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Clusters Containing Ynamine Ligands. 6. Transformations of an Ynamine Ligand in a Dirhenium Complex. Synthesis and Structural Characterization of $Re_2(CO)_8[\mu\text{-}H_2CCHCNMe_2]$, $Re_2(CO)_7[\mu\text{-}H_2CCCNMe_2](\mu\text{-}H)$, and $Re_2(CO)_8[\mu\text{-}H_2C{=}CCNMe_2](\mu\text{-}H)$

Richard D. Adams,* Gong Chen, Yun Chi,† Wengan Wu, and Jianguo Yin

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

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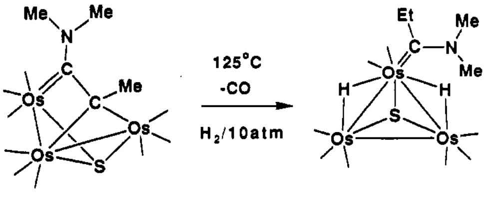
The complex $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ (**1**) was transformed into three new compounds, $Re_2(CO)_7(\mu\text{-}\eta^3\text{-}H_2CCCNMe_2)(\mu\text{-}H)$ (**2**; 17%), $Re_2(CO)_8(\mu\text{-}H_2CCHCNMe_2)$ (**3**; 25%), and $Re_2(CO)_8(\mu\text{-}H_2C{=}CCNMe_2)(\mu\text{-}H)$ (**4**; 0.5%), when heated to 80 °C for 2 h. Compounds **2**–**4** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Compound **2** is a hydride-containing decarbonylation product of **1** formed by a shift of one of the hydrogen atoms on the C-methyl group to the metal atoms. It also contains a η^3 bridging (dimethylamino)allenyl ligand that exhibits carbene-like character at the amine-substituted carbon atom. Compounds **3** and **4** are isomers of **1** formed by a shift of one of the hydrogen atoms on the *C*-methyl group of **1** to one of the alkynyl carbon atoms. Compound **3** contains a bridging vinyl(dimethylamino)carbene ligand in which the vinyl group is π-bonded to one metal atom and the carbene is terminally coordinated to the other metal atom. Compound **4** contains a η^2 bridging (dimethylamino)allenyl ligand in an unusual coordination in which the two coordinated carbon atoms lie parallel to the metal–metal bond. The amine-substituted carbon shows a pronounced carbene-like character. Addition of CO to **2** at 25 °C/1 atm yielded compound **4** (79%) and only a trace **3** (1%). At 75 °C **4** was slowly converted to **3** (54% in 18 h) and the new compound **5** (39% in 18 h). Although it was not possible to isolate **5**, it was unambiguously identified as $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NMe_2]$ on the basis of its ^1H NMR spectrum and comparison with the known compound $Mn_2(CO)_8(\mu\text{-}\eta^2\text{-}C_3H_3NEt_2)$. Over a period of 35 h at 100 °C compound **5** was decarbonylated to yield the new compound $Re_2(CO)_7(\mu\text{-}\eta^4\text{-}C_3H_3NMe_2)$ (**6**; 53%). Compound **6** is assigned a structure analogous to that of the known compound $Mn_2(CO)_7(\mu\text{-}\eta^4\text{-}C_3H_3NEt_2)$ on the basis of its spectral similarities. Crystal data: for **2**, space group $P\bar{1}$, $a = 9.572$ (2) Å, $b = 9.922$ (2) Å, $c = 9.193$ (2) Å, $\alpha = 107.91$ (2)°, $\beta = 101.25$ (1)°, $\gamma = 92.63$ (2)°, $Z = 2$, 1912 reflections, $R = 0.021$; for **3**, space group $P2_1/a$, $a = 15.428$ (4) Å, $b = 16.047$ (6) Å, $c = 15.341$ (4) Å, $\beta = 115.03$ (2)°, $Z = 8$, 3256 reflections, $R = 0.038$; for **4**, space group $P2_1/n$, $a = 9.268$ (2) Å, $b = 18.652$ (4) Å, $c = 10.276$ (2) Å, $\beta = 101.24$ (1)°, $Z = 4$, 1738 reflections, $R = 0.029$.

Introduction

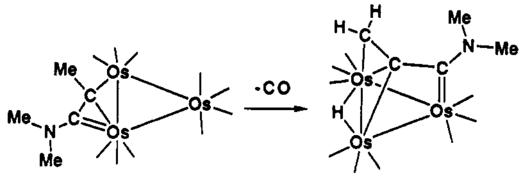
Unsymmetrical ynamines or aminoacetylenes, RC_2NMe_2, have been shown to exhibit unusual coordinations to metal cluster complexes that can be attributed in part to strong interactions of the lone pair of electrons on the nitrogen atom to the alkynyl grouping.[1] It was proposed and demonstrated that the amine-substituted carbon atom in these complexes possesses carbene-like character.[2-6]

We have shown that ynamines can be converted to aminocarbene ligands by reaction of ynamine ligand complexes with hydrogen[6] and by reactions of ynamines with hydride-containing metal cluster complexes[7] in a process that involves the addition of two hydrogen atoms to the alkyl-substituted carbon atom of the ynamine (eq 1).



