)	0.00229 (76)
F(24)	0.03820 (68)	0.21950 (24)	0.09345 (81)
F(25)	0.06512 (65)	0.28051 (22)	−0.03525 (83)
F(26)	0.00498 (66)	0.20808 (22)	−0.14027 (73)
O(1)	0.73817 (83)	0.19427 (29)	0.51441 (86)
O(2)	0.80646 (81)	0.05332 (27)	0.35461 (83)
O(3)	0.70633 (88)	0.18608 (28)	0.06220 (90)
O(4)	−0.10304 (76)	0.11201 (23)	−0.01081 (81)
O(5)	0.18426 (77)	−0.00413 (28)	−0.00457 (80)
O(6)	0.07618 (82)	0.12243 (27)	−0.31422 (76)
O(7)	0.47588 (79)	0.06235 (26)	−0.06309 (78)
N(1)	0.39206 (74)	0.10005 (24)	0.28548 (75)
N(2)	0.33008 (77)	0.17406 (26)	0.10283 (72)
C(1)	0.6620 (11)	0.17110 (34)	0.3999 (12)
C(2)	0.7048 (12)	0.08448 (37)	0.3019 (10)
C(3)	0.6428 (11)	0.16447 (35)	0.1195 (12)
C(4)	0.0333 (11)	0.11076 (31)	0.0177 (10)
C(5)	0.2042 (10)	0.03912 (38)	0.0131 (10)
C(6)	0.1392 (11)	0.11659 (33)	−0.1766 (12)
C(7)	0.4557 (10)	0.08719 (35)	0.0245 (10)
C(11)	0.5438 (12)	0.08009 (42)	0.5798 (11)
C(12)	0.3907 (9)	0.08474 (30)	0.4096 (10)
C(13)	0.2274 (11)	0.07236 (41)	0.4014 (11)
C(21)	0.3965 (12)	0.26574 (38)	0.1333 (13)
C(22)	0.2818 (9)	0.21904 (33)	0.0801 (9)
C(23)	0.0967 (12)	0.23216 (38)	0.0014 (13)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the preceding number.

The crystal selected for the structural study approximated in shape to a distorted hexagonal plate between {100} faces, 0.23 mm apart. Other faces (cyclically) were $(\bar{1}11)$, $(\bar{1}\bar{2}1)$, $(0\bar{1}0)$, $(1\bar{1}\bar{1})$, $(12\bar{1})$, and (010); dimensions were $(\bar{1}11)\rightarrow(1\bar{1}\bar{1})$ = 0.25 mm, $(\bar{1}\bar{2}1)\rightarrow(12\bar{1})$ = 0.36 mm, and $(0\bar{1}0)\rightarrow(010)$ = 0.29 mm. The crystal was mounted along c^*.

Preliminary studies [Weissenberg, rotation, precession, and cone-axis photographs] revealed approximate cell dimensions, showed C_{2h} $(2/m)$ Laue symmetry, and indicated the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. This information is consistent with the crystal belonging to the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14].

The crystal was transferred to a Picker FAC-1 automated diffractometer, was accurately centered, and was aligned precisely along [001].

The intensity of the axial 002 reflection was measured by means of a θ–2θ coupled scan at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The observed variation in intensity as a function of ϕ [(maximum − minimum)/(average) = 40%] indicated that an absorption correction would be necessary. These data were treated along with the primary data set; following correction for absorption, the ϕ dependence of the 002 reflection was essentially eliminated, thereby providing confirmation of the validity of the absorption correction.

Details of the data collection are given in Table I; the apparatus and experimental technique have been described previously.[14] We note here that the intensity data were rather weak; thus, to $2\theta_{max} = 45°$, only 1512 of the 2630 reflections had $I \geq 3\sigma(I)$.

