was then cannulated into a flame-dried, three-neck, 250-mL round-bottom flask fitted with a reflux condenser, nitrogen inlet, magnetic stir bar, and a thermometer. In the dark, the solution was stirred and brought to 50 °C with a thermostated oil bath. A solution of $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$, 0.5785 g (0.00262 equiv of OH), and DBTA, 0.02 mL (0.08 mmol), in 20 mL of THF was then cannulated (under nitrogen) into the Hypol solution (total volume of THF ≈45 mL). The solution was stirred at 54 °C for 2.5 h until all the Hypol 2000 had reacted (determined by monitoring the decrease in the intensity of the NCO stretch at 2275 cm^{-1}). Absolute ethanol (dried over type 4-Å molecular sieves), 0.2 mL (3.4 mmol), was then added by syringe, and the solution was stirred for 15 min. The polymer was then reprecipitated several times from THF with hexane. The THF/hexane mixture was cannula-filtered from the polymer, and the polymer flask was covered with foil and dried in vacuo (~2 mmHg) for 20.5 h, yielding 1.519 g (69%) of red, gummy polymer. The polymer was transferred to and stored in an amber vial in the glovebox. ^1H NMR ($CDCl_3$): δ, ppm 7.74 (br, 2 H, NH), 7.16, 7.04 (2 br resonances, 4 H, aromatic), 6.55 (br, 3 H, NH), 4.63, 4.54 (2 br resonances, 8 H, C_5H_4), 4.34, 4.29 (br, 8 H, $-CH_2OC(O)$), 4.16 (br, 2 H), 3.62 (s, 79 H, $-(C_2H_4O-)_n$), 2.81 (br, 4 H, $C_5H_4CH_2$), 2.16 (s, 7 H, $-CH_3$). $\bar{M}_n$ (VPO, THF) = 3100 g/mol.

Photochemical Reactions. Photochemical reactions and quantum yield measurements were carried out as previously described.[1,2]

Acknowledgment is made to Amoco Chemical Co. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. W. R. Grace Co. is acknowledged for a sample of the Hypol 2000 prepolymer.

Registry No. 1, 138815-35-7; (1)($NCO(CH_2)_6NCO$) (copolymer), 138834-50-1; **2**, 138815-36-8; **5** (copolymer), 138815-37-9; 6 (copolymer), 138876-19-4; CCl_4, 56-23-5; $C_5H_5(CH_2)_2NH_2$, 138816-65-6; $Mo(CO)_6$, 13939-06-5; triethyl phosphite, 122-52-1.

Supplementary Material Available: Textual presentation of complete experimental details for the synthesis of the cyclopentadienylethyl *p*-toluenesulfonate, cyclopentadienylethyl azide, and (cyclopentadienylethyl)amine and tables with spectroscopic data describing the photochemical reaction products of complexes 2, 3, 5, and 6 with CCl_4 and $P(OEt)_3$ (11 pages). Ordering information is given on any current masthead page.

Clusters Containing Ynamine Ligands. 5. Coordination and Transformations of an Ynamine Ligand in a Dimanganese Complex. Synthesis and Structural Characterization of $Mn_2(CO)_8[\mu\text{-}MeC_2NEt_2]$, $Mn_2(CO)_8[\mu\text{-}H_2CCC(H)NEt_2]$, $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$, and $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$

Richard D. Adams,* Gong Chen, and Yun Chi†

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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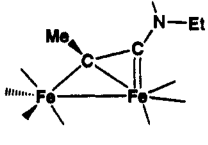
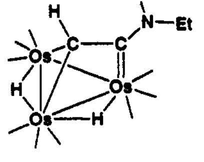
The complex $Mn_2(CO)_8(\mu\text{-}MeC_2NEt_2)$ (1), obtained from the photoreaction of $Mn_2(CO)_{10}$ with MeC_2NEt_2, has been structurally characterized and shown to contain an ynamine ligand asymmetrically bridging the two mutually bonded manganese atoms. The new isomer $Mn_2(CO)_8(\mu\text{-}H_2CCCHNEt_2)$ (2) was isolated in very low yield (0.7%) from this reaction. Compound 2, a second isomer, $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$ (3), and a decarbonylation product of 3, $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$ (4), were obtained in yields of 16%, 8%, and 22%, respectively, by heating 1 to reflux in THF solvent. All three compounds were characterized by crystallographic methods. Compound 2 is the first example of a metal complex containing a aminoallene ligand. This ligand bridges the two metal atoms. Compound 3 contains a bridging η^2 metalated aminoallyl ligand. Compound 4 contains a bridging η^4 metalated aminoallyl ligand. Crystal data: for 1, space group $P2_1/c$, $a = 13.608$ (2) Å, $b = 13.874$ (8) Å, $c = 20.044$ (3) Å, $\beta = 92.32$ (1)°, $Z = 8$, 2293 reflections, $R = 0.053$; for 2, space group $P2_1/n$, $a = 10.414$ (2) Å, $b = 24.02$ (1) Å, $c = 7.618$ (2) Å, $\beta = 107.86$ (1)°, $Z = 4$, 1412 reflections, $R = 0.040$; for 3, space group $P\bar{1}$, $a = 10.999$ (2) Å, $b = 12.684$ (3) Å, $c = 7.076$ (2) Å, $\alpha = 93.08$ (2)°, $\beta = 107.90$ (2)°, $\gamma = 101.63$ (2)°, $Z = 2$, 1891 reflections, $R = 0.022$; for 4, space group $P2_1/n$, $a = 17.904$ (2) Å, $b = 7.509$ (2) Å, $c = 24.555$ (4) Å, $\beta = 91.19$ (1)°, $Z = 8$, 2180 reflections, $R = 0.031$.

Introduction

Since their discovery approximately 30 years ago, ynamines or aminoacetylenes, RC_2NMe_2, have proved to be versatile reagents for a variety of organic syntheses.[1] Studies of their coordination in metal complexes have shown that they generally adopt an unusual asymmetric bridging coordination in which the amine-substituted carbon atom is bonded to only one metal atom,[2-6] as is found in the complexes $Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$,[2a] $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$,[6] and $Os_3(CO)_9(\mu\text{-}HC_2NEt_2)(\mu\text{-}H)_2$.[3]



$Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$



$Os_3(CO)_9(\mu\text{-}HC_2NEt_2)(\mu\text{-}H)_2$

A theoretical analysis of the triosmium complex indicated that the unusual coordination can be attributed in

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[†] On leave from the Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan.

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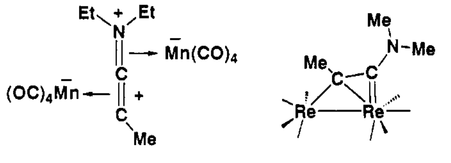
part to strong interactions of the lone pair of electrons on the nitrogen atom with the alkynyl grouping;[7] however, an analysis of the dirhenium complex indicates that the twisted structure results more from a stabilization of the HOMO, which is predominantly metal–metal bonding in character.[8] It was proposed and demonstrated that the amine-substituted carbon atom in most of these complexes possesses a carbene-like character.[2–6,9]

In 1976, King et al. reported a complex having the empirical formula $Mn_2(CO)_8(\mu\text{-}MeC_2NEt_2)$ (1) that was obtained by the UV irradiation of solutions of $Mn_2(CO)_{10}$ and the ynamine $MeC{\equiv}CNEt_2$.[10] On the basis of spectroscopic data structure A was proposed. This structure contrasts with those of the related compound $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$[6] and its mixed metal homologue $MnRe(CO)_8(\mu\text{-}MeC_2NMe_2)$,[8] which were recently prepared and structurally characterized by us and were found to exhibit asymmetric bridging coordination. Accordingly, we have prepared the complex 1 by the previously reported method and have determined its structure by single-crystal X-ray diffraction methods. We have found that in addition to compound 1, small amounts of an unreported isomer, 2, are also formed in the same reaction. This isomer can be obtained by thermal transformation of 1. Compound 2 can be converted thermally to a third isomer, 3, which is subsequently decarbonylated to yield another new complex, 4. Details of the syntheses of compounds 2–4 and the crystal structure analyses and transformations of each of the compounds 1–4 are reported here.