(1)

When the complex is thermally decarbonylated, the unsymmetrically bridged ynamine ligand in $Os_3(CO)_{10}(\mu\text{-}MeC_2NMe_2)$ undergoes CH activation at the *C*-methyl group to yield the complex $Os_3(CO)_{10}(\mu\text{-}H_2CCCNMe_2)(\mu\text{-}H)$, which contains an unusual triply bridging aminoallenyl ligand that shows carbene-like character at the amine-substituted carbon atom (eq 2).[2c]



(2)

Recently, we reported the preparation and structural characterization of the complexes $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ (**1**)[8] and $ReMn(CO)_8(\mu\text{-}MeC_2NMe_2)$,[9] in which the ynamine ligands also exhibit an asymmetrical bridging coordination. Complex **1** reacts with hydrogen to convert the ynamine

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

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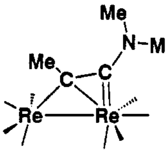
ligand to an enamine ligand by a mechanism that utilizes both rhenium atoms.[10]



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We have also structurally characterized the compound $Mn_2(CO)_8(\mu\text{-}MeC_2NEt_2)$, which was reported by King,[11] and have shown that it also possesses an asymmetrically coordinated ynamine ligand similar to that in 1.[12] In addition, we have shown that $Mn_2(CO)_8(\mu\text{-}MeC_2NEt_2)$ can be thermally isomerized to the aminoallene complex $Mn_2(CO)_8(\mu\text{-}H_2CCC(H)NEt_2)$ and the two monometalated aminoallyl complexes $Mn_2(CO)_8(\mu\text{-}\eta^2\text{-}C_3H_3NEt_2)$ and $Mn_2(CO)_7(\mu\text{-}\eta^4\text{-}C_3H_3NEt_2)$ by hydrogen shifts from the *C*-methyl carbon atom. We have now investigated the thermal transformations of compound 1. These transformations are also characterized by activation of the CH bonds on the *C*-methyl group. These results are reported here.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were stored over 4-Å molecular sieves. 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. Elemental analyses were performed by Desert Analytics, Tucson, AZ. $Re_2(CO)_{10}$ was purchased from Strem Chemical Co. and was used without further purification. $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ was prepared by the previously reported procedure.[8]