Solution and Refinement of the Structure

Scattering factors for neutral atoms were taken from the compilation of Cromer and Waber;[15] both the real and imaginary components of anomalous dispersion were included in the calculation of structure factors, using the values of Cromer and Liberman.[16]

Table III. Anisotropic Thermal Parameters[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[b]
Mn(1)	2.52 (6)	4.31 (7)	3.75 (6)	0.09 (5)	1.46 (5)	0.15 (5)	0.178, 0.224, 0.235
Mn(2)	2.67 (6)	3.69 (7)	3.21 (6)	−0.04 (5)	1.07 (5)	−0.20 (5)	0.180, 0.213, 0.226
F(11)	8.44 (38)	8.32 (40)	4.34 (28)	1.98 (30)	1.81 (27)	−0.37 (26)	0.23, 0.29, 0.39
F(12)	9.64 (40)	6.40 (34)	5.66 (30)	2.63 (29)	3.29 (29)	2.38 (27)	0.21, 0.31, 0.38
F(13)	3.62 (28)	15.34 (57)	4.83 (29)	0.80 (29)	1.09 (24)	2.78 (30)	0.20, 0.28, 0.45
F(14)	7.12 (35)	13.11 (51)	6.10 (32)	−0.93 (31)	4.24 (28)	2.35 (32)	0.21, 0.30, 0.43
F(15)	5.58 (30)	7.45 (38)	10.60 (42)	1.84 (27)	5.38 (31)	1.52 (31)	0.21, 0.30, 0.38
F(16)	5.84 (31)	7.39 (37)	8.76 (37)	−2.23 (27)	3.83 (29)	−1.62 (31)	0.23, 0.32, 0.35
F(21)	7.73 (36)	5.57 (33)	9.35 (38)	−1.35 (26)	4.28 (31)	−3.22 (29)	0.22, 0.31, 0.38
F(22)	4.19 (30)	5.33 (31)	10.11 (39)	−1.11 (23)	2.10 (27)	−0.49 (27)	0.21, 0.28, 0.40
F(23)	7.79 (36)	5.99 (34)	8.26 (37)	−1.39 (27)	3.22 (30)	1.32 (29)	0.24, 0.31, 0.38
F(24)	4.74 (30)	10.69 (45)	9.85 (41)	1.10 (28)	4.50 (30)	1.17 (35)	0.21, 0.34, 0.38
F(25)	4.98 (30)	4.69 (33)	13.09 (50)	1.46 (24)	2.11 (31)	0.70 (31)	0.21, 0.28, 0.46
F(26)	4.79 (30)	7.25 (36)	7.27 (35)	1.62 (25)	0.02 (26)	−0.55 (29)	0.21, 0.29, 0.41
O(1)	5.46 (37)	7.98 (46)	6.38 (42)	−1.11 (33)	0.90 (33)	−2.63 (35)	0.21, 0.32, 0.38
O(2)	5.28 (39)	7.22 (46)	7.66 (44)	2.04 (33)	2.56 (34)	1.10 (34)	0.22, 0.33, 0.33
O(3)	7.55 (45)	7.26 (46)	9.22 (48)	0.55 (34)	5.74 (39)	2.21 (36)	0.24, 0.29, 0.37
O(4)	3.48 (31)	6.32 (39)	8.15 (41)	−0.15 (28)	2.27 (31)	−0.25 (30)	0.21, 0.28, 0.34
O(5)	5.33 (36)	5.41 (39)	7.21 (41)	−0.96 (31)	1.74 (31)	−1.58 (34)	0.22, 0.28, 0.35
O(6)	6.18 (38)	9.84 (52)	3.43 (31)	0.68 (32)	1.62 (30)	0.22 (31)	0.21, 0.30, 0.36
O(7)	5.75 (37)	8.37 (46)	5.48 (36)	0.85 (31)	3.17 (32)	−1.19 (32)	0.23, 0.27, 0.34
N(1)	3.67 (33)	3.72 (37)	3.62 (33)	−0.19 (26)	1.92 (28)	−0.43 (28)	0.20, 0.21, 0.23
N(2)	3.68 (33)	4.07 (41)	3.29 (32)	−0.29 (29)	1.80 (27)	−0.41 (28)	0.20, 0.22, 0.23
C(1)	3.44 (45)	4.84 (57)	5.43 (53)	0.28 (39)	1.75 (42)	−0.38 (43)	0.21, 0.24, 0.29
C(2)	4.65 (51)	5.32 (55)	3.90 (45)	0.04 (41)	2.04 (41)	−0.18 (39)	0.22, 0.25, 0.26
C(3)	5.01 (52)	4.86 (55)	6.15 (56)	0.76 (42)	3.20 (46)	0.97 (44)	0.23, 0.24, 0.29
C(4)	3.37 (44)	4.28 (46)	3.96 (42)	−0.08 (37)	1.29 (37)	−0.24 (35)	0.20, 0.23, 0.25
C(5)	3.12 (44)	5.74 (58)	3.49 (44)	−0.67 (41)	0.94 (36)	−1.07 (42)	0.18, 0.24, 0.28
C(6)	4.65 (49)	5.55 (59)	4.59 (50)	0.49 (39)	2.45 (43)	−0.53 (43)	0.22, 0.24, 0.28
C(7)	4.31 (47)	5.05 (53)	3.79 (46)	0.43 (38)	1.85 (40)	−0.11 (38)	0.22, 0.23, 0.26
C(11)	4.51 (55)	6.90 (64)	3.96 (50)	0.76 (45)	2.09 (44)	1.15 (48)	0.21, 0.24, 0.30
C(12)	3.58 (42)	3.99 (43)	3.50 (42)	0.30 (32)	2.18 (36)	0.06 (34)	0.19, 0.22, 0.30
C(13)	4.29 (52)	6.36 (66)	3.99 (49)	−0.56 (47)	2.15 (43)	0.26 (44)	0.22, 0.23, 0.29
C(21)	4.60 (56)	4.44 (61)	5.78 (56)	0.24 (41)	2.47 (48)	0.11 (45)	0.23, 0.25, 0.28
C(22)	3.13 (43)	3.32 (46)	2.97 (38)	−0.15 (34)	0.97 (33)	−0.23 (32)	0.18, 0.21, 0.23
C(23)	4.08 (53)	4.50 (57)	5.89 (58)	0.51 (43)	1.64 (47)	0.17 (46)	0.22, 0.25, 0.30

