

STRUCTURAL INVESTIGATIONS OF ALUMINO-METALLOAMINOCARBENE COMPLEXES

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Summary

$[\text{Al}(\text{NMe}_2)_3]_2$ combines with $\text{Fe}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ forming bimetallic compounds $\text{Fe}_2(\text{CO})_8[\text{C}(\text{NMe}_2)\text{OAl}(\text{NMe}_2)_2]_2$ and $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$. X-ray diffraction analyses reveal the formation of aluminometallobene compounds with central connectivities, $\text{MC}[\text{NMe}_2][\text{OAl}(\text{NMe}_2)(\mu\text{-NMe}_2)_2]$.

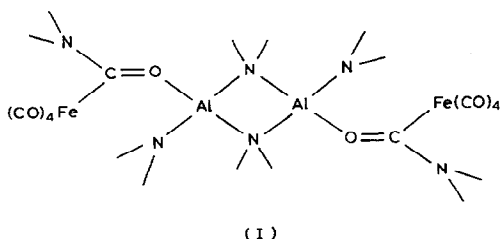
Introduction

It has been recognized for some time that CO ligands in mononuclear and polynuclear metal carbonyls possess latent basicity on the oxygen atom [1–3]. For related compounds, it has been observed that the O-carbonyl basicity is a function of carbon atom connectivity with face bridging CO groups being more basic than edge bridging CO groups which, in turn, are more basic than terminal CO groups [1]. The basicity trend has been tested with a number of acceptors with the most attention given to Group IIIA species including boron halides, aluminum halides and alkyl aluminums. Interest in the structural properties of the acid–base complexes continues; however, the realization that Group IIIA acceptors activate and modify the reactivity of coordinated CO has generated a broader interest in these interactions [1].

Several years ago, Schmid and Petz [4–6] reported studies of the reactions of aminoalanes with several metal carbonyls. In particular, they noted that $\text{Fe}(\text{CO})_5$ and $[\text{Al}(\text{NMe}_2)_3]_2$ combined to form a yellow crystalline complex [4]. Based upon analytical and spectroscopic data, they proposed the formation not of a simple acid–base complex, but instead a metallobene compound (I) schematically represented here. The dimeric formulation was proposed to account for ^1H NMR spectra which resolved bridging and terminal amide groups bound to aluminum. Subsequently Petz reported the formation of a closely related dimeric complex with $\text{Ni}(\text{CO})_4$ [5].

Our own interests in reactivity modifications of coordinated ligands by Lewis acids, and the unusual structural proposals for the products of the reactions of

aluminum amides with $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ stimulated a reinvestigation of the reaction of $[\text{Al}(\text{NMe}_2)_3]_2$ with $\text{Fe}(\text{CO})_5$ and a study of the reaction with $\text{Mn}_2(\text{CO})_{10}$.



Experimental

$\text{Fe}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ were purchased from Strem Chemicals and $[\text{Al}(\text{NMe}_2)_3]_2$ was prepared by literature methods [7]. Solvents were treated with appropriate drying agents, distilled and stored under nitrogen. All reactions were performed in Schlenk vessels under nitrogen. Infrared spectra were recorded on a Nicolet 6000 FT-IR and NMR spectra were recorded on a Varian FT-80A or Nicolet 360 NMR spectrometer.

Preparation of $\text{Fe}_2(\text{CO})_8[\text{C}(\text{NMe}_2)\text{OAl}(\text{NMe}_2)_2]_2$

The complex was prepared in a manner similar to that described by Petz and Schmid [4]. In a typical experiment 1.72 g (5.4 mmol) $[\text{Al}(\text{NMe}_2)_3]_2$ was dissolved in 50 ml of a 1/1 mixture of benzene and pentane, the solution cooled to 0°C and 2.13 g (10.9 mmol) $\text{Fe}(\text{CO})_5$ was added slowly with stirring. The mixture was stirred while protected from light for 30 min, and then warmed to 25°C . During this time the solution became yellow in color and a yellow solid precipitated. The mixture was filtered and the solid washed with pentane (2×15 ml) and dried in vacuo. Yield 3.5 g (91%). A small, second crop of crystalline product was collected by cooling the solution in the refrigerator for several days. In our experience, solutions of the product are unstable producing a dark brown oil. The decomposition seems to be accelerated by light exposure and the solid does not sublime without significant decomposition. The solid is stable for approximately one week in the refrigerator before decomposition is detected. IR (CH_2Cl_2): 2040(m), 1950(sh,m), 1923(s), 1512(br,w) cm^{-1} ; (THF) 2035(m), 1945(m), 1929(m), 1908(m), 1520(br,wk) cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 45.0, 38.5, 36.4; ^1H NMR: δ 3.53, 3.14, 2.86 ppm.

Preparation of $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$

$[\text{Al}(\text{NMe}_2)_3]_2$ (1.61 g, 5.06 mmol) was dissolved in 50 ml hexane cooled to 0°C and a solution of $\text{Mn}_2(\text{CO})_{10}$ (1.97 g, 5.05 mmol) in 50 ml hexane, was added slowly with stirring and protection from light. The solution was stirred for 1 h at 0°C and then warmed to 25°C . The mixture was filtered to remove a small amount of insoluble material and evaporation of the solvent left an orange solid. Recrystallization from cold hexane gave orange crystals (2.96 g, 82% yield). Unreacted $\text{Mn}_2(\text{CO})_{10}$ was removed by gentle sublimation. The product is significantly more stable in solution and the solid state compared to the iron analog. IR (benzene): 2046(m), 2010(s), 1980(m), 1928(w), 1910(w), 1483(m) cm^{-1} ; ^1H NMR (C_6D_6): δ 2.97, 2.64, 2.24 ppm.