Thermolysis of Complex 1. A cyclohexane (65 mL) solution of $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ (1; 108 mg, 0.159 mmol) was heated to reflux for 2 h. After the solution was cooled to room temperature, the solvent was evaporated to dryness and the residue was chromatographed with a mixture of hexane/dichloromethane (4/1) on silica gel TLC plates to give the following four complexes in the order of elution: 0.5 mg of colorless $Re_2(CO)_8(\mu\text{-}H_2C{=}CCNMe_2)(\mu\text{-}H)$ (4; 0.5%), 17.7 mg of colorless $Re_2(CO)_7(\mu\text{-}\eta^3\text{-}H_2CCCNMe_2)(\mu\text{-}H)$ (2; 17%), 2.5 mg of orange 1, and 26.6 mg of pale yellow $Re_2(CO)_8(\mu\text{-}H_2CCHCNMe_2)$ (3; 25%). For complexes 1 and 3, their relative abundances were calculated on the basis of ^1H NMR integration and their total weight, since these complexes separated very poorly on the TLC plates. Pure complex 3, free of any undesired complex 1, was easily obtained by heating the above mixture in refluxing cyclohexane solvent for 2 h followed by TLC separation. Spectral data for 2 are as follows. IR (C_6H_{12}): $\nu(CO)$ 2092 (w), 2031 (s), 1998 (s), 1976 (vs), 1961 (s), 1953 (w), 1940 (m) cm^{-1}; $\nu(CN)$ 1654 (vw) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.01 (d, 1 H, $J_{H\text{-}H}$ = 2.9 Hz), 4.12 (d, 1 H, $J_{H\text{-}H}$ = 2.9 Hz), 3.66 (s, 3 H), 3.43 (s, 3 H), −15.66 (s, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 225.3 ($H_2CC\mathit{C}NMe_2$), 109.7 ($H_2C\mathit{C}CNMe_2$), 62.1 ($H_2\mathit{C}CCNMe_2$), 48.7 (NMe), 46.7 (NMe); Re(CO), δ 192.4, 191.9, 188.8, 186.2, 185.2, 183.4, 182.8. Anal. Calcd (found) for $Re_2C_{12}H_9NO_7$: C, 22.12 (22.27); H, 1.39 (1.27); N, 2.15 (2.07). Spectral data for 3 are as follows. IR (C_6H_{12}): $\nu(CO)$ 2085 (m), 2044 (s), 1991 (s), 1983 (vs), 1974 (s), 1964 (m), 1949 (w), 1931 (s) cm^{-1}; $\nu(CN)$ 1522 (vw) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.43 (s, 3 H), 3.42 (s, 3 H), 3.33 (dd, 1 H, $J_{H\text{-}H}$ = 8.6 and 13.2 Hz), 1.98 (dd, 1 H, $J_{H\text{-}H}$ = 2.2 and 8.6 Hz), 1.40 (dd, 1 H, $J_{H\text{-}H}$ = 2.2 and 13.2 Hz). Anal. Calcd (found) for $Re_2C_{13}H_9NO_8$: C, 22.97 (22.94); H, 1.33 (1.24); N, 2.06 (2.01). Spectral data for 4 are as follows. IR (C_6H_{12}): $\nu(CO)$ 2105 (w), 2082 (m), 2012 (vs), 1998 (vs), 1992 (s), 1979 (w), 1966 (s), 1959 (s) cm^{-1}; $\nu(CN)$ 1522 (vw) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.25 (d, 1 H, $J_{H\text{-}H}$ = 3.0 Hz), 5.06 (d, 1 H, $J_{H\text{-}H}$ = 3.0 Hz), 3.60 (s, 3 H), 3.42 (s, 3 H), −15.80 (s, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 212.7 ($H_2CC\mathit{C}NMe_2$), 150.4 ($H_2C\mathit{C}CNMe_2$), 108.1 ($H_2\mathit{C}CCNMe_2$), 50.1 (NMe), 41.3 (NMe); Re(CO), δ 187.9, 186.4, 186.1, 186.0, 185.9, 185.5, 185.3, 184.2. Anal. Calcd (found) for $Re_2C_{13}H_9NO_8$: C, 22.97 (23.06); H, 1.33 (1.28); N, 2.06 (2.03). We have also recorded the $^{13}C\{^1H\}$ NMR spectrum of 1. It is reported here for the first time (δ, in $CDCl_3$): 229.5 ($MeC\mathit{C}NMe_2$), 121.6 ($Me\mathit{C}CNMe_2$), 32.7 ($\mathit{Me}CCNMe_2$), 47.5 (NMe), 46.6 (NMe); Re(CO), 197.2 (1 CO), 194.4 (1 CO), 193.4 (1 CO), 191.4 (1 CO), 191.3 (br, 4 CO).

Table I.

t, min	amt, %			
	1	2	3	5
0	100			
10	99	1	trace	trace
30	90	3	4	3
60	72	3	12	13

Reaction of Compound 2 with Carbon Monoxide. In a 50-mL reaction flask, 20.4 mg of 2 was dissolved in a mixture of benzene (5 mL) and cyclohexane (25 mL). The solution was then stirred under 1 atm of carbon monoxide at room temperature. Ten hours later, the solvent was removed and the residue was separated by thin-layer chromatography with a hexane/dichloromethane mixture (4/1), giving 16.8 mg of colorless 4 (0.025 mmol, 79%), 1.0 mg of 2 (0.002 mmol, 5%), and 0.3 mg of 3 (0.0004 mmol, 1%).

Synthesis of Complexes 5 and 6. A deuterated benzene (0.7 mL) solution of $Re_2(CO)_8(H_2CCHCNMe_2)$ (3; 11.8 mg, 0.0174 mmol) was added to a 5-mm NMR tube. The tube was then placed in a constant-temperature oil bath at 100 °C. After 35 h, the ^1H NMR spectrum indicated the formation of $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}C_3H_3NMe_2)$ (5) and $Re_2(CO)_7(\mu\text{-}\eta^4\text{-}C_3H_3NMe_2)$ (6) in a molar ratio of 0.58/1. The solvent was evaporated, and the residue was eluted with a mixture of hexane/dichloromethane (3/1) on silica gel plates, giving 6.3 mg of light yellow 6 (53%). We were unable to purify complex 5, since it decomposed rapidly when eluted on silica gel TLC plates. Compound 6 was recrystallized from a mixture of hexane and dichloromethane at room temperature. Spectral data for 5 are as follows. ^1H NMR (C_6D_6): δ 7.11 (d, 1 H, $J_{H\text{-}H}$ = 11.6 Hz), 5.12 (d, 1 H, $J_{H\text{-}H}$ = 10.8 Hz), 3.13 (dd, 1 H, $J_{H\text{-}H}$ = 10.8 and 11.6 Hz), 1.46 (s, 3 H), 1.37 (s, 3 H). Spectral data for 6 are as follows. MS (EI, ^{187}Re): m/z 653 − 28x, x = 0–7 ($M^+ - x$ CO). IR (C_6H_{12}): $\nu(CO)$ 2078 (m), 2026 (vs), 2004 (s), 1972 (vs), 1947 (s), 1944 (m), 1896 (vw) cm^{-1}. ^1H NMR (C_6D_6): δ 7.66 (dd, 1 H, $J_{H\text{-}H}$ = 2.6 and 6.3 Hz), 6.20 (dd, 1 H, $J_{H\text{-}H}$ = 3.2 and 6.3 Hz), 2.90 (dd, 1 H, $J_{H\text{-}H}$ = 2.6 and 3.2 Hz), 1.95 (s, 3 H), 1.48 (s, 3 H). Anal. Calcd (found) for $Re_2C_{12}H_9NO_7$: C, 22.12 (22.05); H, 1.39 (1.18); N, 2.15 (2.10).