A

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Reagent grade solvent tetrahydrofuran was distilled from sodium/benzophenone before use. All chromatographic separations were performed in air on TLC plates (0.25 mm silica gel 60 F_{254}). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer. UV irradiations were performed by using an externally positioned Gates (Long Island, NY) 360-W high-pressure mercury lamp on reaction solutions in Pyrex glassware. Elemental analyses were performed by Desert Analytics, Tucson, AZ. $Mn_2(CO)_{10}$ was purchased from Strem Chemicals Co. MeC_2NEt_2 was prepared by the reported procedure.[11]

Reaction of MeC_2NEt_2 with $Mn_2(CO)_{10}$. A mixture of MeC_2NEt_2 (0.6 mL) and $Mn_2(CO)_{10}$ (470 mg, 1.205 mmol) in 60 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 14 h at 25 °C. After irradiation, the solvent was removed and the residue was chromatographed over a short column of Florisil with a mixture of hexane/CH_2Cl_2 (2/1) to remove the unreacted $Mn_2(CO)_{10}$ (150 mg, 0.385 mmol) and a red-orange oily material. The latter was separated by TLC on silica gel with hexane/CH_2Cl_2 (2/1) to yield 65 mg of red-orange $Mn_2(CO)_8(MeCCNEt_2)$ (1; 0.0146 mmol, 18%) and 2.6 mg of orange $Mn_2(CO)_8(\mu\text{-}H_2CCCHNEt_2)$ (2; 0.006 mmol, 0.7%). The yield of 1 and 2 was calculated on the basis of the $Mn_2(CO)_{10}$ consumed in the reaction. Spectral data for 1 are as follows. MS (EI, ^{55}Mn): m/z 445 (M^+). IR (in C_6H_{12}, cm^{-1}) $\nu(CO)$ 2070 (m), 2018 (s), 1981 (vs), 1967 (s), 1958 (s), 1944 (m), 1935 (s); $\nu(CN)$ 1625 (vw). ^1H NMR (in $CDCl_3$, ppm): 3.67 (4 H, br), 2.77 (3 H, s), 1.35 (6 H, m). ^1H NMR (in C_6D_6, ppm): 2.90 (1 H, m, $^3J_{H-H}$ = 7.3 Hz), 2.70 (3 H, m), 2.48 (3 H, s), 0.61 (3 H, t, $^3J_{H-H}$ = 7.3 Hz), 0.44 (3 H, t, J_{H-H} = 7.3 Hz). Spectral data for 2 are as follows. IR (in C_6H_{12}, cm^{-1}): $\nu(CO)$ 2066 (m), 2013 (vs), 1977 (s), 1968 (vs), 1956 (s), 1943 (w), 1935 (m); $\nu(CN)$ 1554 (vw). ^1H NMR (in $CDCl_3$, ppm): 7.45 (s, 1 H), 3.49 (4 H, br), 2.74 (1 H, s), 2.54 (1 H, s), 1.40 (3 H, br), 1.26 (3 H, br). ^1H NMR (in C_6D_6, ppm): 7.18 (1 H, s), 2.66 (1 H, m, $^3J_{H-H}$ = 7.4 Hz), 2.57 (1 H, m, $^3J_{H-H}$ = 7.4 Hz), 2.43 (1 H, s), 2.17 (2 H, q, $^3J_{H-H}$ = 7.4 Hz), 1.97 (1 H, s), 0.57 (3 H, t, $^3J_{H-H}$ = 7.4 Hz), 0.42 (3 H, t, $^3J_{H-H}$ = 7.4 Hz). Anal. Calcd (found) for 1: C, 40.47 (40.03); H, 2.94 (2.80); N, 3.15 (3.01). Calcd (found) for 2: C, 40.47 (39.20); H, 2.94 (2.68); N, 3.15 (3.01).

Thermolysis of 1. A solution of 1 (23.0 mg, 0.0517 mmol) in 40 mL of THF was heated to reflux for 1.5 h. After the solution was cooled, the solvent was removed in vacuo and the residue was separated by TLC. Elution with a CH_2Cl_2/hexane (1/1) solvent mixture first separated a yellow band of $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$ (3; 2.8 mg, 8%). With a CH_2Cl_2/hexane (1/9) mixture a yellow band of $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$ (4; 6.8 mg, 22%) and an orange band of 2 (5.4 mg, 16%) were separated. Spectral data for 3 are as follows. IR (in hexane, cm^{-1}): $\nu(CO)$ 2068 (m), 2016 (m), 1979 (vs), 1962 (m), 1950 (m), 1935 (m); $\nu(CN)$ 1577 (vw). ^1H NMR (in C_6D_6, ppm): 7.71 (1 H, d, $^3J_{H-H}$ = 11.2 Hz), 5.25 (1 H, d, $^3J_{H-H}$ = 10.8 Hz), 3.10 (1 H, dd, $^3J_{H-H}$ = 11.2 Hz, $^3J_{H-H}$ = 10.8 Hz), 2.09 (2 H, m), 1.85 (2 H, m), 0.34 (3 H, t, $^3J_{H-H}$ = 7.35 Hz), 0.31 (3 H, t, $^3J_{H-H}$ = 7.17 Hz). Spectral data for 4 are as follows. IR (in hexane, cm^{-1}): $\nu(CO)$ 2061 (m), 2015 (vs), 1989 (m), 1970 (s), 1953 (m), 1875 (w). ^1H NMR (in C_6D_6, ppm): 8.24 (1 H, s, br), 5.18 (1 H, s, br), 3.13 (1 H, s, br), 2.43 (1 H, dq, $^3J_{H-H}$ = 7.3 Hz, $^2J_{H-H}$ = 13.6 Hz), 2.20 (1 H, dq, $^3J_{H-H}$ = 7.3 Hz, $^2J_{H-H}$ = 13.6 Hz), 1.45 (1 H, dq, $^3J_{H-H}$ = 7.3 Hz, $^2J_{H-H}$ = 13.6 Hz), 1.04 (1 H, dq, $^3J_{H-H}$ = 7.3 Hz, $^2J_{H-H}$ = 13.6 Hz), 0.14 (3 H, t, $^3J_{H-H}$ = 7.3 Hz), 0.12 (3 H, t, $^3J_{H-H}$ = 7.3 Hz). Anal. Calcd (found) for 3: C, 40.47 (40.58); H, 2.94 (2.84); N, 3.15 (3.00). Calcd (found) for 4: C, 40.27 (39.72); H, 3.12 (3.03); N, 3.36 (3.17).

Thermolysis of 2. A solution of 2 (23.0 mg in 40 mL of THF) was heated to reflux for 1.5 h. After it was cooled, the mixture was worked up (same procedure as described above) to yield unreacted 2 (8.0 mg), 1.5 mg of 3 (7%), and 3.0 mg of 4 (14%).