Collection of X-ray data

$Fe_2(CO)_8[C(NMe_2)OAl(NMe_2)_2]_2$. A small yellow crystal of dimensions $0.18 \times 0.37 \times 0.60$ mm was sealed in a glass capillary under nitrogen. The crystal was centered on a Syntex P3/F automated diffractometer and determination of the crystal class, orientation matrix and accurate unit cell parameters were performed in a standard manner [8]. The data were collected at 20°C by the omega scan method using Mo- K_α radiation, a scintillation counter and pulse height analyzer. Details of the data collection are summarized in Table 1. Inspection of a short data set indicated it to be triclinic in space group $P\bar{1}$ or its noncentric counterpart $P1$. The lattice constants were obtained from a least-squares fit to the automatically centered settings for 25 reflections ($11.9^\circ < 2\theta < 48.2^\circ$). The data were corrected for Lorentz and polarization effects and an empirical absorption correction based upon 360

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $Fe_2(CO)_8[C(NMe_2)OAl(NMe_2)_2]_2$ (I) AND $Mn_2(CO)_9[C(NMe_2)OAl_2(NMe_2)_5]$ (II)

	I	II
<i>(A) Crystallographic parameters</i>		
Formula	$FeAlO_5N_3C_{11}H_{18}$	$Mn_2Al_2O_{10}N_6C_{22}H_{36}$
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
<i>a</i> (Å)	9.373(2)	8.994(2)
<i>b</i> (Å)	9.606(2)	14.233(4)
<i>c</i> (Å)	10.257(2)	14.905(4)
α (°)	88.98(2)	65.85(2)
β (°)	78.43(2)	74.81(2)
γ (°)	65.36(1)	82.08(2)
<i>V</i> (Å ³)	820.2(2)	1679.2(7)
<i>Z</i>	2	2
mol. wt.	355.15	549.25
<i>D</i> (calcd) (g cm ⁻³)	1.44	1.09
μ (Mo- K_α) (cm ⁻¹)	9.9	8.6
<i>(B) Measurement of intensity data</i>		
Diffractometer:	Syntex P3/F	
Radiation:	Mo- K_α (λ 0.71069 Å)	
Monochromator:	highly oriented graphite crystal	
Reflections collected:	$\pm h \pm k \pm l$	$+ h \pm k \pm l$
2θ limits:	$2^\circ < \pm h, \pm k, \pm l < 60^\circ$	$2^\circ < + h, \pm k \pm l < 60^\circ$
Scan range:	0.7° below $\omega(0)$ to 0.7° above $\omega(0)$	1.25° below $2\theta(K_{a1})$ to 1.25° above $2\theta(K_{a2})$
Scan speed:	6–30 deg m ⁻¹	4–30 deg min ⁻¹
Background counting time/ total scan time:	0.5	0.5
Standard reflections:	3 measured every 141 [–500, 070, 007] no significant changes in intensity	3 measured every 141 [500, 040, 005] no significant changes in intensity
Reflections collected:	12,166 total merged to 5947 unique data	9546 total merged to 9023 unique data
Reflections observed:	4307 with $F > 3\sigma(F)$	4679 with $F > 3\sigma(F)$

azimuthal (ψ) scans was applied. The R before correction was 2.9% and R after correction was 2.6%. The maximum and minimum transmissions were 0.53 and 0.46, respectively. Redundant and equivalent reflections were averaged and converted to unscaled $|F_o|$ values.

$Mn_2(CO)_9[C(NMe_2)OAl_2(NMe_2)_5]$. An orange crystal, shaped as a triangular plate $0.46 \times 0.46 \times 0.68$ mm on its sides and 0.24 mm thick, was lodged in a glass capillary under nitrogen. The crystal was treated as described above. A short data set indicated the triclinic space group $P\bar{1}$ or $P1$. Lattice constants were obtained from automatically centered settings for 25 reflections in the 2θ range 5.09 to 34.39° . Data were corrected for Lorentz and polarization effects and an empirical absorption correction based upon 288 azimuthal (ψ) scans was applied. The R before correction was 3.1% and R after correction was 3.1%. The maximum and minimum transmissions were 0.77 and 0.68, respectively.

Solution and refinement of the structure

All calculations were performed on the Syntex R3/XTL structure solution system. Scattering factors for neutral atoms were resident in the program, and both real ($\Delta f'$) and imaginary ($\Delta f''$) components of the anomalous dispersion were included. The function minimized during the least squares refinement process was $\sum w(|F_o| - |F_c|)^2$.

$Fe_2(CO)_8[C(NMe_2)OAl(NMe_2)_2]_2$. The structure was solved by direct methods in the space group $P1$ which gave reasonable starting positions for $Fe(CO)_2$ and AlN_3 fragments. Subsequent difference maps revealed the rest of the structure. Isotropic refinement with 4307 data above the $3\sigma(F)$ threshold gave $R = 13\%$ on 85

TABLE 2

POSITIONAL PARAMETERS FOR $Fe_2(CO)_8[C(NMe_2)OAl(NMe_2)_2]_2$

Atom	x/a	y/b	z/c
Fe	0.19135(4)	0.04792(4)	0.78262(4)
C(1)	0.3360(4)	-0.0514(3)	0.6370(3)
O(1)	0.4266(3)	-0.1188(3)	0.5423(2)
C(2)	0.1934(3)	0.0897(3)	0.9510(3)
O(2)	0.1940(3)	0.1164(3)	1.0593(2)
C(3)	-0.0111(3)	0.1292(3)	0.7567(3)
O(3)	-0.1395(2)	0.1640(3)	0.7459(3)
C(4)	0.1885(4)	-0.1294(3)	0.8304(3)
O(4)	0.1940(4)	-0.2462(2)	0.8607(3)
C(5)	0.2529(3)	0.2213(3)	0.7368(2)
O(5)	0.1680(2)	0.3436(2)	0.6783(2)
Al	-0.00993(8)	0.46002(7)	0.63322(7)
N(1)	-0.0282(3)	0.3793(2)	0.4690(2)
C(6)	0.1015(6)	0.2238(3)	0.4182(3)
C(7)	-0.1875(5)	0.3769(5)	0.4737(4)
N(2)	-0.1767(3)	0.5272(3)	0.7696(3)
C(8)	-0.1645(8)	0.4958(5)	0.9035(4)
C(9)	-0.3410(4)	0.6199(5)	0.7656(5)
N(3)	0.3824(2)	0.2288(2)	0.7611(2)
C(10)	0.4197(4)	0.3615(3)	0.7339(3)
C(11)	0.5076(3)	0.1046(3)	0.8125(3)