Reaction of 6 with Carbon Monoxide. A deuterated benzene (0.75 mL) solution of 6 (4.8 mg) was added to a 5-mm NMR tube under 1 atm of carbon monoxide. The tube was then placed in an oil bath maintained at 100 °C. The reaction was terminated after 40 min. ^1H NMR analysis indicated that there is no evidence for the formation of any complex 5.

^1H NMR Analysis of the Pyrolysis of 1. A deuterated benzene (0.8 mL) solution of complex 4 (8.0 mg) was added to a 5-mm NMR tube under nitrogen. The tube was then placed in an oil bath maintained at 100 °C. The progress of the reaction was monitored regularly by ^1H NMR spectroscopy over a period of 60 min. The results of this analysis are listed in Table I.

Analysis of the Pyrolysis Products of 1. A cyclohexane (10 mL) solution of 1 (10 mg, 0.0015 mmol) was heated to reflux for 90 min. The solvent was evaporated to dryness, and the residue was redissolved in benzene-d_6 solvent. The ^1H NMR analysis of this sample indicated that the molar ratio of complexes 1, 2, 3, and 5 is 0.02/0.56/0.20/0.22.

^1H NMR Analysis of the Thermolysis of 2. A deuterated benzene (0.7 mL) solution of 2 (5 mg) was added to a 5-mm NMR tube. The tube was then placed in a constant-temperature oil bath at 100 °C for 10 min. The ^1H NMR analysis of this sample indicated that the molar ratio of complexes 2, 3, 5, and 6 is 0.54/0.05/0.14/0.27. Formation of a small amount of one unidentified decomposition product was also noticed.

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Table II.

	amt, %			
	0 h	12 h	20 h	30 h
3	100	25	17	13
5		60	63	56
6		15	20	31

Table III.

	amt, %					
	0 h	1.4 h	3.8 h	6 h	9 h	12 h
3	100	96	71	61	45	37
5		4	27	37	51	58
6		trace	2	2	4	5

Table IV.

	amt, %				
t	**1**	**2**	**3**	**4**	**5**
0				100	
10 min		2	trace	98	
25 min		4	1	95	
40 min	trace	5	3	91	1
1 h	1	8	6	81	4
1.6 h	1	7	10	74	8
2.4 h	1	6	16	64	13
3.5 h	2	5	22	52	19
6.5 h	3	3	35	31	28
18 h	3	trace	54	3	39

^{1}H NMR Analysis of the Thermolysis of 3. A deuterated benzene (0.7 mL) solution of complex **3** (12 mg) was added to a 5-mm NMR tube. The tube was then placed in an oil bath maintained at 100 °C. The progress of the reaction was monitored regularly by ^{1}H NMR spectroscopy over a period of 30 h. The results of this analysis are listed in Table II.

^{1}H NMR Analysis of the Thermolysis of 3 under CO. A deuterated benzene (0.85 mL) solution of complex **3** (25 mg) was added to a 5-mm NMR tube under 1 atm of carbon monoxide. The tube was then placed in an oil bath maintained at 100 °C. The progress of the reaction was monitored regularly by ^{1}H NMR spectroscopy over a period of 12 h. The results of this analysis are listed in Table III.

Thermolysis of 4 under N_2 Purge. A cyclohexane (20 mL) solution of **4** (19 mg, 0.028 mmol) was heated at 70 °C with a slow stream of N_2 bubbled into the solution. Six hours later the solvent was evaporated, and the residue was chromatographed with a mixture of hexane/dichloromethane (4/1) on silica gel TLC plates, giving 10.6 mg of **4** (56%), 1.8 mg of **2** (9.5%), and 0.9 mg of **3** (4.7%).

^{1}H NMR Analysis of the Thermolysis of 4. A deuterated benzene (0.8 mL) solution of **4** (8 mg) was added to a 5-mm NMR tube under nitrogen. The tube was then placed in an oil bath maintained at 75 °C. The progress of the reaction was monitored regularly by ^{1}H NMR spectroscopy over a period of 18 h. The results of this analysis are listed in Table IV.