Thermolysis of 3. A THF solution (40 mL) of 3 (15.5 mg, 0.0348 mmol) was heated to reflux for 1.5 h. After the solution was cooled and the solvent was removed in vacuo, separation by TLC (as described above) yielded 2.2 mg of unreacted 3 and 3.9 mg of 4 (27%).

Crystallographic Analyses. Orange crystals of 1 and 2 suitable for X-ray diffraction analyses were grown from solution in hexane/CH_2Cl_2 solvent mixtures by slow evaporation of the solvent at 25 °C. Yellow crystals of 3 and orange crystals of 4 were grown from hexane/CH_2Cl_2 solvent mixtures by slow evaporation of solvent at 0 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromatized Mo Kα radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was

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Table I. Crystallographic Data for Compounds 1-4

	1	2	3	4
formula	$Mn_2O_8NC_{15}H_{13}$	$Mn_2O_8NC_{15}H_{13}$	$Mn_2O_8NC_{15}H_{13}$	$Mn_2O_7NC_{14}H_{13}$
fw	445.15	445.15	445.15	417.14
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
lattice params				
a, Å	13.608 (2)	10.414 (2)	10.999 (2)	17.904 (2)
b, Å	13.874 (8)	24.02 (1)	12.684 (3)	7.509 (2)
c, Å	20.044 (3)	7.618 (2)	7.076 (2)	24.555 (4)
α, deg			93.08 (2)	
β, deg	92, 32 (1)	107.86 (2)	107.90 (2)	91.19 (1)
γ, deg			101.63 (2)	
V, Å^3	3781 (2)	1814 (1)	912.9 (8)	3300.6 (9)
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Z	8	4	2	8
D_{calc}, g/cm^3	1.56	1.63	1.62	1.68
μ(Mo Kα), cm^{-1}	13.21	13.77	13.68	15.03
temp, °C	20	20	20	20
$2\theta_{max}$, deg	40.1	48.5	44.0	40.0
no. of observns ($I > 3\sigma(I)$)	2293	1412	1891	2180
no. of variables	469	247	287	381
residuals: R, R_w	0.053, 0.060	0.040, 0.044	0.022, 0.024	0.031, 0.030
goodness-of-fit indicator	2.19	2.41	1.45	1.30
max shift in final cycle	0.00	0.04	0.00	0.04
largest peak in final diff map, e/Å^3	0.73	0.44	0.18	0.30
abs corr	empirical	empirical	empirical	empirical
max/min	1.00/0.68	1.00/0.88	1.00/0.84	1.00/0.95

performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] Lorentz–polarization (Lp) and empirical absorption corrections were applied in structure analysis. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compounds 1, 2, and 4 each crystallized in the monoclinic crystal system. The space group $P2_1/c$ or $P2_1/n$ for each was determined uniquely from the systematic absences observed during the collection of data. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The metal atoms were located in an E-map. Nonmetal atoms were obtained from difference Fourier syntheses. For 1 and 2 all of the non-hydrogen atoms were refined with anisotropic thermal parameters. For 4 all non-hydrogen atoms except carbon atoms of carbonyl ligands were refined with anisotropic thermal parameters. For 1, 2, and 4 the positions of hydrogen atoms were located from difference Fourier maps. For 1 the scattering contributions of all hydrogen atoms were added to the structure factor calculations, but their positions were not refined. For 2 and 4 the hydrogen atoms bonded to the atoms C(1), C(2), and C(3) were successfully refined; the scattering contributions of all other hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 3 crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods and difference Fourier syntheses. The coordinates of the manganese atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms and hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were refined with isotropic thermal parameters.

Results

The UV irradiation of $Mn_2(CO)_{10}$ in the presence of MeC_2NEt_2 does yield the compound 1 (18%) as reported by King in 1976.[10] The identity of this product was unambiguously established by comparison with its previously reported ^{1}H NMR and IR spectra. The formula established by King was correct, but the structure that was proposed was not. The structure of 1 was established by a single-crystal X-ray analysis that was a part of this study. In the solid state compound 1 contains two symmetry-independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP drawing of one of these molecules is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV, respectively. The structure of 1 is analogous to that of two related members of this series, $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$[6] and its mixed-metal homologue $MnRe(CO)_8(\mu\text{-}MeC_2NMe_2)$.[8] The ynamine ligand bridges the two manganese atoms in the previously established asymmetric fashion. The two manganese atoms are joined by a metal–metal single bond, and the Mn–Mn distance of 2.780 (2) Å (2.791 (2) Å) is slightly shorter than that found in $Mn_2(CO)_{10}$ (2.92 Å).[13] This shortening can be attributed

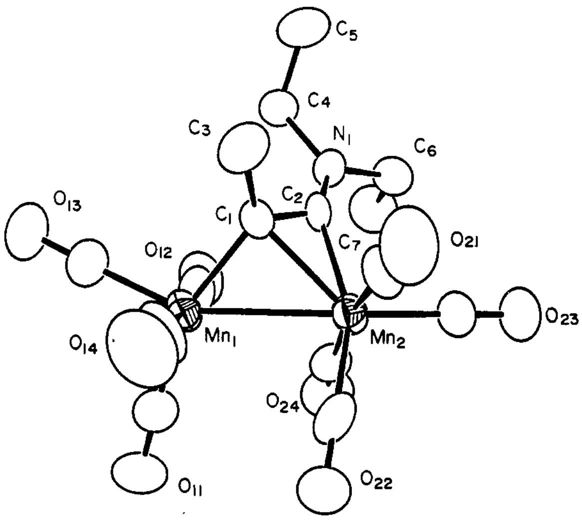

Figure 1. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}MeC_2NEt_2]$ (1) showing 50% probability thermal ellipsoids.

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(12) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