[a] These parameters have units of Å² and enter the expression for the calculated structure factor in the following form: $\exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. [b] These are the root-mean-square amplitudes of vibration (in Å) along the principal axes (minor, median, major, respectively) of the atomic vibration ellipsoids. For relative orientations, see Figure 1.

Discrepancy indices used below are defined by the equations

$$R_F = \left[\frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}\right] \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w[F(hkl)] = \sigma^{-2}[F(hkl)]$.

Computer programs used during the solution and refinement of the crystal structure include FORDAP (Fourier synthesis, by A. Zalkin), LSHF (least-squares refinement, by B. G. DeBoer), STAN1 (distances and angles, with esd's, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson). All calculations were carried out on the IBM 370/158 computer at the Computer Center of the University of Illinois at Chicago Circle.

The positions of the two independent manganese atoms were determined from a three-dimensional Patterson synthesis. A Fourier synthesis, phased by these two atoms, revealed the positions of the remaining 34 atoms of the $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$ molecule. Full-matrix least-squares refinement of individual positional and isotropic thermal parameters along with the overall scale factor [145 parameters in all] led to convergence with $R_F = 16.57\%$ and $R_{wF} = 14.49\%$. Continued refinement, now using anisotropic thermal parameters for the manganese and fluorine atoms [215 variable parameters], led to reduction in the discrepancy indices to $R_F = 12.75\%$ and $R_{wF} = 7.55\%$. Further refinement, using anisotropic thermal parameters for all 36 atoms [325 variables] led to final convergence with $(\Delta/\sigma)_{max} = 0.023$ and discrepancy indices of $R_F = 10.91\%$ and $R_{wF} = 6.23\%$. The final "goodness of fit" defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was 1.485, where m (the number of observables)

Table IV. Interatomic Distances (in Å) for $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$[a,b]

(a) Distances Involving Mn Atoms			
Mn(1)-Mn(2)	2.5183 (24)	Mn(2)-N(1)	1.999 (7)
Mn(1)-N(1)	2.021 (7)	Mn(2)-N(2)	1.972 (7)
Mn(1)-N(2)	2.036 (7)	Mn(2)-C(4)	1.800 (9)
Mn(1)-C(1)	1.869 (10)	Mn(2)-C(5)	1.789 (10)
Mn(1)-C(2)	1.801 (10)	Mn(2)-C(6)	1.832 (10)
Mn(1)-C(3)	1.826 (10)	Mn(2)-C(7)	2.173 (9)
Mn(1)-C(7)	1.944 (9)		
(b) Distances within Carbonyl Ligands			
C(1)-O(1)	1.131 (11)	C(5)-O(5)	1.164 (10)
C(2)-O(2)	1.160 (9)	C(6)-O(6)	1.140 (9)
C(3)-O(3)	1.145 (9)	C(7)-O(7)	1.154 (9)
C(4)-O(4)	1.152 (9)		
(c) Nitrogen-Carbon Distances			
N(1)-C(12)	1.259 (9)	N(2)-C(22)	1.258 (9)
(d) Carbon-Carbon Distances			
C(11)-C(12)	1.516 (11)	C(21)-C(22)	1.543 (12)
C(12)-C(13)	1.516 (11)	C(22)-C(23)	1.521 (11)
(e) Carbon-Fluorine Distances			
C(11)-F(11)	1.337 (10)	C(21)-F(21)	1.317 (10)
C(11)-F(12)	1.332 (10)	C(21)-F(22)	1.308 (9)
C(11)-F(13)	1.311 (10)	C(21)-F(23)	1.331 (10)
C(13)-F(14)	1.320 (9)	C(23)-F(24)	1.294 (11)
C(13)-F(15)	1.301 (10)	C(23)-F(25)	1.326 (10)
C(13)-F(16)	1.322 (10)	C(23)-F(26)	1.333 (10)