Crystallographic Analyses. Crystals of **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a mixture of dichloromethane and hexane at room temperature. Crystals of **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a mixture of benzene and heptane at room temperature. Crystals of **4** were obtained by slow evaporation of solvent from a mixture of dichloromethane and heptane at room temperature. The data 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. The 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 refinements are listed in Table V. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[13a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[13b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

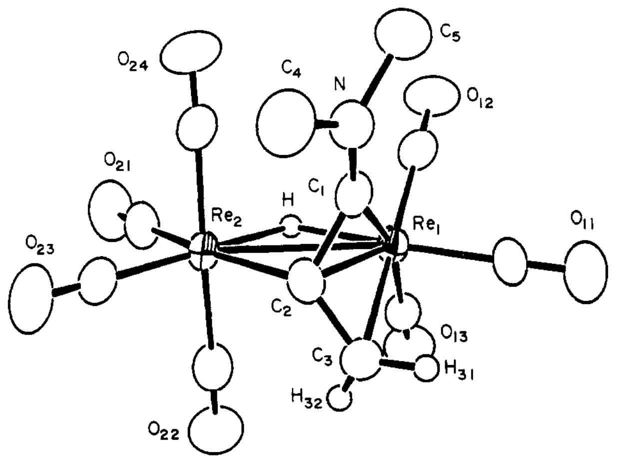

Figure 1. ORTEP diagram of $Re_2(CO)_7[\mu\text{-}H_2CCCNMe_2](\mu\text{-}H)$ (**2**) showing 50% probablity thermal ellipsoids.

Compound **2** crystallized in the triclinic crystal system. The 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 (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located and refined on their positional parameters with a constant thermal parameter, $B = 5.0$ Å^2.

Compound **3** crystallized in the monoclinic crystal system with two symmetry-independent molecules in the asymmetric crystal unit. The space group $P2_1/a$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the vinyl groupings were obtained from a difference Fourier synthesis. These atoms were refined by least squares. The hydrogen atoms on the methyl groups were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but thier positions were not refined.

Compound **4** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydride ligand was located at refined on its position. The positions of the remaining hydrogen atoms were obtained from a difference Fourier synthesis or were calculated by assuming idealized geometries. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results

The complex $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ (**1**) was transformed into three new compounds, $Re_2(CO)_7[\mu\text{-}H_2C{=}CCNMe_2](\mu\text{-}H)$ (**2**; 17%), $Re_2(CO)_8[\mu\text{-}H_2C{=}CHCNMe_2]$ (**3**; 25%), and $Re_2(CO)_8[\mu\text{-}H_2C{=}CCNMe_2](\mu\text{-}H)$ (**4**; 0.5%), when heated to 80 °C for 2 h. Compounds **2**–**4** were characterized by IR and ^{1}H NMR spectroscopy and by single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **2** is shown in Figure 1. Final atomic positional parameters are listed in Table VI. Selected interatomic distances and angles are listed in

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[13] (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.

Table V. Crystallographic Data for Diffraction Studies

	2	3	4
empirical formula	$Re_2O_7NC_{12}H_9$	$Re_2O_8NC_{13}H_9$	$Re_2O_8NC_{13}H_9$
fw	651.62	679.63	679.63
cryst syst	triclinic	monoclinic	monoclinic
lattice params			
a, Å	9.572 (2)	15.428 (4)	9.268 (2)
b, Å	9.922 (2)	16.047 (6)	18.652 (4)
c, Å	9.193 (2)	15.341 (4)	10.276 (2)
α, deg	107.91 (2)	90.0	90.0
β, deg	101.25 (1)	115.03 (2)	101.24 (1)
γ, deg	92.63 (2)	90.0	90.0
V, $Å^3$	809.5 (3)	3441 (2)	1742.4 (6)
space group	$P\bar{1}$ (No. 2)	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
Z	2	8	4
D_{calc}, g/cm^3	2.67	2.62	2.59
μ(Mo Kα), cm^{-1}	151.74	142.88	187.15
radiation	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)
abs cor	empirical	empirical	empirical
temp, °C	20	20	20
$2\theta_{max}$, deg	46.0	44.0	43.0
no. of observns ($I > 3\sigma(I)$)	1912	3256	1738
no. of variables	226	457	220
residuals: R, R_w	0.021, 0.024	0.038, 0.039	0.029, 0.033
goodness-of-fit indicator	1.43	2.04	2.09
max shift in final cycle	0.06	0.50	0.01
largest peak in final diff map, θ/Å^3	1.10	1.28	0.75