variables. Anisotropic refinement on all nonhydrogen atoms gave R 7.7% on 190 variables. The hydrogen atoms were included in idealized positions (riding model) and subsequent refinements gave R 7.0%. All hydrogen atoms were then allowed to vary in position and the refinement converged at R 6.7%. The positions of the hydrogen atoms on C(9) were not those expected: bond lengths C(9)–H(9a) 0.58(7) Å, C(9)–H(9b) 0.95(4) Å and C(9)–H(9c) 1.11(5) Å. Therefore, all hydrogens were allowed to vary freely except those on C(9) which were calculated using the riding model. The U_{iso} 's for the hydrogen atoms were set to 1.2 times the last U_{equiv} of their

TABLE 3

POSITIONAL PARAMETERS FOR $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$

Atom	x/a	y/b	z/c
Mn(1)	0.32523(8)	0.21972(5)	0.17786(5)
Mn(2)	0.05812(8)	0.35682(5)	0.19848(5)
Al(1)	0.45200(15)	-0.11409(9)	0.29436(9)
N(1)	0.6392(4)	0.1213(2)	0.1255(3)
C(1)	0.7137(6)	0.2198(3)	0.0733(4)
C(2)	0.7451(5)	0.0337(3)	0.1234(4)
N(2)	0.2515(4)	-0.1674(3)	0.3660(2)
C(3)	0.1160(5)	-0.0978(4)	0.3450(6)
C(4)	0.2368(9)	-0.2099(6)	0.4770(4)
N(3)	0.5856(4)	-0.1384(3)	0.3706(3)
C(5)	0.6333(7)	-0.0592(4)	0.3926(5)
C(6)	0.6349(9)	-0.2409(4)	0.4362(4)
Al(2)	0.27872(15)	-0.26873(9)	0.30363(10)
N(4)	0.4681(4)	-0.1954(2)	0.2155(2)
C(7)	0.6147(5)	-0.2576(4)	0.2078(4)
C(8)	0.4499(6)	-0.1344(4)	0.1116(3)
N(5)	0.3233(4)	-0.3962(3)	0.3855(3)
C(9)	0.4140(8)	-0.4706(4)	0.3510(6)
C(10)	0.2289(9)	-0.4495(5)	0.4847(4)
N(6)	0.1312(4)	-0.2611(3)	0.2401(3)
C(11)	0.0516(7)	-0.1731(5)	0.1768(5)
C(12)	0.0536(7)	-0.3523(4)	0.2632(6)
C(13)	0.4894(5)	0.1110(3)	0.1716(3)
O(1)	0.4462(3)	0.0139(2)	0.2139(2)
C(14)	0.4357(5)	0.2887(3)	0.2182(3)
O(2)	0.5053(4)	0.3303(3)	0.2442(3)
C(15)	0.2111(5)	0.1568(3)	0.1350(3)
O(3)	0.1445(4)	0.1175(3)	0.1046(3)
C(16)	0.3819(5)	0.3123(3)	0.0462(4)
O(4)	0.4154(4)	0.3692(3)	-0.0353(3)
C(17)	0.2525(5)	0.1407(3)	0.3124(4)
O(5)	0.2122(5)	0.0923(3)	0.3961(3)
C(18)	0.1099(5)	0.3388(4)	0.3169(4)
O(6)	0.1391(4)	0.3301(3)	0.3892(3)
C(19)	0.1977(6)	0.4603(4)	0.1286(4)
O(7)	0.2808(4)	0.5255(3)	0.0853(3)
C(20)	-0.0491(5)	0.2380(4)	0.2622(3)
O(8)	-0.1195(4)	0.1654(3)	0.3016(3)
C(21)	-0.1071(6)	0.4402(4)	0.2149(4)
O(9)	-0.2109(4)	0.4937(3)	0.2246(3)
C(22)	0.0418(5)	0.3606(3)	0.0771(4)
O(10)	0.0278(4)	0.3630(3)	0.0017(3)

parent atom. A final series of refinements with 235 parameters and 4307 reflections with $F > 3\sigma(F)$ resulted in: $R_F = \sum \|F_o| - |F_c| \| / \sum |F_o| = 6.73\%$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 5.17\%$, $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2} = 1.49$, $m = 4307$, $n = 235$, $w^{-1} = [\sigma(F)^2]$. A final difference map showed seven peaks ($0.64\text{--}0.39 \text{ e}\text{\AA}^{-3}$) with the top six within 0.97 \AA of the iron atom. Positional parameters are listed in Table 2.

$\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$. The structure was solved by using a sharpened Patterson (E^*F) map which provided trial positions for the two Mn atoms and an Al atom. A difference map obtained by phasing on these atom positions gave trial positions for the rest of the non-hydrogen atoms. Isotropic refinement with 4679 data above the $3\sigma(F)$ threshold gave $R = 13\%$ on 169 parameters. Anisotropic refinement on the non-hydrogen atoms gave R 9.1% on 379 parameters. The hydrogen atoms were included in idealized positions (riding model) with their U_{iso} 's set at 1.2 times U_{equiv} of their parent atom and subsequent refinements gave R 8.0%. All hydrogen atoms were then allowed to vary in U_{iso} and refinement converged at R_F 8.0%, R_{wF} 4.8%, $\text{GOF} = 1.77$, $m = 4679$, $n = 415$, $w^{-1} = [\sigma^2(F) + |g|F^2]$, $g = 0.00001$. A final difference map showed no peaks above the ripple amplitude, $0.593 \text{ e}\text{\AA}^{-3}$. Positional parameters are listed in Table 3.