[a] Estimated standard deviations (shown in parentheses) were calculated from the full positional correlation matrix using the Fortran IV program STAN1, by Dr. B. G. DeBoer. Errors in the unit cell parameters are included. [b] Bond lengths are not corrected for any possible effects of thermal motion.

Table V. Interatomic Angles (in deg) for $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$

	(a) Angles around Manganese Atoms		
Mn(2)-Mn(1)-N(1)	50.82 (18)	Mn(1)-Mn(2)-N(1)	51.61 (19)
Mn(2)-Mn(1)-N(2)	49.95 (19)	Mn(1)-Mn(2)-N(2)	52.20 (19)
Mn(2)-Mn(1)-C(1)	133.68 (27)	Mn(1)-Mn(2)-C(4)	145.35 (27)
Mn(2)-Mn(1)-C(2)	120.37 (30)	Mn(1)-Mn(2)-C(5)	114.90 (26)
Mn(2)-Mn(1)-C(3)	120.31 (30)	Mn(1)-Mn(2)-C(6)	115.48 (29)
Mn(2)-Mn(1)-C(7)	56.53 (26)	Mn(1)-Mn(2)-C(7)	48.28 (24)
N(1)-Mn(1)-N(2)	75.83 (25)	N(1)-Mn(2)-N(2)	77.78 (25)
N(1)-Mn(1)-C(1)	95.06 (34)	N(1)-Mn(2)-C(4)	103.84 (32)
N(1)-Mn(1)-C(2)	96.74 (34)	N(1)-Mn(2)-C(5)	94.52 (32)
N(1)-Mn(1)-C(3)	169.87 (34)	N(1)-Mn(2)-C(6)	167.09 (34)
N(1)-Mn(1)-C(7)	92.34 (32)	N(1)-Mn(2)-C(7)	86.51 (28)
N(2)-Mn(1)-C(1)	96.94 (32)	N(2)-Mn(2)-C(4)	103.65 (32)
N(2)-Mn(1)-C(2)	170.21 (36)	N(2)-Mn(2)-C(5)	167.08 (33)
N(2)-Mn(1)-C(3)	94.56 (33)	N(2)-Mn(2)-C(6)	93.83 (34)
N(2)-Mn(1)-C(7)	91.76 (31)	N(2)-Mn(2)-C(7)	87.04 (31)
C(1)-Mn(1)-C(2)	89.98 (39)	C(4)-Mn(2)-C(5)	88.17 (36)
C(1)-Mn(1)-C(3)	89.21 (42)	C(4)-Mn(2)-C(6)	87.57 (37)
C(1)-Mn(1)-C(7)	169.73 (39)	C(4)-Mn(2)-C(7)	166.37 (36)
C(2)-Mn(1)-C(3)	92.44 (40)	C(5)-Mn(2)-C(6)	91.83 (38)
C(2)-Mn(1)-C(7)	82.08 (37)	C(5)-Mn(2)-C(7)	82.10 (36)
C(3)-Mn(1)-C(7)	84.66 (40)	C(6)-Mn(2)-C(7)	83.24 (35)
	(b) Angles Involving Bridging Atoms		
Mn(1)-N(1)-Mn(2)	77.57 (25)	Mn(2)-N(2)-C(22)	140.33 (56)
Mn(1)-N(1)-C(12)	142.71 (56)	Mn(1)-C(7)-Mn(2)	75.19 (34)
Mn(2)-N(1)-C(12)	139.72 (57)	Mn(1)-C(7)-O(7)	150.96 (77)
Mn(1)-N(2)-Mn(2)	77.85 (26)	Mn(2)-C(7)-O(7)	133.83 (71)
Mn(1)-N(2)-C(22)	141.81 (56)		
	(c) Angles within Terminal Carbonyl Ligands		
Mn(1)-C(1)-O(1)	178.12 (66)	Mn(2)-C(4)-O(4)	174.25 (83)
Mn(1)-C(2)-O(2)	177.76 (70)	Mn(2)-C(5)-O(5)	178.94 (59)
Mn(1)-C(3)-O(3)	178.73 (71)	Mn(2)-C(6)-O(6)	178.41 (70)
	(d) N-C-C Angles		
N(1)-C(12)-C(11)	125.12 (78)	N(2)-C(22)-C(21)	125.80 (75)
N(1)-C(12)-C(13)	121.14 (75)	N(2)-C(22)-C(23)	121.07 (75)
	(e) C-C-C Angles		
C(11)-C(12)-C(13)	113.62 (77)	C(21)-C(22)-C(23)	113.06 (76)
	(f) C-C-F Angles		
C(12)-C(11)-F(11)	112.86 (79)	C(22)-C(21)-F(21)	111.02 (79)
C(12)-C(11)-F(12)	112.24 (84)	C(22)-C(21)-F(22)	112.95 (79)
C(12)-C(11)-F(13)	113.20 (77)	C(22)-C(21)-F(23)	109.87 (77)
C(12)-C(13)-F(14)	113.98 (78)	C(22)-C(23)-F(24)	111.67 (80)
C(12)-C(13)-F(15)	112.64 (80)	C(22)-C(23)-F(25)	113.18 (81)
C(12)-C(13)-F(16)	111.18 (78)	C(22)-C(23)-F(26)	111.15 (80)
	(g) F-C-F Angles		
F(11)-C(11)-F(12)	105.34 (75)	F(21)-C(21)-F(22)	107.20 (81)
F(11)-C(11)-F(13)	106.59 (88)	F(21)-C(21)-F(23)	108.02 (87)
F(12)-C(11)-F(13)	106.01 (82)	F(22)-C(21)-F(23)	107.59 (82)
F(14)-C(13)-F(15)	107.17 (81)	F(24)-C(23)-F(25)	108.53 (88)
F(14)-C(13)-F(16)	105.10 (81)	F(24)-C(23)-F(26)	106.85 (86)
F(15)-C(13)-F(16)	106.19 (78)	F(25)-C(23)-F(26)	105.06 (82)