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	−0.24615 (03)	0.16240 (03)	0.04511 (03)	2.77 (1)
Re(2)	−0.32195 (03)	0.24061 (03)	0.36769 (04)	2.99 (1)
O(11)	−0.0577 (08)	0.1532 (08)	−0.1909 (08)	6.1 (3)
O(12)	−0.5075 (07)	0.1760 (07)	−0.1996 (08)	5.7 (3)
O(13)	−0.2715 (07)	−0.1679 (07)	−0.0568 (08)	5.4 (3)
O(21)	−0.6954 (08)	0.1165 (09)	0.4172 (08)	6.7 (3)
O(22)	−0.1713 (07)	−0.0213 (07)	0.4175 (09)	6.0 (3)
O(23)	−0.2072 (08)	0.4173 (09)	0.7145 (08)	7.2 (3)
O(24)	−0.4889 (08)	0.4862 (08)	0.3060 (09)	6.9 (3)
N	−0.1922 (07)	0.5120 (07)	0.1987 (08)	3.8 (3)
C(1)	−0.1893 (08)	0.3797 (08)	0.1809 (09)	2.9 (3)
C(2)	−0.1367 (08)	0.3024 (08)	0.2863 (09)	2.9 (3)
C(3)	−0.0278 (09)	0.2187 (10)	0.2458 (11)	3.5 (3)
C(4)	−0.1303 (11)	0.6242 (10)	0.3473 (12)	4.7 (4)
C(5)	−0.2664 (12)	0.5632 (11)	0.0744 (13)	5.0 (4)
C(11)	−0.1274 (09)	0.1583 (09)	−0.0997 (10)	3.9 (3)
C(12)	−0.4118 (09)	0.1669 (09)	−0.1097 (10)	3.8 (3)
C(13)	−0.2627 (09)	−0.0473 (10)	−0.0181 (10)	3.8 (3)
C(21)	−0.5002 (10)	0.1617 (10)	0.4008 (10)	4.4 (4)
C(22)	−0.2256 (10)	0.0732 (10)	0.3972 (10)	4.2 (3)
C(23)	−0.2523 (09)	0.3482 (11)	0.5885 (11)	4.4 (4)
C(24)	−0.4255 (09)	0.3964 (10)	0.3269 (10)	4.3 (4)
H	−0.397 (08)	0.128 (08)	0.153 (09)	5.0
H(31)	0.040 (09)	0.233 (09)	0.179 (10)	5.0

Table VII. Intramolecular Distances for 2[a]

Re(1)–Re(2)	3.0642 (7)	Re(2)–C(23)	1.94 (1)
Re(1)–C(1)	2.116 (8)	Re(2)–C(24)	1.97 (1)
Re(1)–C(2)	2.239 (7)	N–C(1)	1.27 (1)
Re(1)–C(3)	2.418 (8)	N–C(4)	1.46 (1)
Re(1)–C(11)	1.907 (8)	N–C(5)	1.46 (1)
Re(1)–C(12)	1.92 (1)	C(1)–C(2)	1.44 (1)
Re(1)–C(13)	1.97 (1)	C(2)–C(3)	1.40 (1)
Re(2)–C(2)	2.186 (7)	H–Re(2)	1.92 (8)
Re(2)–C(21)	1.96 (1)	H–Re(1)	1.97 (8)
Re(2)–C(22)	2.00 (1)	O–C (av)	1.14 (1)

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

Table VIII. Intramolecular Bond Angles for 2[a]

Re(2)–Re(1)–C(1)	66.1 (2)	Re(1)–Re(2)–C(23)	144.0 (3)
Re(2)–Re(1)–C(2)	45.5 (2)	Re(1)–Re(2)–C(24)	90.9 (2)
Re(2)–Re(1)–C(3)	70.8 (2)	C(2)–Re(2)–C(21)	169.4 (3)
Re(2)–Re(1)–C(11)	156.0 (3)	C(2)–Re(2)–C(22)	88.3 (3)
Re(2)–Re(1)–C(12)	109.5 (2)	C(2)–Re(2)–C(23)	97.2 (3)
Re(2)–Re(1)–C(13)	101.9 (2)	C(2)–Re(2)–C(24)	92.9 (3)
C(1)–Re(1)–C(2)	38.6 (3)	C(1)–N–C(4)	123.0 (7)
C(1)–Re(1)–C(3)	63.4 (3)	C(1)–N–C(5)	122.2 (8)
C(1)–Re(1)–C(11)	96.7 (3)	C(4)–N–C(5)	114.7 (8)
C(1)–Re(1)–C(12)	103.2 (3)	Re(1)–C(1)–N	151.4 (6)
C(1)–Re(1)–C(13)	161.1 (3)	Re(1)–C(1)–C(2)	75.3 (4)
C(2)–Re(1)–C(3)	34.7 (3)	N–C(1)–C(2)	133.1 (7)
C(2)–Re(1)–C(11)	110.6 (3)	Re(1)–C(2)–Re(2)	87.6 (3)
C(2)–Re(1)–C(12)	136.1 (3)	Re(1)–C(2)–C(1)	66.1 (4)
C(2)–Re(1)–C(13)	122.6 (3)	Re(1)–C(2)–C(3)	79.7 (5)
C(3)–Re(1)–C(11)	86.7 (3)	Re(2)–C(2)–C(1)	106.1 (5)
C(3)–Re(1)–C(12)	165.7 (3)	Re(2)–C(2)–C(3)	126.4 (6)
C(3)–Re(1)–C(13)	99.4 (3)	C(1)–C(2)–C(3)	115.1 (7)
Re(1)–Re(2)–C(2)	46.9 (2)	Re(1)–C(3)–C(2)	65.6 (4)
Re(1)–Re(2)–C(21)	122.6 (2)	Re(2)–H–Re(1)	104 (4)
Re(1)–Re(2)–C(22)	87.3 (2)	Re–C–O (av)	177 (1)