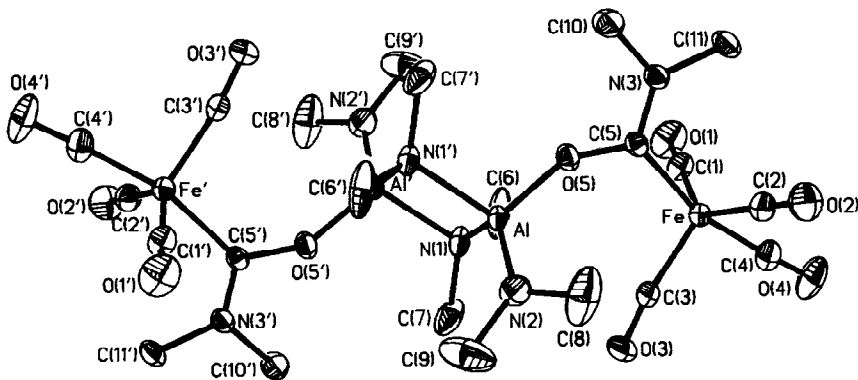


Fig. 1. Molecular structure and labelling scheme for $\text{Fe}_2(\text{CO})_8[\text{C}(\text{NMe}_2)\text{OAl}(\text{NMe}_2)_2]_2$.

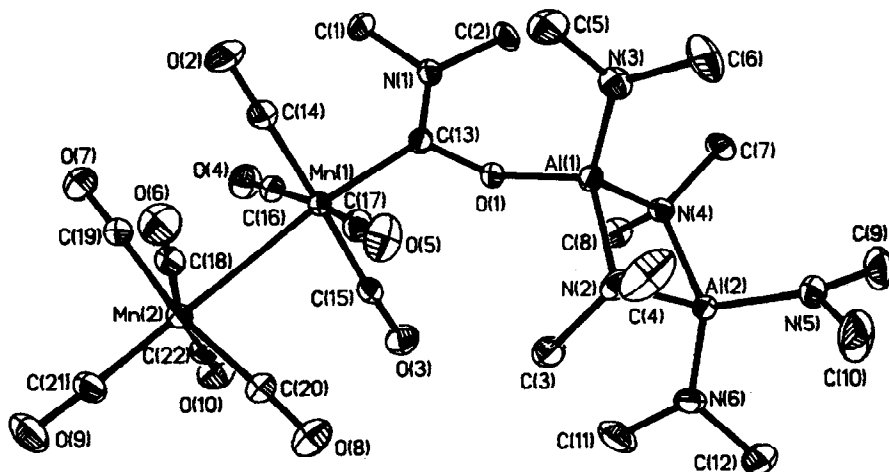


Fig. 2. Molecular structure and labelling scheme for $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$.

Description of the structures

The molecular structure of $\text{Fe}_2(\text{CO})_8[\text{C}(\text{NMe}_2)\text{OAl}(\text{NMe}_2)_2]_2$ (I) can be considered to be a dimer of $\text{Fe}(\text{CO})_4[\text{C}(\text{NMe}_2)\text{OAl}(\text{NMe}_2)_2]$ with dimerization occurring through a central $\text{Al}_2(\text{NMe}_2)_2$ ring. The ring is planar within experimental error. The aluminum atoms each have two *exo* substituents: a NMe_2 group and a $(\text{CO})_4\text{FeC}(\text{NMe}_2)\text{O}$ group, with *trans* orientations across the four-membered ring. The $\text{C}(\text{NMe}_2)\text{O}$ substituent on the $\text{Fe}(\text{CO})_4$ fragment occupies an axial position. A view of the molecule is shown in Fig. 1. Bond distances and angles are summarized in Table 4.

The molecular structure of $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$ (II) also contains an $\text{Al}_2(\text{NMe}_2)_2$ ring, but the substituent arrangement on this ring does not parallel the symmetrical arrangement found in I. One aluminum atom is bonded to two *exo*- NMe_2 groups while the second aluminum atom is bonded to one *exo*- NMe_2

TABLE 4
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $\text{Fe}_2(\text{CO})_8[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_2]_2$

Fe–C(1)	1.772(3)	Fe–C(2)	1.786(3)
Fe–C(3)	1.800(3)	Fe–C(4)	1.773(3)
Fe–C(5)	1.998(3)	C(1)–O(1)	1.147(3)
C(2)–O(2)	1.145(4)	C(3)–O(3)	1.135(4)
C(4)–O(4)	1.142(4)	C(5)–O(5)	1.327(3)
C(5)–N(3)	1.318(4)	O(5)–Al	1.726(2)
Al–N(1)	1.934(3)	Al–N(2)	1.769(2)
Al–Ala	2.817(1)	Al–N(1a)	1.965(2)
N(1)–C(6)	1.496(3)	N(1)–C(7)	1.494(6)
N(1)–Ala	1.965(2)	N(2)–C(8)	1.418(5)
N(2)–C(9)	1.431(4)	N(3)–C(10)	1.464(4)
N(3)–C(11)	1.462(3)		
C(1)–Fe–C(2)	136.4(1)	C(1)–Fe–C(3)	113.0(1)
C(2)–Fe–C(3)	110.6(1)	C(1)–Fe–C(4)	88.5(1)
C(2)–Fe–C(4)	88.4(1)	C(3)–Fe–C(4)	94.3(1)
C(1)–Fe–C(5)	85.6(1)	C(2)–Fe–C(5)	86.4(1)
C(3)–Fe–C(5)	100.7(1)	C(4)–Fe–C(5)	165.0(1)
Fe–C(1)–O(1)	177.5(4)	Fe–C(2)–O(2)	179.6(4)
Fe–C(3)–O(3)	171.5(3)	Fe–C(4)–O(4)	177.0(3)
Fe–C(5)–O(5)	125.2(1)	Fe–C(5)–N(3)	124.3(2)
O(5)–C(5)–N(3)	111.5(2)	C(5)–O(5)–Al	150.0(2)
O(5)–Al–N(1)	111.2(1)	O(5)–Al–N(2)	113.2(1)
N(1)–Al–N(2)	119.6(1)	O(5)–Al–Ala	116.9(1)
N(1)–Al–Ala	44.2(1)	N(2)–Al–Ala	129.5(1)
O(5)–Al–N(1a)	107.0(1)	N(1)–Al–N(1a)	87.5(1)
N(2)–Al–N(1a)	115.3(1)	Ala–Al–N(1a)	43.3(1)
Al–N(1)–C(6)	114.5(2)	Al–N(1)–C(7)	114.1(2)
C(6)–N(1)–C(7)	108.8(3)	Al–N(1)–Ala	92.5(1)
C(6)–N(1)–Ala	110.8(2)	C(7)–N(1)–Ala	115.5(2)
Al–N(2)–C(8)	123.5(3)	Al–N(2)–C(9)	127.2(3)
C(8)–N(2)–C(9)	109.2(4)	C(5)–N(3)–C(10)	123.2(2)
C(5)–N(3)–C(11)	124.2(2)	C(10)–N(3)–C(11)	112.5(2)