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Table II. Positional Parameters and *B*(eq) Values for $Mn_2(CO)_8(MeC_2NEt_2)$ (1)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1A)	0.29474 (12)	0.20410 (13)	0.27880 (08)	4.7 (1)
Mn(1B)	0.96740 (12)	0.27261 (14)	0.61114 (08)	5.1 (1)
Mn(2A)	0.48425 (11)	0.25543 (12)	0.32214 (07)	3.93 (8)
Mn(2B)	0.77597 (11)	0.22265 (12)	0.56936 (08)	4.01 (9)
O(11A)	0.2415 (07)	0.3337 (08)	0.1671 (05)	9.1 (7)
O(11B)	1.0290 (08)	0.1422 (10)	0.7224 (06)	13 (1)
O(12A)	0.1926 (07)	0.3339 (07)	0.3699 (05)	7.8 (6)
O(12B)	1.0658 (06)	0.1407 (07)	0.5190 (05)	8.1 (6)
O(13A)	0.1177 (07)	0.0829 (08)	0.2790 (05)	9.7 (7)
O(13B)	1.1475 (06)	0.3841 (07)	0.6052 (04)	7.6 (6)
O(14A)	0.3804 (08)	0.0644 (08)	0.1844 (05)	10.1 (7)
O(14B)	0.8854 (08)	0.4085 (09)	0.7093 (05)	11.1 (8)
O(21A)	0.6165 (07)	0.0877 (07)	0.3117 (05)	8.4 (6)
O(21B)	0.6040 (06)	0.1345 (06)	0.5022 (05)	6.5 (5)
O(22A)	0.5164 (06)	0.2923 (07)	0.1791 (04)	8.3 (6)
O(22B)	0.7476 (07)	0.1847 (08)	0.7135 (04)	9.7 (7)
O(23A)	0.6501 (06)	0.3559 (07)	0.3905 (04)	7.1 (6)
O(23B)	0.6438 (07)	0.3913 (06)	0.5862 (05)	8.1 (6)
O(24A)	0.3847 (07)	0.4482 (07)	0.3180 (05)	7.9 (6)
O(24B)	0.8688 (07)	0.0287 (07)	0.5694 (05)	8.2 (6)
N(1A)	0.3866 (06)	0.2325 (06)	0.4603 (04)	3.8 (4)
N(1B)	0.8724 (06)	0.2469 (06)	0.4317 (04)	4.0 (5)
C(1A)	0.3796 (07)	0.1473 (07)	0.3512 (05)	3.4 (6)
C(1B)	0.8813 (07)	0.3318 (09)	0.5403 (06)	4.6 (7)
C(2A)	0.4106 (07)	0.2135 (07)	0.4004 (06)	3.4 (6)
C(2B)	0.8472 (08)	0.2664 (08)	0.4937 (06)	4.1 (6)
C(3A)	0.4001 (09)	0.0416 (08)	0.3621 (06)	6.1 (7)
C(3B)	0.8599 (08)	0.4393 (09)	0.5316 (06)	5.5 (7)
C(4A)	0.3111 (08)	0.1758 (09)	0.4927 (05)	5.0 (6)
C(4B)	0.9509 (09)	0.3032 (09)	0.4009 (06)	5.6 (7)
C(5A)	0.3527 (09)	0.0981 (09)	0.5387 (06)	6.6 (8)
C(5B)	0.9094 (11)	0.3815 (12)	0.3566 (07)	9 (1)
C(6A)	0.4356 (08)	0.3082 (08)	0.5009 (05)	5.1 (6)
C(6B)	0.8251 (08)	0.1712 (09)	0.3905 (06)	5.4 (7)
C(7A)	0.3735 (10)	0.3948 (10)	0.5077 (07)	7.8 (9)
C(7B)	0.8859 (11)	0.0814 (10)	0.3856 (07)	8 (1)
C(11A)	0.2625 (09)	0.2809 (10)	0.2098 (07)	7.1 (9)
C(11B)	1.0038 (09)	0.1906 (12)	0.6796 (06)	7.8 (9)
C(12A)	0.2367 (09)	0.2821 (10)	0.3334 (08)	7 (1)
C(12B)	1.0254 (09)	0.1890 (09)	0.5530 (06)	5.1 (7)
C(13A)	0.1855 (10)	0.1311 (10)	0.2789 (07)	6.7 (8)
C(13B)	1.0760 (09)	0.3410 (09)	0.6087 (05)	5.1 (7)
C(14A)	0.3483 (10)	0.1209 (11)	0.2221 (06)	6.9 (9)
C(14B)	0.9149 (10)	0.3592 (12)	0.6703 (07)	8 (1)
C(21A)	0.5637 (08)	0.1519 (09)	0.3177 (06)	5.3 (7)
C(21B)	0.6712 (08)	0.1685 (08)	0.5293 (05)	3.9 (6)
C(22A)	0.5035 (08)	0.2773 (09)	0.2353 (07)	6.0 (7)
C(22B)	0.7574 (08)	0.1980 (10)	0.6593 (06)	6.3 (8)
C(23A)	0.5879 (09)	0.3155 (09)	0.3636 (06)	5.0 (7)
C(23B)	0.6956 (09)	0.3305 (09)	0.5799 (06)	5.1 (7)
C(24A)	0.4171 (09)	0.3713 (10)	0.3195 (06)	5.3 (7)
C(24B)	0.8398 (10)	0.1066 (11)	0.5699 (06)	6.2 (8)

Table III. Intramolecular Distances for 1[a]

Mn(1A)–Mn(2A)	2.780 (2)	Mn(2B)–C(1B)	2.18 (1)
Mn(1A)–C(1A)	1.98 (1)	Mn(2B)–C(2B)	1.93 (1)
Mn(1A)–C(11A)	1.79 (1)	Mn(2B)–C(21B)	1.78 (1)
Mn(1A)–C(12A)	1.75 (2)	Mn(2B)–C(22B)	1.86 (1)
Mn(1A)–C(13A)	1.80 (1)	Mn(2B)–C(23B)	1.87 (1)
Mn(1A)–C(14A)	1.80 (1)	Mn(2B)–C(24B)	1.83 (2)
Mn(1B)–Mn(2B)	2.791 (2)	N(1A)–C(2A)	1.28 (1)
Mn(1B)–C(1B)	1.98 (1)	N(1A)–C(4A)	1.47 (1)
Mn(1B)–C(11B)	1.84 (1)	N(1A)–C(6A)	1.47 (1)
Mn(1B)–C(12B)	1.84 (1)	N(1B)–C(2B)	1.33 (1)
Mn(1B)–C(13B)	1.76 (1)	N(1B)–C(4B)	1.48 (1)
Mn(1B)–C(14B)	1.85 (2)	N(1B)–C(6B)	1.47 (1)
Mn(2A)–C(1A)	2.16 (1)	C(1A)–C(2A)	1.40 (1)
Mn(2A)–C(2A)	1.98 (1)	C(1A)–C(3A)	1.51 (1)
Mn(2A)–C(21A)	1.80 (1)	C(1B)–C(2B)	1.37 (1)
Mn(2A)–C(22A)	1.80 (1)	C(1B)–C(3B)	1.53 (2)
Mn(2A)–C(23A)	1.81 (1)	O–C (av)	1.15 (2)
Mn(2A)–C(24A)	1.85 (1)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Intramolecular Bond Angles for 1[a]

Mn(2A)–Mn(1A)–C(1A)	50.7 (3)	Mn(2A)–C(1A)–C(3A)	126.4 (7)
Mn(2B)–Mn(1B)–C(1B)	51.0 (3)	C(2A)–C(1A)–C(3A)	119 (1)
Mn(1A)–Mn(2A)–C(1A)	45.1 (3)	Mn(1B)–C(1B)–C(2B)	112.9 (9)
Mn(1A)–Mn(2A)–C(2A)	71.3 (3)	Mn(1B)–C(1B)–C(3B)	126.2 (8)
Mn(1B)–Mn(2B)–C(1B)	44.9 (3)	Mn(2B)–C(1B)–C(2B)	60.9 (6)
Mn(1B)–Mn(2B)–C(2B)	70.4 (3)	Mn(2B)–C(1B)–C(3B)	125.7 (7)
C(2A)–N(1A)–C(4A)	120.9 (9)	C(2B)–C(1B)–C(3B)	121 (1)
C(2A)–N(1A)–C(6A)	122.5 (9)	Mn(2A)–C(2A)–N(1A)	146.7 (8)
C(4A)–N(1A)–C(6A)	116.6 (8)	Mn(2A)–C(2A)–C(1A)	77.4 (6)
C(2B)–N(1B)–C(4B)	120 (1)	N(1A)–C(2A)–C(1A)	135 (1)
C(2B)–N(1B)–C(6B)	123 (1)	Mn(2B)–C(2B)–N(1B)	146 (1)
C(4B)–N(1B)–C(6B)	116.8 (8)	Mn(2B)–C(2B)–C(1B)	80.7 (7)
Mn(1A)–C(1A)–C(2A)	113.9 (7)	N(1B)–C(2B)–C(1B)	133 (1)
Mn(1A)–C(1A)–C(3A)	126.3 (8)	Mn–C–O (av)	177 (2)
Mn(2A)–C(1A)–C(2A)	63.4 (6)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