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

Tables VII and VIII, respectively. The molecule contains two rhenium atoms joined by a hydride-bridged metal–metal bond (Re(1)–Re(2) = 3.0642 (7) Å) and a μ-η^3-(dimethylamino)allenyl ligand. The three carbon atoms of the allenyl ligand C(1), C(2), and C(3) are π-bonded to Re(1), while C(2) serves as the bridge to Re(2). The Re(1)–C(1) distance of 2.116 (8) Å is much shorter than the other two distances Re(1)–C(2) = 2.239 (7) Å and Re(1)–C(3) = 2.418 (8) Å. Carbon C(1) has only one substituent, the dimethylamino group, which is planar at the nitrogen and has a short C–N distance to the allenyl carbon atom C(1) (C(1)–N = 1.27 (1) Å). This indicates the presence of substantial C–N multiple-bond character. In solution the *N*-methyl groups are inequivalent due to hindered rotation about the C–N bond. The combination of evidence suggests the existence of carbene-like character at the C(1) site. This is also supported by the ^{13}C NMR resonance of carbon C(1), which was observed at the low-field value of +225.3 ppm in the region characteristic of aminocarbene ligands.[14] In fact, this ligand could alternatively and perhaps more accurately be described as an η^3-vinyl(dimethylamino)carbene ligand that is metallated at C(2). We have also recorded the ^{13}C NMR spectrum of **1** for the first time. It shows a very low field resonance,