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$

Mn(1)–Mn(2)	2.913(1)	Mn(1)–C(13)	2.000(4)
Mn(1)–C(14)	1.837(6)	Mn(1)–C(15)	1.824(6)
Mn(1)–C(16)	1.841(4)	Mn(1)–C(17)	1.840(4)
Mn(2)–C(18)	1.851(6)	Mn(2)–C(19)	1.844(5)
Mn(2)–C(20)	1.830(5)	Mn(2)–C(21)	1.799(5)
Mn(2)–C(22)	1.832(6)	Al(1)–N(2)	1.916(3)
Al(1)–N(3)	1.771(5)	Al(1)–Al(2)	2.806(2)
Al(1)–N(4)	1.928(4)	Al(1)–O(1)	1.726(3)
N(1)–C(1)	1.453(5)	N(1)–C(2)	1.467(6)
N(1)–C(13)	1.340(5)	N(2)–C(3)	1.475(6)
N(2)–C(4)	1.486(6)	N(2)–Al(2)	1.971(5)
N(3)–C(5)	1.440(9)	N(3)–C(6)	1.470(6)
Al(2)–N(4)	1.978(3)	Al(2)–N(5)	1.785(3)
Al(2)–N(6)	1.790(5)	N(4)–C(7)	1.489(5)
N(4)–C(8)	1.474(5)	N(5)–C(9)	1.427(8)
N(5)–C(10)	1.444(6)	N(6)–C(11)	1.453(7)
N(6)–C(12)	1.431(8)	C(13)–O(1)	1.328(5)
C(14)–O(2)	1.144(8)	C(15)–O(3)	1.148(7)
C(16)–O(4)	1.137(5)	C(17)–O(5)	1.136(5)
C(18)–O(6)	1.128(8)	C(19)–O(7)	1.133(6)
C(20)–O(8)	1.141(6)	C(21)–O(9)	1.139(6)
C(22)–O(10)	1.150(8)		
Mn(2)–Mn(1)–C(13)	172.6(1)	Mn(2)–Mn(1)–C(14)	90.4(1)
C(13)–Mn(1)–C(14)	95.2(2)	Mn(2)–Mn(1)–C(15)	87.4(1)
C(13)–Mn(1)–C(15)	87.1(2)	C(14)–Mn(1)–C(15)	177.4(2)
Mn(2)–Mn(1)–C(16)	86.6(1)	C(13)–Mn(1)–C(16)	98.2(2)
C(14)–Mn(1)–C(16)	90.4(2)	C(15)–Mn(1)–C(16)	88.0(2)
Mn(2)–Mn(1)–C(17)	86.4(1)	C(13)–Mn(1)–C(17)	89.0(2)
C(14)–Mn(1)–C(17)	87.4(2)	C(15)–Mn(1)–C(17)	94.0(2)
C(16)–Mn(1)–C(17)	172.6(2)	Mn(1)–Mn(2)–C(18)	84.0(2)
Mn(1)–Mn(2)–C(19)	84.7(2)	C(18)–Mn(2)–C(19)	89.3(2)
Mn(1)–Mn(2)–C(20)	84.4(2)	C(18)–Mn(2)–C(20)	91.1(2)
C(19)–Mn(2)–C(20)	168.9(2)	Mn(1)–Mn(2)–C(21)	178.4(2)
C(18)–Mn(2)–C(21)	94.5(3)	C(19)–Mn(2)–C(21)	95.9(2)
C(20)–Mn(2)–C(21)	95.1(2)	Mn(1)–Mn(2)–C(22)	85.0(1)
C(18)–Mn(2)–C(22)	168.9(2)	C(19)–Mn(2)–C(22)	88.4(2)
C(20)–Mn(2)–C(22)	89.1(2)	C(21)–Mn(2)–C(22)	96.5(3)
N(2)–Al(1)–N(3)	115.0(2)	N(2)–Al(1)–Al(2)	44.6(1)
N(3)–Al(1)–Al(2)	123.0(1)	N(2)–Al(1)–N(4)	88.6(2)
N(3)–Al(1)–N(4)	119.0(2)	Al(2)–Al(1)–N(4)	44.8(1)
N(2)–Al(1)–O(1)	113.1(1)	N(3)–Al(1)–O(1)	111.6(2)
Al(2)–Al(1)–O(1)	125.3(1)	N(4)–Al(1)–O(1)	107.5(2)
C(1)–N(1)–C(2)	113.1(3)	C(1)–N(1)–C(13)	123.7(4)
C(2)–N(1)–C(13)	123.2(3)	Al(1)–N(2)–C(3)	118.1(3)
Al(1)–N(2)–C(4)	111.2(4)	C(3)–N(2)–C(4)	107.0(5)
Al(1)–N(2)–Al(2)	92.4(2)	C(3)–N(2)–Al(2)	111.7(4)
C(4)–N(2)–Al(2)	116.3(4)	Al(1)–N(3)–C(5)	122.6(3)
Al(1)–N(3)–C(6)	125.4(4)	C(5)–N(3)–C(6)	110.7(5)
Al(1)–Al(2)–N(2)	43.0(1)	Al(1)–Al(2)–N(4)	43.4(1)
N(2)–Al(2)–N(4)	85.7(2)	Al(1)–Al(2)–N(5)	115.1(2)
N(2)–Al(2)–N(5)	113.3(2)	N(4)–Al(2)–N(5)	111.3(2)
Al(1)–Al(2)–N(6)	130.7(1)	N(2)–Al(2)–N(6)	114.2(2)
N(4)–Al(2)–N(6)	115.0(2)	N(5)–Al(2)–N(6)	114.2(2)
Al(1)–N(4)–Al(2)	91.9(1)	Al(1)–N(4)–C(7)	114.5(3)