was 2630 and n (the number of variables) was 325; the ratio $m{:}n$ is 8.09:1. The function $\sum w(|F_o| - |F_c|)^2$ was not markedly dependent either upon $|F_o|$ or upon $((\sin\theta)/\lambda)$; the weighting scheme is thus acceptable.

The correctness of the determined structure was confirmed by means of a final difference-Fourier synthesis on which the strongest features were peaks of 0.71 e Å^{-3} at (0.81, 0.01, 0.48) and 0.67 e Å^{-3} at (0.72, 0.13, 0.45).

As a test, we took the 1512 data for which $I \geq 3\sigma(I)$ and refined the structure to convergence once again. Not one parameter changed by more than 0.5σ, but estimated standard deviations increased by ca. 40%. The resulting discrepancy indices were R_F = 5.17% and R_{wF} = 5.67%, the goodness of fit was 1.870, and the highest features on the associated difference-Fourier map were of height 0.55 e Å^{-3} (at 0.54, 0.13, 0.36) and 0.52 e Å^{-3} (at 0.38, 0.17, 0.19). These results were discarded.

A table of observed and calculated structure factor amplitudes is available.[17] Table II gives the final positional parameters and their estimated standard deviations. Anisotropic thermal parameters and their esd's are collected in Table III.

Molecular Structure

Interatomic distances and their esd's are given in Table IV, while bond angles and their esd's are listed in Table V. The stereochemistry and numbering of atoms within the $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$ molecule is shown in Figure 1.