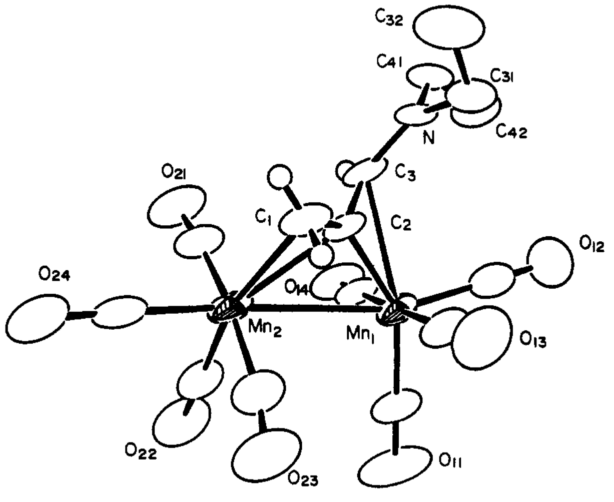

Figure 2. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}H_2CCC(H)NEt_2]$ (2) showing 50% probability thermal ellipsoids.

to the presence of the bridging ynamine ligand. Similar shortenings of the metal–metal bonds compared to those in the parent carbonyls were also observed for $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ and $MnRe(CO)_8(\mu\text{-}MeC_2NMe_2)$. There is partial multiple bonding between the alkynyl carbon C(1) and the nitrogen atom; C(1)–N = 1.28 (1) Å (1.33 (1) Å). The nitrogen atom has a planar geometry, and there is a hindered rotation about the C–N bond in solution, as indicated by observation of separate resonances for the ethyl groups. Similar effects were found for $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ and $MnRe(CO)_8(\mu\text{-}MeC_2NMe_2)$. The ^1H NMR spectrum of 1 in $CDCl_3$ is of poor quality due to overlapping of the resonances and the possible formation of paramagnetic impurities in this solvent. A much better resolved spectrum was obtained in C_6D_6. There are four linear terminal carbonyl ligands coordinated to each metal atom.

The second product, obtained in a very low yield, has been identified as the isomer $Mn_2(CO)_8(\mu\text{-}H_2CCCHNEt_2)$ (2; 0.7%). This compound can be obtained in much larger amounts (16% yield) by heating solutions of 1 to reflux in THF. Compound 2 was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses, and an ORTEP drawing of its molecular structure is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. The molecule contains two manganese atoms bridged by a (dimethylamino)allene ligand. The coordination is similar to that found for other bridging allene ligands; namely, one π-bond donates to one metal atom and the other π-bond donates to the other metal atom.[14] However, there are some significant distortions

Table V. Positional Parameters and *B*(eq) Values for 2

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1)	0.65423 (10)	0.15097 (04)	0.67093 (13)	3.44 (6)
Mn(2)	0.76056 (09)	0.08828 (04)	0.98590 (13)	3.53 (6)
O(11)	0.8975 (06)	0.1772 (02)	0.5651 (09)	8.8 (4)
O(12)	0.4580 (06)	0.2022 (02)	0.3509 (07)	6.3 (3)
O(13)	0.6725 (05)	0.2585 (02)	0.8701 (07)	6.3 (3)
O(14)	0.6207 (05)	0.0433 (02)	0.4688 (07)	6.0 (3)
O(21)	0.6227 (05)	−0.0211 (02)	0.9138 (08)	6.6 (3)
O(22)	0.9632 (06)	0.0424 (02)	0.8249 (08)	7.4 (4)
O(23)	0.9394 (05)	0.1877 (02)	1.0871 (08)	6.6 (4)
O(24)	0.8847 (05)	0.0543 (02)	1.3707 (08)	5.6 (3)
N	0.3259 (06)	0.1135 (02)	0.7216 (07)	3.8 (3)
C(1)	0.6019 (08)	0.1369 (03)	1.0482 (11)	4.3 (5)
C(2)	0.5699 (06)	0.1237 (03)	0.8632 (09)	3.1 (4)
C(3)	0.4522 (07)	0.0970 (03)	0.7571 (09)	3.5 (4)
C(11)	0.8037 (08)	0.1669 (03)	0.6027 (10)	4.9 (4)
C(12)	0.5363 (07)	0.1823 (03)	0.4795 (10)	4.3 (4)
C(13)	0.6688 (07)	0.2169 (03)	0.7953 (10)	4.4 (4)
C(14)	0.6358 (07)	0.0838 (03)	0.5496 (10)	4.2 (4)
C(21)	0.6721 (07)	0.0222 (03)	0.9387 (09)	4.3 (4)
C(22)	0.8855 (08)	0.0600 (03)	0.8845 (10)	4.6 (4)
C(23)	0.8651 (07)	0.1518 (03)	1.0390 (10)	4.5 (4)
C(24)	0.8333 (06)	0.0674 (03)	1.2186 (11)	3.9 (4)
C(31)	0.2928 (07)	0.1676 (03)	0.7883 (11)	5.5 (5)
C(32)	0.2287 (08)	0.1616 (04)	0.9359 (12)	7.9 (6)
C(41)	0.2167 (06)	0.0828 (03)	0.5917 (10)	4.5 (4)
C(42)	0.2101 (08)	0.0946 (03)	0.3948 (11)	6.0 (5)

Table VI. Intramolecular Distances for 2[a]

Mn(1)–Mn(2)	3.042 (2)	Mn(2)–C(22)	1.658 (8)
Mn(1)–C(2)	1.830 (6)	Mn(2)–C(23)	1.917 (9)
Mn(1)–C(3)	2.557 (7)	Mn(2)–C(24)	1.99 (1)
Mn(1)–C(11)	1.685 (8)	N–C(3)	1.400 (9)
Mn(1)–C(12)	2.05 (1)	N–C(31)	1.438 (8)
Mn(1)–C(13)	1.853 (8)	N–C(41)	1.68 (1)
Mn(1)–C(14)	1.869 (8)	C(1)–C(2)	1.48 (1)
Mn(2)–C(1)	2.079 (7)	C(2)–C(3)	1.60 (1)
Mn(2)–C(2)	2.354 (7)	O–C (av)	1.15 (1)
Mn(2)–C(21)	1.870 (8)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table VII. Intramolecular Bond Angles for 2[a]

C(2)–Mn(1)–C(11)	140.5 (4)	Mn(1)–C(2)–C(1)	125.2 (6)
C(2)–Mn(1)–C(12)	114.4 (3)	Mn(1)–C(2)–C(3)	96.1 (4)
C(2)–Mn(1)–C(13)	86.4 (3)	C(1)–C(2)–C(3)	137.5 (5)
C(2)–Mn(1)–C(14)	92.1 (3)	N–C(3)–C(2)	134.7 (6)
C(1)–Mn(2)–C(21)	97.4 (3)	N–C(31)–C(32)	109.0 (7)
C(1)–Mn(2)–C(22)	163.8 (3)	C(2)–Mn(1)–C(3)	38.5 (3)
C(1)–Mn(2)–C(23)	87.5 (3)	C(2)–Mn(1)–Mn(2)	50.6 (2)
C(1)–Mn(2)–C(24)	103.9 (3)	C(3)–Mn(1)–C(1)	62.5 (2)
C(3)–N–C(31)	114.4 (6)	C(3)–Mn(1)–Mn(2)	81.1 (2)
C(3)–N–C(41)	128.8 (5)	C(1)–Mn(2)–Mn(1)	67.2 (2)
C(31)–N–C(41)	116.3 (6)	C(2)–Mn(2)–Mn(1)	36.9 (1)
Mn(2)–C(1)–C(2)	80.9 (4)	Mn–C–O (av)	176 (1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table VIII. Positional Parameters and *B*(eq) Values for 3