TABLE 5 (continued)

Al(2)-N(4)-C(7)	117.8(2)	Al(1)-N(4)-C(8)	113.7(3)
Al(2)-N(4)-C(8)	111.7(3)	C(7)-N(4)-C(8)	106.9(3)
Al(2)-N(5)-C(9)	123.8(4)	Al(2)-N(5)-C(10)	123.4(4)
C(9)-N(5)-C(10)	108.7(4)	Al(2)-N(6)-C(11)	131.3(4)
Al(2)-N(6)-C(12)	119.4(3)	C(11)-N(6)-C(12)	108.5(5)
Mn(1)-C(13)-N(1)	129.3(3)	Mn(1)-C(13)-O(1)	117.2(3)
N(1)-C(13)-O(1)	113.3(4)	Al(1)-O(1)-C(13)	155.2(3)
Mn(1)-C(14)-O(2)	179.0(4)	Mn(1)-C(15)-O(3)	177.0(4)
Mn(1)-C(16)-O(4)	179.2(5)	Mn(1)-C(17)-O(5)	177.6(5)
Mn(2)-C(18)-O(6)	178.1(4)	Mn(2)-C(19)-O(7)	178.5(4)
Mn(2)-C(20)-O(8)	178.2(4)	Mn(2)-C(21)-O(9)	179.3(4)
Mn(2)-C(22)-O(10)	178.4(4)		

group and a $\text{Mn}_2(\text{CO})_9\text{C}(\text{NMe}_2)\text{O}$ group. The $\text{C}(\text{NMe}_2)\text{O}$ fragment is bonded to Mn(1) in an axial position on the $\text{Mn}_2(\text{CO})_9$ fragment, and the four equatorial CO groups on each Mn form approximate planes with the CO groups in the two planes staggered with respect to each other. A view of the molecule is shown in Fig. 2. Bond distances and angles are summarized in Table 5.

Discussion

Combination of $[\text{Al}(\text{NMe}_2)_3]_2$ with $\text{Fe}(\text{CO})_5$ in a 1/1 mole ratio results in the formation of yellow, crystalline $\text{Fe}_2(\text{CO})_8[\text{C}(\text{NMe}_2)\text{OAl}(\text{NMe}_2)_2]_2$ (I). The crystalline complex is relatively unstable with respect to decomposition which results in several products including the starting reagents. We have observed that the infrared spectra for I are very sensitive to solvent. In THF, four carbonyl bands are typically seen at 2035, 1945, 1929 and 1908 cm^{-1} . This is one more band than expected and one more than reported by Petz and Schmid in THF solutions: 2031, 1949, 1912 cm^{-1} . This observation is consistent with the presence of an impurity in these solutions. With CH_2Cl_2 solutions, three carbonyl bands are typically resolved: 2040, 1950 and 1923 cm^{-1} . In the previous study and in our investigation a relatively broad, weak band between 1530–1505 cm^{-1} is also found, and it has been assigned to a $\text{C}=\text{OAl}$ stretch. The ^1H NMR spectra reported by Petz and Schmid show four resonances at δ 3.63, 3.12, 2.78 and 2.67 ppm which were assigned to terminal carbene amide methyl protons in a *trans* isomer, terminal carbene amide methyl protons in a *cis* isomer, terminal aluminum amide methyl protons and bridging aluminum amide methyl protons, respectively. In the present study, only three resonances are resolved in ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra obtained from fresh solutions of the crystalline compound. It is possible in view of the crystal structure determination, that these solutions contain only the *trans* isomer and hence only three resonances would be expected.

Reaction of $[\text{Al}(\text{NMe}_2)_3]_2$ with $\text{Mn}_2(\text{CO})_{10}$ in a 1/1 ratio results in the formation of an orange crystalline product $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5]$ (II). Unlike I, II is relatively stable surviving reflux in hexane for at least several hours. Infrared spectra for the crystals in benzene show carbonyl bands at 2046(m), 2010(s), 1980(m), 1928(w) and 1910(w) cm^{-1} and a broad band centered at 1483 cm^{-1} which is assigned to a $\text{C}=\text{OAl}$ stretching vibration. The ^1H NMR spectra for II show rather broad resonances centered at δ 2.97, 2.64 and 2.24 ppm.