The $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$ molecule consists of two $Mn(CO)_3$ moieties which are linked together via two bridging $[(CF_3)_2C{=}N]$ ligands and a bridging carbonyl ligand. The manganese atoms are best regarded as in an oxidation state of zero, with a d^7 outer electronic configuration. The 18-electron configuration for each Mn atom is attained by the donation of two electrons from each carbonyl ligand and three electrons from each $[(CF_3)_2C{=}N]$ ligand, with concomitant formation of a manganese–manganese bond. Evidence for the existence of a bonding Mn–Mn interaction comes both from the short interatomic distance [Mn(1)–Mn(2) = 2.5183 (24) Å] and from the acute metal–ligand–metal angles centered on the three bridging ligands, viz., Mn(1)–N(1)–Mn(2) = 77.57 (25)°, Mn(1)–N(2)–Mn(2) = 77.85 (26)°, and Mn(1)–C(7)–Mn(2) = 75.19 (34)°. The M(μ-X)$_3$M central portion of the molecule can, to a first approximation, be represented as a resonance hybrid of V and VI.

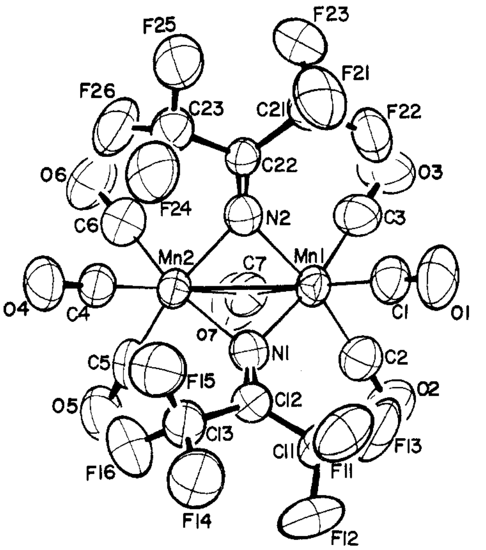
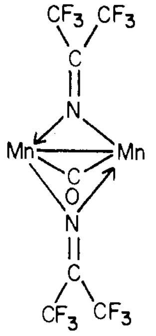
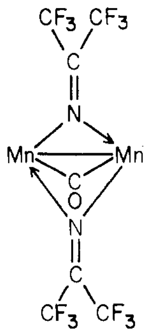


Figure 1. Stereochemistry and atomic labeling for the $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$ molecule [ORTEP diagram, 50% probability ellipsoids].



V

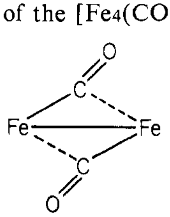


VI

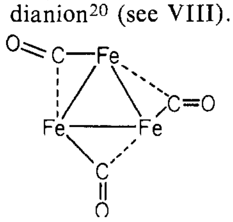
An unexpected feature of the present structure is the gross asymmetry of the bridging carbonyl ligand, which is characterized by the metal–carbon distances Mn(1)–C(7) = 1.944 (9) Å and Mn(2)–C(7) = 2.173 (9) Å [difference 0.229 ± 0.013 Å or ca. 18σ] and the bond angles Mn(1)–C(7)–O(7) = 150.96 (77)° and Mn(2)–C(7)–O(7) = 133.83 (71)° [difference 17.13 ± 1.05° or ca. 16σ].

Highly asymmetric or "semibridging" carbonyl groups have been known for some time, having been observed in the crystal structures of $Fe_2(CO)_6(COH{=}CMe)_2$,[18] $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$,[19] $[Fe_4(CO)_{13}{}^{2-}]$,[20] $Fe_3(CO)_{11}(PPh_3)$,[21] $Fe_3(CO)_{12}$,[22] $Fe(CO)_3(PhC_2C_6H_4C_2Ph)_2Fe(CO)$,[23] $(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$,[24] $(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}$,[25] $[Fe_6(CO)_{16}C^{2-}]$,[26] $\alpha\text{-}H_2Ru_4(CO)_{13}$,[27] $(\pi\text{-}C_5H_5)_2V_2(CO)_5$,[28] $(C_{12}H_{16})Fe_2(CO)_6$,[29] and $Fe_2(CO)_7(dipy)$.[30]

As Cotton has pointed out,[31] "semibridging" carbonyl groups occur only in association with a metal–metal bond; while their function is usually to relieve excessive buildup of charge in a certain portion of a molecule,[30] they also occur in such otherwise symmetric systems as the $Fe(\mu\text{-}CO)_2Fe$ bridge of the $Fe_3(CO)_{12}$ molecule[22] (see VII) and the basal $Fe_3(\mu\text{-}CO)_3$ portion of the $[Fe_4(CO)_{13}{}^{2-}]$ dianion[20] (see VIII).