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1)	0.96864 (04)	0.28143 (03)	0.61339 (06)	3.02 (2)
Mn(2)	0.76751 (04)	0.17455 (03)	0.74867 (06)	3.00 (2)
O(11)	0.9103 (02)	0.06668 (19)	0.3673 (03)	5.3 (1)
O(12)	1.0072 (03)	0.50800 (19)	0.7893 (04)	6.6 (1)
O(13)	0.7536 (02)	0.33336 (19)	0.2913 (03)	5.7 (1)
O(14)	1.1844 (02)	0.3548 (02)	0.4526 (04)	7.7 (1)
O(21)	0.8383 (02)	−0.03948 (18)	0.7475 (03)	5.7 (1)
O(22)	0.6417 (02)	0.09631 (19)	1.0405 (03)	5.5 (1)
O(23)	0.5307 (02)	0.10263 (18)	0.3891 (03)	5.4 (1)
O(24)	0.7001 (02)	0.38629 (19)	0.8126 (04)	6.2 (1)
N	1.3062 (02)	0.2714 (02)	0.9987 (03)	4.2 (1)
C(1)	0.9505 (03)	0.2444 (02)	0.8988 (04)	3.1 (1)
C(2)	1.0654 (02)	0.2137 (02)	0.8875 (04)	3.0 (1)
C(3)	1.1892 (03)	0.2869 (02)	0.9749 (04)	3.6 (1)
C(11)	0.9304 (03)	0.1448 (03)	0.4701 (04)	3.6 (1)
C(12)	0.9947 (03)	0.4202 (03)	0.7295 (04)	4.1 (1)
C(13)	0.8350 (03)	0.3109 (02)	0.4169 (04)	3.9 (1)
C(14)	1.1011 (03)	0.3257 (03)	0.5156 (04)	4.5 (1)
C(21)	0.8136 (03)	0.0436 (03)	0.7390 (04)	3.7 (1)
C(22)	0.6903 (03)	0.1271 (02)	0.9257 (04)	3.6 (1)
C(23)	0.6226 (03)	0.1299 (02)	0.5261 (04)	3.7 (1)
C(24)	0.7273 (03)	0.3059 (03)	0.7857 (04)	3.9 (1)
C(41)	1.3297 (03)	0.1663 (03)	0.9371 (05)	4.6 (1)
C(42)	1.3469 (04)	0.1619 (04)	0.7354 (06)	5.8 (2)
C(51)	1.4227 (04)	0.3635 (04)	1.0859 (07)	6.5 (2)
C(52)	1.4679 (05)	0.3800 (05)	1.3021 (08)	8.5 (2)

Table IX. Intramolecular Distances for 3[a]

Mn(1)–Mn(2)	2.8072 (7)	Mn(2)–C(24)	1.833 (3)
Mn(1)–C(1)	2.156 (3)	N–C(3)	1.302 (3)
Mn(1)–C(2)	2.216 (3)	N–C(41)	1.476 (4)
Mn(1)–C(11)	1.860 (3)	N–C(51)	1.490 (4)
Mn(1)–C(12)	1.831 (3)	C(1)–C(2)	1.418 (4)
Mn(1)–C(13)	1.804 (3)	C(2)–C(3)	1.418 (4)
Mn(1)–C(14)	1.802 (3)	C(41)–C(42)	1.496 (5)
Mn(2)–C(1)	1.957 (3)	C(51)–C(52)	1.445 (6)
Mn(2)–C(21)	1.836 (3)	Mn(1)–C(3)	2.921 (3)
Mn(2)–C(22)	1.784 (3)	O–C (av)	1.140 (3)
Mn(2)–C(23)	1.828 (3)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles for 3[a]

Mn(2)–Mn(1)–C(1)	44.06 (7)	C(1)–Mn(2)–C(23)	156.0 (1)
Mn(2)–Mn(1)–C(2)	73.50 (7)	C(1)–Mn(2)–C(24)	87.7 (1)
C(1)–Mn(1)–C(2)	37.8 (1)	C(3)–N–C(41)	122.9 (2)
C(1)–Mn(1)–C(11)	102.9 (1)	C(3)–N–C(51)	119.5 (3)
C(1)–Mn(1)–C(12)	81.6 (1)	C(41)–N–C(51)	117.6 (3)
C(1)–Mn(1)–C(13)	112.0 (1)	Mn(1)–C(1)–Mn(2)	85.9 (1)
C(1)–Mn(1)–C(14)	136.4 (1)	Mn(1)–C(1)–C(2)	73.4 (2)
C(2)–Mn(1)–C(11)	88.8 (1)	Mn(2)–C(1)–C(2)	128.0 (2)
C(2)–Mn(1)–C(12)	97.5 (1)	Mn(1)–C(2)–C(1)	68.8 (2)
C(2)–Mn(1)–C(13)	157.3 (1)	Mn(1)–C(2)–C(3)	104.8 (2)
C(2)–Mn(1)–C(14)	102.7 (1)	C(1)–C(2)–C(3)	119.5 (3)
Mn(1)–Mn(2)–C(1)	50.01 (9)	N–C(3)–C(2)	129.3 (3)
C(1)–Mn(2)–C(21)	89.4 (1)	Mn–C–O (av)	176.0 (2)
C(1)–Mn(2)–C(22)	107.3 (1)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

that deserve comment. In particular, the central carbon C(2) is much more strongly bonded to the metal atom Mn(1) than Mn(2) (Mn(1)–C(2) = 1.830 (6) Å vs Mn(2)–C(2) = 2.354 (7) Å) and the amine-substituted carbon C(3) is only very weakly coordinated (Mn(1)–C(3) = 2.557 (7) Å vs Mn(2)–C(1) = 2.079 (7) Å). This may be due to a significant interaction of the nitrogen atom with C(3). This is indicated by the short distance C(3)–N = 1.400 (9) Å and the planar geometry at the nitrogen atom. The observation of separate NMR resonances for the ethyl groups in solution also indicates that there is a hindered rotation about the C–N bond. The metal–metal bond (Mn(1)–Mn(2) = 3.042 (2) Å) is significantly longer than that in 1 and even longer than that in $Mn_2(CO)_{10}$. There are four linear terminal carbonyl ligands coordinated to each metal atom.

In their uncomplexed form aminoallenes are thermally unstable and isomerize to ynamines in solution.[15] Compound 2 is apparently the first example of an aminoallene

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Table XI. Positional Parameters and *B*(eq) Values for 4