Spectroscopic data do not provide unambiguous structural assignments for either I or II, consequently single crystal X-ray analyses were undertaken. As described above, the molecular structure of I is identical to that proposed by Petz and Schmid [4]. The interaction of $[\text{Al}(\text{NMe}_2)_3]_2$ results in the coordination of each aluminum atom in the dimer to the oxygen atom of an axial CO ligand of the $\text{Fe}(\text{CO})_5$. Accompanying this coordination, an amide group apparently migrates from an aluminum atom to the carbon atom of the aluminum bonded CO group. The resulting $\text{Al}-\text{O}-\text{C}(\text{NMe}_2)\text{Fe}(\text{CO})_4$ unit can be considered to be an alumino-ferr-amino carbene complex. The Al_2N_2 ring is a parallelogram with $\text{Al}(1)-\text{N}(1)$ 1.934(3) Å, $\text{Al}(1)-\text{N}(1')$ 1.965(2) Å, $\text{N}(1)-\text{Al}(1)-\text{N}(1')$ 87.5(1)° and $\text{Al}(1)-\text{N}(1)-\text{Al}(1')$ 92.5(1)°. These parameters may be compared with related distances and angles in the dimeric compounds $[\text{Me}_2\text{AlNMe}_2]_2$ [9] 1.955(2) Å, 1.972(2) Å, 88.4(3)° and 91.6(3)° and $[(\text{Me}_2\text{N})_2\text{AlNMe}_2]_2$ [10] 1.959(2) Å, 1.980(2) Å, 88.1(1)° and 91.9(1)°. As expected, the terminal $\text{Al}-\text{NMe}_2$ distance $\text{Al}(1)-\text{N}(2)$ in I, 1.769(2) Å, is considerably shorter than the bridging $\text{Al}-\text{N}$ bond distances. It is also significantly shorter than the average terminal $\text{Al}-\text{NMe}_2$ distance in $[(\text{Me}_2\text{N})_2\text{AlNMe}_2]_2$, 1.814 Å. The $\text{Al}(1)-\text{O}(5)$ distance, 1.726(2) Å, is much shorter than the $\text{Al}-\text{O}(\text{carbonyl})$ distances in $\text{Fe}_2\text{Cp}_2(\text{CO})_2[\text{COAlEt}_3]_2$ [11] 2.00(2) Å, in $\text{Mn}[\text{C}(\text{OAlBrBr}_2)\text{CH}_3](\text{CO})_4$ [12] 1.81(1) Å, in $\text{Al}[\text{Mn}(\text{CO})_4(\text{C}(\text{O})\text{CH}_3)_2]_3$ [13] 1.87(1) Å and in $\text{Cp}(\text{CO})\text{Fe}[\text{C}(\text{Me})\text{OAl}(\text{Et})_2\text{N}(\text{t-BuPPh}_2)]$ [14] 1.842(2) Å.

The metallocarbene fragment, $(\text{CO})_4\text{Fe}[\text{C}(\text{NMe}_2)(\text{OAl} \leftarrow)]$ has structural features similar to several other classical carbene complexes. The carbene carbon atom C(5) and amide nitrogen atom N(3) are planar (sums of angles 360.0° and 359.9° respectively) and the C(10)N(3)C(11) and FeC(5)O(5) units are nearly coplanar (interplanar angle 5.8°). The Al(1) atom lies only 0.14 Å out of the least-squares plane containing FeC(5)O(5)C(10)N(3) and C(11). The six atom plane bisects the C(1)FeC(2) angle and makes an angle of 90.2° with the $\text{Fe}(\text{CO})_3$ trigonal plane. A view of the molecule looking down the Fe-C(5) bond is shown in Fig. 3.

The carbene fragment occupies an axial position on an $\text{Fe}(\text{CO})_4$ group. The Fe-C(5) bond distances, 1.998(3) Å, can be compared with Fe-C(carbene) distances in the acyclic complex $(\text{CO})_4\text{Fe}[\text{C}(\text{i-Pr}_2\text{N})\text{OEt}]$ [15] 2.013(3) Å, in the cyclic analog $(\text{CO})_3\text{Fe}[\text{C}(\text{i-Pr}_2\text{N})\text{OCO}(\text{Et})]$ [15] 1.904(6) Å, in $(\text{CO})_4\text{FeCN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)$ [16] 2.007(5) Å and in $\text{Fe}_2(\text{CO})_7\text{C}(\text{OEt})\text{C}_6\text{H}_3(\text{OMe})_2$ [17] 2.00 Å. As expected, this distance is significantly longer than the average Fe-C(carbonyl) distance, 1.783 Å. It is interesting to note that the *trans*-Fe-C(carbonyl) distance, 1.773(3) Å, does not significantly deviate from the average Fe-C(carbonyl) distance which suggests that the carbene fragment is not making unusual electronic demands on the $\text{Fe}(\text{CO})_4$ fragment. The C(5)-O(5) distance in I, 1.327(3) Å is long compared to the range of distances, 1.19–1.21 Å, found in η^1 -acetyl compounds [12]; however, the distance is comparable to the related distances found in $(\text{CO})_4\text{Fe}[\text{C}(\text{i-Pr}_2\text{N})\text{OEt}]$ 1.336(3) Å and in $(\text{CO})_5\text{Cr}[\text{C}(\text{NMe}_2)(\text{OEt})]$ [18] 1.346(5) Å. The C(5)-O(5) distance in I is significantly shorter than the C(carbene)-O distance in the cyclic compound $(\text{CO})_3\text{Fe}[\text{C}(\text{i-Pr}_2\text{N})\text{OCO}(\text{Et})]$ 1.395(7) Å. The C(5)-N(3) distance, 1.318(4) Å, also is similar to the respective C(carbene)-NR₂ distances in the two carbene iron complexes listed above, acyclic 1.326(4) and cyclic 1.329(7) Å, as well as in $(\text{CO})_5\text{Cr}[\text{C}(\text{NMe}_2)(\text{OEt})]$ 1.328(5) Å. The short C-N distances are consistent with a degree of delocalized multiple bond character in the unit $\text{Fe} \equiv \text{C} \equiv \text{NR}_2$ [19].