VII



VIII

There are no electronic reasons for the occurrence of a "semibridging" carbonyl ligand in $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$. It apparently results from a complex set of *inter*molecular and *intra*molecular repulsions between CF_3 groups and CO ligands. (Among these, the contact F(24)···C(4) is, in part, responsible for the angle Mn(1)–Mn(2)–C(4) = 145.35 (27)° being 11.67 ± 0.38° greater than the "pseudomirror" related angle Mn(2)–Mn(1)–C(1).)

The presence of this grossly asymmetric bridging ligand necessarily causes other perturbations within the molecule. Its effect is apparently balanced by a considerably smaller and opposing distortion in the geometry of the alkylidenimino ligands; thus the bond Mn(2)–N(1) = 1.999 (7) Å is 0.022 Å (or ca. 2.2σ) shorter than the Mn(1)–N(1) bond length of 2.021 (7) Å, and the Mn(2)–N(2) bond length of 1.972 (7) Å is 0.064 Å (or ca. 6.5σ) shorter than the Mn(1)–N(2) bond length of 2.036 (7) Å. Angles at the nitrogen atoms confirm this pattern of distortions. Thus, the angle Mn(2)–N(1)–C(12) is 139.72 (57)° and is 2.99° smaller than the angle Mn(1)–N(1)–C(12), which is 142.71 (56)°; similarly Mn(2)–N(2)–C(22) = 140.33 (56)° and is 1.48° smaller than Mn(1)–N(2)–C(22) = 141.81 (56)°.

To our knowledge, the present molecule represents the first example of a system in which the asymmetry of a "semibridging" carbonyl ligand is balanced by opposing asymmetries in another type of ligand.

The asymmetry of the "semibridging" carbonyl ligand, C(7)–O(7), is further reflected by the manganese–carbonyl distances which are trans to it. Thus, Mn(1)–C(1) = 1.869 (10) Å and is 0.069 Å or ca. 5σ longer than Mn(2)–C(4) = 1.800 (9) Å [appropriate angles are C(7)–Mn(1)–C(1) = 169.73 (39)° and C(7)–Mn(2)–C(4) = 166.37 (36)°]. For carbonyl ligands trans to the alkylidenimino ligands we have Mn(1)–C(2) = 1.801 (10) Å, Mn(1)–C(3) = 1.826 (10) Å, Mn(2)–C(5) = 1.789 (10) Å, and Mn(2)–C(6) = 1.832 (10) Å [corresponding angles are N(2)–Mn(1)–C(2) = 170.21 (36)°, N(1)–Mn(1)–C(3) = 169.87 (34)°, N(2)–Mn(2)–C(5) = 167.08 (33)°, and N(1)–Mn(2)–C(6) = 167.09 (34)°].

The six terminal carbonyl ligands have carbon–oxygen distances varying from C(1)–O(1) = 1.131 (11) Å to C(5)–O(5) = 1.164 (10) Å, while the corresponding bond within the "semibridging" carbonyl ligand, C(7)–O(7), has a length of 1.154 (9) Å. Angles within the terminal carbonyl ligands range from Mn(2)–C(4)–O(4) = 174.25 (83)° to Mn(2)–C(5)–O(5) = 178.94 (59)°.

Distances within the alkylidenimino ligands are essentially as expected. The nitrogen–carbon distances, N(1)–C(12) = 1.259 (9) Å and N(2)–C(22) = 1.258 (9) Å, are self-consistent and in keeping with the formulation of these linkages as N=C. The carbon–carbon bonds range from C(11)–C(12) = C(12)–C(13) = 1.516 (11) Å to C(21)–C(22) = 1.543 (12) Å and average 1.524 Å—in keeping with the recognized $C(sp^2)\text{–}C(sp^3)$ distance of 1.51 Å. Despite substantial librational motion of the perfluoromethyl groups, individual carbon–fluorine distances range only from C(23)–F(24) = 1.294 (11) Å up to C(11)–F(11) = 1.337 (10) Å.

Angles within the $[(CF_3)_2C{=}N]$ ligands are all normal and lie in the ranges N–C–C = 121.07 (75)–125.80 (75)°, C–C–C = 113.06 (76)–113.62 (77)°, C–C–F = 109.87 (77)–113.98 (78)°, and F–C–F = 105.06 (82)–108.53 (88)°.