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1A)	0.16004 (05)	0.81190 (13)	0.03182 (04)	3.09 (5)
Mn(1B)	0.59710 (05)	0.81169 (13)	0.26299 (04)	3.06 (5)
Mn(2A)	0.26730 (05)	0.90807 (13)	−0.03636 (04)	2.98 (5)
Mn(2B)	0.45383 (05)	0.73937 (12)	0.27867 (04)	3.08 (5)
O(11A)	0.0217 (02)	0.6229 (07)	0.06008 (19)	5.7 (3)
O(11B)	0.7386 (03)	0.9936 (07)	0.2913 (02)	7.3 (3)
O(12A)	0.0683 (03)	1.1397 (07)	0.0266 (02)	6.9 (3)
O(12B)	0.6572 (03)	0.4833 (06)	0.31374 (20)	5.8 (3)
O(13A)	0.2005 (03)	0.8016 (07)	0.14866 (19)	6.0 (3)
O(13B)	0.6493 (02)	0.7779 (06)	0.15063 (18)	5.4 (3)
O(14A)	0.2671 (02)	1.1132 (06)	0.06843 (17)	4.4 (2)
O(14B)	0.5271 (02)	0.4980 (06)	0.19915 (17)	4.1 (2)
O(21A)	0.3050 (02)	0.8190 (07)	−0.15015 (18)	5.4 (3)
O(21B)	0.3464 (03)	0.8685 (07)	0.3605 (02)	7.3 (3)
O(22A)	0.1927 (02)	1.2268 (06)	−0.08077 (17)	5.0 (3)
O(22B)	0.4780 (03)	0.4328 (07)	0.35084 (20)	6.2 (3)
O(23A)	0.4142 (02)	1.0860 (06)	−0.02122 (18)	5.0 (3)
O(23B)	0.3382 (02)	0.5530 (07)	0.21231 (20)	5.4 (3)
N(1A)	0.3021 (02)	0.6577 (06)	−0.00079 (18)	2.8 (2)
N(1B)	0.4568 (02)	0.9727 (06)	0.22792 (19)	2.7 (3)
C(1A)	0.1721 (03)	0.7734 (09)	−0.0515 (03)	3.3 (4)
C(1B)	0.5259 (03)	0.8836 (10)	0.3249 (03)	3.6 (4)
C(2A)	0.1712 (04)	0.6078 (10)	−0.0261 (03)	3.5 (4)
C(2B)	0.5486 (03)	1.0367 (09)	0.2982 (03)	3.4 (4)
C(3A)	0.2778 (04)	0.5891 (09)	0.0148 (03)	3.3 (4)
C(3B)	0.5319 (03)	1.0387 (09)	0.2424 (03)	3.3 (4)
C(11A)	0.0759 (04)	0.6983 (09)	0.0491 (03)	3.9 (1)
C(11B)	0.6833 (04)	0.9201 (10)	0.2806 (03)	4.9 (2)
C(12A)	0.1040 (04)	1.0132 (10)	0.0275 (03)	4.1 (2)
C(12B)	0.6344 (03)	0.6129 (10)	0.2944 (03)	3.7 (1)
C(13A)	0.1849 (03)	0.8053 (09)	0.1029 (03)	4.0 (1)
C(13B)	0.6302 (03)	0.7901 (09)	0.1947 (03)	3.6 (1)
C(14A)	0.2503 (03)	1.0070 (09)	0.0364 (03)	3.2 (1)
C(14B)	0.5201 (03)	0.6172 (09)	0.2290 (03)	3.1 (1)
C(21A)	0.2902 (03)	0.8490 (09)	−0.1062 (03)	3.6 (1)
C(21B)	0.3865 (04)	0.8239 (10)	0.3281 (03)	4.4 (2)
C(22A)	0.2237 (03)	1.1046 (10)	−0.0633 (03)	3.5 (1)
C(22B)	0.4665 (03)	0.5519 (10)	0.3223 (03)	4.0 (2)
C(23A)	0.3580 (04)	1.0128 (09)	−0.0273 (03)	3.5 (1)
C(23B)	0.3816 (04)	0.6303 (09)	0.2380 (03)	3.8 (2)
C(41A)	0.3331 (03)	0.5244 (08)	−0.0412 (02)	3.4 (3)
C(41B)	0.4028 (03)	1.1207 (08)	0.2420 (03)	3.7 (3)
C(42A)	0.4114 (03)	0.5638 (09)	−0.0589 (03)	4.6 (4)
C(42B)	0.3220 (03)	1.0842 (09)	0.2263 (03)	4.7 (4)
C(51A)	0.3530 (03)	0.6745 (08)	0.0470 (03)	3.5 (3)
C(51B)	0.4505 (03)	0.9312 (08)	0.1683 (02)	3.3 (3)
C(52A)	0.3722 (03)	0.5062 (09)	0.0778 (03)	4.4 (4)
C(52B)	0.4634 (04)	1.0872 (11)	0.1297 (03)	5.3 (4)

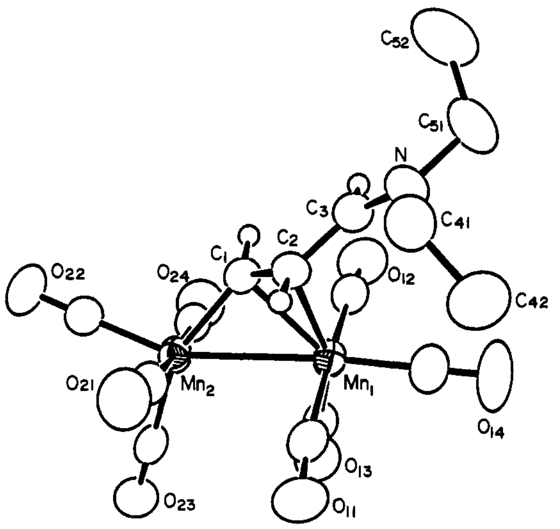

Figure 3. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$ (**3**) showing 50% probability thermal ellipsoids.

Table XII. Intramolecular Distances for 4[a]

Mn(1A)–Mn(2A)	2.673 (1)	Mn(2A)–C(22A)	1.790 (7)
Mn(1A)–C(1A)	2.081 (6)	Mn(2A)–C(23A)	1.813 (7)
Mn(1A)–C(2A)	2.103 (7)	Mn(2B)–N(1B)	2.151 (5)
Mn(1A)–C(3A)	2.114 (7)	Mn(2B)–C(1B)	2.017 (7)
Mn(1A)–C(11A)	1.791 (7)	Mn(2B)–C(14B)	1.949 (7)
Mn(1A)–C(12A)	1.816 (8)	Mn(2B)–C(21B)	1.842 (7)
Mn(1A)–C(13A)	1.794 (7)	Mn(2B)–C(22B)	1.780 (8)
Mn(1A)–C(14A)	2.183 (7)	Mn(2B)–C(23B)	1.813 (7)
Mn(1B)–Mn(2B)	2.658 (1)	N(1A)–C(3A)	1.484 (7)
Mn(1B)–C(1B)	2.075 (6)	N(1A)–C(41A)	1.522 (7)
Mn(1B)–C(2B)	2.095 (6)	N(1A)–C(51A)	1.476 (7)
Mn(1B)–C(3B)	2.122 (7)	N(1B)–C(3B)	1.469 (7)
Mn(1B)–C(11B)	1.790 (8)	N(1B)–C(41B)	1.518 (7)
Mn(1B)–C(12B)	1.803 (8)	N(1B)–C(51B)	1.499 (7)
Mn(1B)–C(13B)	1.797 (7)	C(1A)–C(2A)	1.391 (9)
Mn(1B)–C(14B)	2.164 (7)	C(1B)–C(2B)	1.389 (9)
Mn(2A)–N(1A)	2.160 (5)	C(2A)–C(3A)	1.419 (9)
Mn(2A)–C(1A)	2.009 (6)	C(2B)–C(3B)	1.396 (9)
Mn(2A)–C(14A)	1.965 (7)	O–C (av)	1.15 (1)
Mn(2A)–C(21A)	1.825 (7)	C(Et)–C (av)	1.510 (8)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table XIII. Intramolecular Bond Angles for 4[a]