The molecular structure for II reveals that the $[\text{Al}(\text{NMe}_2)_3]_2$ dimer has attacked

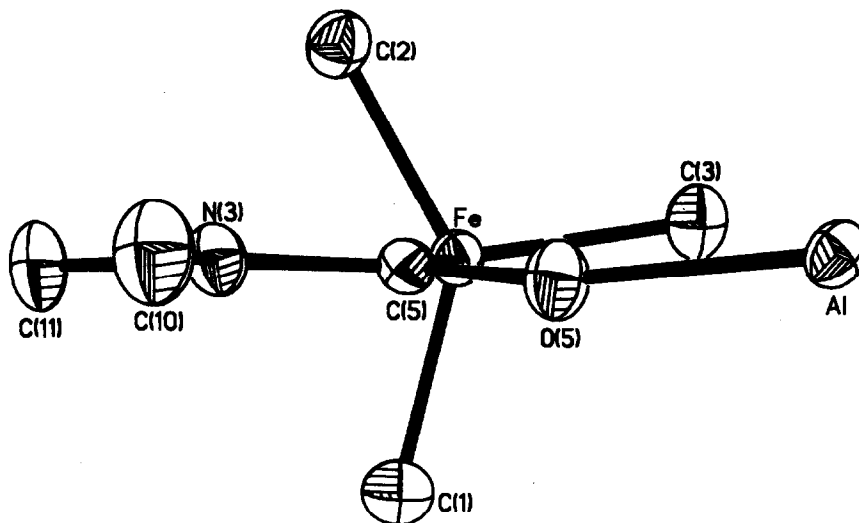


Fig. 3. A partial view of $\text{Fe}_2(\text{CO})_8[\text{C}(\text{NMe}_2)\text{OAl}(\text{NMe}_2)_2]_2$ looking down the Fe–C(5) bond.

one of the axial carbonyls of the parent $\text{Mn}_2(\text{CO})_{10}$. One amide group has transferred to C(13) and one aluminum atom, Al(1), is bonded to the O(1) atom which, in turn, is bonded to C(13). The Al_2N_2 ring is very distorted with short aluminum-bridging amide nitrogen bond distances, Al(1)–N(2) 1.916(3) Å and Al(1)–N(4) 1.928(4) Å, associated with the Al atom which is also bonded to the carbene oxygen atom. The long aluminum-bridging amide nitrogen distances, Al(2)–N(2) 1.971(5) Å and Al(2)–N(4) 1.978(3) Å, are associated with the AlN_4 unit. The internal ring angles N(2)–Al(1)–N(4) 88.6(2)°, N(2)–Al(2)–N(4) 85.7(2)°, Al(1)–N(2)–Al(2) 92.4(2)° and Al(1)–N(4)–Al(2) 91.9(1)° are comparable with the angles in I with the N(2)–Al(2)–N(4) angle being more compressed than the N(2)–Al(1)–N(4) angle. This is consistent with the longer Al–N(ring) bond distance involving Al(2). The terminal Al(2)–NMe₂ distances, 1.785(3) and 1.790(5) Å, are slightly longer than the terminal Al(1)–N(3) distance, 1.771(5) Å, in II as well as the terminal Al–NMe₂ distance in I. The Al(1)–O(1) distance in II is identical with the distance in I. In both cases then, a relatively strong Al–O(carbonyl) bond is implicated.

The $(\text{CO})_4\text{Mn}[\text{C}(\text{NMe}_2)(\text{OAl}(\leftarrow))]$ fragment in II resembles in part the carbene fragment in I, as well as the heavy atom cores in several other carbene manganese compounds. The sums of the angles about the carbene carbon atom C(13) and nitrogen atom N(1) are 359.8 and 360.0° respectively, and the Mn(1)–C(13)–O(1) and N(1)–C(1)–C(2) planes are nearly coplanar (interplanar angle 2.8°). The Al(1) atom lies only 0.59 Å out of the least-squares plane containing Mn, C(13), O(1), N(1), C(1) and C(2). This six atom plane nearly bisects the C(15)–Mn–C(17) and C(16)–Mn–C(14) angles.

The Mn(1)–C(13) bond distance, 2.000(4) Å, is slightly longer than most Mn–C(carbene) distances, 1.83–1.99 Å [12,17,20]. In particular, the Mn–C(carbene) distances in $(\text{CO})_4\text{Mn}[\text{C}(\text{OAlBr}_2)\text{CH}_3]$ [12] and the bimetallic compound $(\text{CO})_5\text{Mn}–\text{Mn}(\text{CO})_4[\text{C}(\text{OEt})\text{Ph}]$ [20] are 1.95(2) and 1.950(5) Å, respectively. This

distance is significantly longer than the average *cis*-Mn(1)-CO distances, 1.836 Å, and Mn(2)-CO, 1.839 Å. Furthermore, the *trans*-Mn(2)-C(21)O distance 1.799(5) is the shortest of all the Mn-CO distances in II. A similar trend in axial and equatorial Mn-CO distances is also seen in (CO)₅Mn-Mn(CO)₄[C(OEt)Ph] and Mn₂(CO)₁₀ [21]. The Mn-Mn bond distance in II is 2.913(1) Å and this distance is comparable with the Mn-Mn distance in Mn₂(CO)₁₀, 2.9038(6) Å.

The remaining structural features of the carbene fragment in II can be compared with the appropriate distances in I. The C(13)-O(1) distance in II, 1.328(5) Å, is identical to the related C(5)-O(5) distance in I, and comparable with the MnC(Ph)-OMe distance, 1.315(6) Å in (CO)₅Mn-Mn(CO)₄[C(OEt)Ph]. The C(13)-N(1) distance 1.340(5) Å in II is considerably longer than the related C(5)-N(3) distance in I.

These studies confirm and extend the interesting amide migration process first proposed to occur between aluminum amides and selected metal carbonyls by Petz and Schmid. The general extent and utility of this reaction is under further study in our laboratory.

Supplementary material. Listings of thermal parameters and structure factor tables can be obtained from R.T.P.

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