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Registry No. $[(CF_3)_2C{=}N]_2Mn_2(CO)_7$, 54713-78-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC407485.

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Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Transition Metal σ-Acyls. III.[1,2] Crystal Structure and Molecular Geometry of $[C_5H_4C_6H_6CO]Fe_2(CO)_5$, Including the Location and Refinement of All Hydrogen Atoms

MELVYN ROWEN CHURCHILL* and SHIRLEY W.-Y. CHANG

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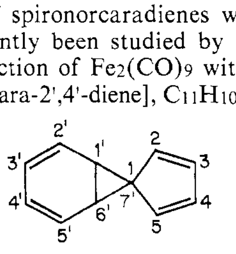
The complex $[C_5H_4C_6H_6CO]Fe_2(CO)_5$, prepared by Moriarty and coworkers by the reaction of $Fe_2(CO)_9$ and spiro[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene], crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with $a = 6.562$ (1) Å, $b = 21.690$ (5) Å, $c = 11.399$ (2) Å, and $\beta = 96.78$ (2)°. The observed density of 1.71 (2) g cm^{-3} is consistent with the value of 1.739 g cm^{-3} calculated for mol wt 421.96 and $Z = 4$. X-Ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogen atoms, have been successfully located. The final discrepancy indices are $R_F = 5.02\%$ and $R_{wF} = 4.24\%$ for the 2852 independent reflections (none rejected). The structural analysis shows that the original spiro[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene] framework has undergone 1,6' bond scission with incorporation of a $-C(=O)-$ moiety at position 6'. The resulting molecule consists of a 5,6-*cis*-disubstituted-1,3-cyclohexadieneiron tricarbonyl residue, where the substituents are defined by the framework $-(\eta^5\text{-}C_5H_4)Fe(CO)_2C(=O)-$. Atom Fe(1) is linked to three terminal carbonyl groups and the η^4-cyclohexadiene fragment, iron–carbon distances around the diene (cyclically) being 2.097 (3), 2.048 (3), 2.049 (3), and 2.098 (3) Å and carbon–carbon distances within the diene system (taken cyclically) being 1.429 (4), 1.387 (5), and 1.428 (4) Å. Atom Fe(2) is linked to two terminal carbonyl ligands, to an η^5-cyclopentadienyl ligand (Fe–C = 2.068 (3)–2.128 (4) Å and C–C = 1.403 (6)–1.436 (5) Å), and to a σ-acyl residue. The iron–σ-acyl bond distance of 1.9596 (30) Å is significantly shorter than the accepted Fe–C (sp^3) distances of 2.0977 (23) Å for an $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ species.

Introduction

The reactions of spironorcaradienes with diiron enneacarbonyl have recently been studied by Moriarty and coworkers.[3] The reaction of $Fe_2(CO)_9$ with spiro[2,4-cyclopentadiene-1,7'-norcara-2',4'-diene], $C_{11}H_{10}$, I, in diethyl ether



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at 36° for 30 hr produces as its principal product (28% yield) a compound of stoichiometry $(C_{11}H_{10})Fe_2(CO)_6$. This complex has an infrared spectrum which suggests the presence of terminal carbonyl ligands (ν 1965–1985, 2005, 2032 cm^{-1}) and an acyl carbonyl group (ν 1630 cm^{-1}). In order to determine the overall stereochemistry of this new complex and in view of our previous interest in σ-acyl derivatives of the transition metals,[1,2] we decided to subject this material to a single-crystal X-ray structural analysis. Our results are reported below.

Collection of the X-Ray Diffraction Data

Crystals of the complex were provided by Professor R. M. Moriarty of the University of Illinois at Chicago Circle. The crystal used was a platelike parallelepiped having the dimensions $(010) \rightarrow (0\bar{1}0) = 0.12$ mm, $(100) \rightarrow (\bar{1}00) = 0.295$ mm, and $(001) \rightarrow (00\bar{1}) = 0.34$ mm. The crystal was sealed into a Lindemann tube, which was fixed into a brass "pin" on a eucentric goniometer. Preliminary (0–2)*kl* Weissenberg photographs, an *a*-axis rotation photograph, *h*(0–2)*l* and *hk*(0–2) precession photographs, and *b* and *c* cone-axis photographs yielded approximate cell dimensions, indicated C_{2h} (2/*m*) Laue symmetry,