Mn(2A)–Mn(1A)–C(1A)	48.0 (2)	Mn(1A)–C(1A)–Mn(2A)	81.6 (2)
Mn(2A)–Mn(1A)–C(2A)	72.2 (2)	Mn(1B)–C(1B)–Mn(2B)	81.0 (2)
Mn(2A)–Mn(1A)–C(3A)	70.6 (2)	C(1A)–C(2A)–C(3A)	113.0 (6)
Mn(2B)–Mn(1B)–C(1B)	48.5 (2)	C(1B)–C(2B)–C(3B)	114.4 (6)
Mn(2B)–Mn(1B)–C(2B)	72.3 (2)	Mn(1A)–C(3A)–N(1A)	107.3 (4)
Mn(2B)–Mn(1B)–C(3B)	70.8 (2)	N(1A)–C(3A)–C(2A)	114.4 (5)
Mn(1A)–Mn(2A)–N(1A)	73.5 (1)	Mn(1B)–C(3B)–N(1B)	106.4 (4)
N(1A)–Mn(2A)–C(1A)	82.7 (2)	N(1B)–C(3B)–C(2B)	114.3 (6)
Mn(1B)–Mn(2B)–N(1B)	73.4 (1)	Mn(1A)–C(14A)–O(14A)	132.9 (5)
N(1B)–Mn(2B)–C(1B)	82.3 (2)	Mn(1B)–C(14B)–O(14B)	133.2 (5)
Mn(2A)–N(1A)–C(3A)	98.9 (4)	Mn–C–O (av)	177 (1)
Mn(2B)–N(1B)–C(3B)	99.7 (4)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

complexed to metal atoms. The isomerization of 1 to 2 shows that this thermodynamic equilibrium between ynamine and aminoallene is significantly changed by the process of complexation.

In addition to the formation of compound 2, the thermolysis of 1 yielded two other products, a third isomer identified as $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$ (3; 8%) and the decarbonylated form $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$ (4; 22%). Compounds 3 and 4 were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of 3 is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. The two manganese atoms are joined by a metal–metal bond (Mn(1)–Mn(2) = 2.8072 (8) Å) and a monometalated bridging (diethylamino)allyl ligand. Carbon C(1) is bonded to both metal atoms (Mn(1)–C(1) = 2.156 (3) Å and Mn(2)–C(1) = 1.957 (3) Å), while C(2) is bonded only to Mn(1) (Mn(1)–C(2) = 2.216 (3) Å). C(3) is not coordinated (Mn(1)–C(3) = 2.921 (3) Å). The short C(3)–N distance (1.302 (3) Å) and planar nitrogen atom are indicative of C–N multiple bonding. The observation of separate NMR resonances for the ethyl groups in solution also indicates that there is a hindered rotation about the C–N bond. The unusual coordination of this ligand suggests a zwitterionic representation for the structure that would place a positive charge on the nitrogen atom and a negative charge on the metal Mn(2). Related to this ligand are the nonmetalated μ-η^2-aminoallyl ligands that have been reported previously.[9,16]

The crystal of 4 also contains two symmetry-independent molecules in the asymmetric crystal unit. Both mol-

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(16) Yin, J.; Chen, J.; Xu, W.; Xu, X.; Tang, Y. *Acta Chim. Sin. (Engl. Ed.)* 1988, *4*, 279.

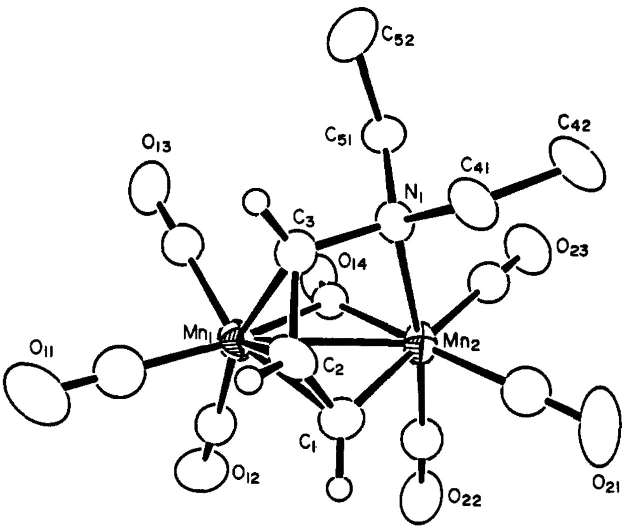


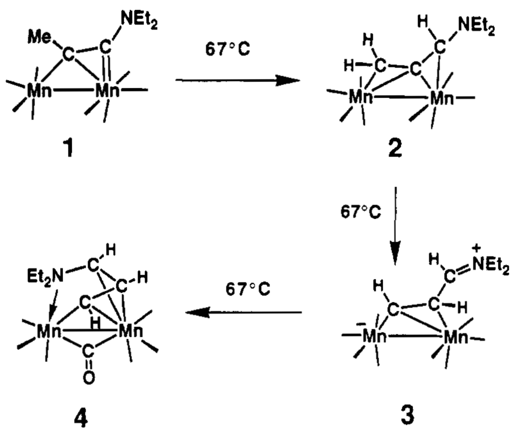
Figure 4. ORTEP diagram of $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$ (4) showing 40% probability thermal ellipsoids.

ecules are structurally similar, and an ORTEP diagram of one of the two molecules of 4 found in the solid is shown in Figure 4. Final atomic positional parameters are listed in Table XI. Selected interatomic distances and angles are listed in Tables XII and XIII. This molecule is simply a decarbonylation product of **3**. As a result, the lone pair of electrons on the nitrogen atom has become coordinated to one of the metal atoms. The aminoallyl ligand in 4 is an η^4-bridging ligand in which the three carbon atoms are π-bonded to Mn(1). Atom C(1) is a bridge to Mn(2), and the nitrogen atom is coordinated to Mn(2) (Mn(2)–N = 2.160 (5) Å (2.151 (5) Å)). The C(3)–N distance has been lengthened to a normal single-bond value, 1.484 (7) Å (1.469 (7) Å). The two manganese atoms are joined by a short metal–metal bond (Mn(1)–Mn(2) = 2.673 (1) Å (2.658 (1) Å)). The unusual shortness can be attributed both to the presence of the bridging metalated (diethylamino)allyl ligand and to an asymmetric bridging carbonyl ligand, C(14)–O(14). The metalated (diethylamino)allyl ligand serves as a 6-electron donor; thus, both metal atoms achieve 18-electron configurations. Each metal atom contains three linear terminal carbonyl ligands.

Discussion

A summary of the results of this study are shown in Scheme I. The structure of complex 1 has now been established as an ynamine complex in which the metal atoms are bonded to one another and the ynamine ligand exhibits the asymmetric bridging coordination that was observed previously for the complexes $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$[6] and $MnRe(CO)_8(\mu\text{-}MeC_2NMe_2)$.[8] Interestingly, compound 1 can be isomerized to the compound 2 by a 1,3-hydrogen shift from the methyl group to the amine-substituted carbon to yield the aminoallene complex 2. Although no intermediates were observed in this transformation, it is believed that the shift occurs by a metal-mediated activation process and may traverse a hydride-containing species. We have shown previously that decarbonylation of the compound $Os_3(CO)_{10}(\mu\text{-}MeC_2NMe_2)$ leads to the hydride-containing complex $Os_3(CO)_9(\mu_3\text{-}H_2CCCNMe_2)(\mu\text{-}H)$ by the activation of one C–H bond on the *C*-methyl group.[2c] Compound 2 is subsequently isomerized to the zwitterionic species 3 by a 1,2-hydrogen shift. In this transformation, we also suspect a metal-mediated CH activation and transfer. Finally, compound 3 is decarbonylated and the iminium grouping in 3 becomes coordinated to the metal atoms.

Scheme I



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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for 1–4 (15 pages); listings of structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.