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[14] (a) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 299. (b) Adams, R. D.; Babin, J. E.; Kim, H. S.; Tanner, J. T.; Wolfe, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 3426.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1A)	0.79098 (05)	0.02378 (04)	−0.07093 (05)	3.95 (3)
Re(1B)	0.33847 (05)	0.12428 (05)	0.61798 (05)	3.93 (3)
Re(2A)	0.72596 (04)	0.05470 (04)	0.08856 (04)	3.35 (3)
Re(2B)	0.26068 (06)	0.15971 (05)	0.40331 (05)	5.10 (4)
O(11A)	0.8969 (09)	0.0104 (09)	−0.1985 (09)	6.8 (7)
O(11B)	0.4458 (10)	0.1120 (09)	0.8359 (09)	7.1 (7)
O(12A)	0.6454 (11)	0.1498 (11)	−0.2128 (10)	9 (1)
O(12B)	0.4637 (11)	−0.0181 (10)	0.6033 (10)	7.7 (8)
O(13A)	0.6404 (11)	−0.1094 (11)	−0.1874 (11)	10 (1)
O(13B)	0.1827 (10)	−0.0049 (10)	0.6005 (10)	7.6 (8)
O(14A)	0.9269 (10)	−0.1133 (08)	0.0582 (10)	6.5 (7)
O(14B)	0.2072 (11)	0.2607 (10)	0.6416 (11)	8.0 (8)
O(21A)	0.5514 (09)	−0.0460 (08)	−0.0514 (09)	6.3 (6)
O(21B)	0.0736 (12)	0.0892 (14)	0.3978 (12)	10 (1)
O(22A)	0.8040 (10)	−0.1123 (09)	0.1914 (10)	6.9 (7)
O(22B)	0.3187 (11)	−0.0200 (09)	0.3741 (10)	7.7 (8)
O(23A)	0.6397 (09)	0.1020 (08)	0.2295 (08)	5.9 (6)
O(23B)	0.1787 (12)	0.1988 (10)	0.1880 (10)	8.9 (9)
O(24A)	0.6482 (12)	0.2202 (09)	−0.0230 (10)	8.6 (8)
O(24B)	0.2045 (13)	0.3298 (12)	0.4509 (10)	10 (1)
N(1A)	0.9010 (11)	0.1906 (10)	0.0196 (13)	5.9 (8)
N(1B)	0.4504 (10)	0.2880 (09)	0.6124 (09)	4.9 (7)
C(1A)	0.8555 (13)	0.1338 (14)	0.1901 (14)	5 (1)
C(1B)	0.3982 (18)	0.2248 (16)	0.4033 (17)	7 (1)
C(2A)	0.8835 (11)	0.0901 (11)	0.1264 (12)	4.0 (7)
C(2B)	0.4216 (14)	0.1838 (13)	0.4917 (13)	6 (1)
C(3A)	0.8723 (11)	0.1169 (11)	0.0318 (12)	4.1 (8)
C(3B)	0.4194 (11)	0.2129 (12)	0.5791 (12)	4.5 (8)
C(4A)	0.8836 (15)	0.2232 (12)	−0.0746 (18)	7 (1)
C(4B)	0.4456 (15)	0.3235 (13)	0.6975 (16)	7 (1)
C(5A)	0.9557 (16)	0.2485 (13)	0.0989 (19)	9 (1)
C(5B)	0.4969 (16)	0.3453 (13)	0.5702 (16)	8 (1)
C(11A)	0.8556 (15)	0.0143 (16)	−0.1512 (15)	8 (1)
C(11B)	0.4027 (13)	0.1169 (12)	0.7498 (14)	5.4 (9)
C(12A)	0.6977 (14)	0.1028 (13)	−0.1586 (13)	5 (1)
C(12B)	0.405 (02)	0.0447 (17)	0.5966 (19)	12 (2)
C(13A)	0.6960 (14)	−0.0609 (14)	−0.1424 (13)	6 (1)
C(13B)	0.2411 (14)	0.0407 (12)	0.6082 (12)	5.0 (9)
C(14A)	0.8758 (13)	−0.0619 (11)	0.0123 (13)	4.5 (8)
C(14B)	0.2566 (14)	0.2121 (12)	0.6327 (12)	5.2 (9)
C(21A)	0.6151 (12)	−0.0064 (11)	−0.0025 (12)	4.0 (7)
C(21B)	0.150 (03)	0.1146 (16)	0.4015 (16)	10 (2)
C(22A)	0.7771 (12)	−0.0495 (12)	0.1544 (12)	4.6 (8)
C(22B)	0.2999 (14)	0.0461 (12)	0.3852 (12)	5.3 (9)
C(23A)	0.6725 (13)	0.0853 (10)	0.1775 (13)	5.2 (8)
C(23B)	0.2084 (15)	0.1839 (11)	0.2674 (15)	6 (1)
C(24A)	0.6736 (14)	0.1589 (13)	0.0169 (13)	6 (1)
C(24B)	0.2225 (14)	0.251 (02)	0.4363 (13)	12 (2)

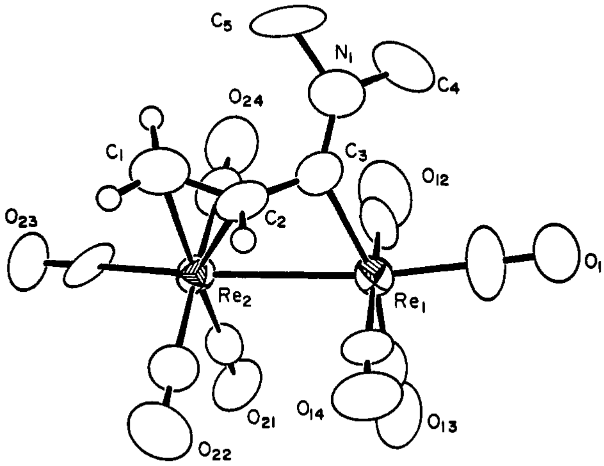

Figure 2. ORTEP diagram of $Re_2(CO)_8[\mu\text{-}H_2CCHCNMe_2]$ (**3**) showing 50% probability thermal ellipsoids.

Table X. Intramolecular Distances for 3[a]

Re(1A)–Re(2A)	3.052 (1)	Re(2A)–C(24A)	1.98 (2)
Re(1A)–C(2A)	2.95 (2)	Re(2B)–C(1B)	2.36 (2)
Re(1A)–C(3A)	2.15 (2)	Re(2B)–C(2B)	2.30 (2)
Re(1A)–C(11A)	1.89 (2)	Re(2B)–C(3B)	2.90 (2)
Re(1A)–C(12A)	1.96 (2)	Re(2B)–C(21B)	1.85 (4)
Re(1A)–C(13A)	1.96 (2)	Re(2B)–C(22B)	1.98 (2)
Re(1A)–C(14A)	1.96 (2)	Re(2B)–C(23B)	1.93 (2)
Re(1B)–Re(2B)	3.044 (1)	Re(2B)–C(24B)	1.73 (3)
Re(1B)–C(2B)	2.90 (2)	N(1A)–C(3A)	1.30 (2)
Re(1B)–C(3B)	2.14 (2)	N(1A)–C(4A)	1.45 (2)
Re(1B)–C(11B)	1.84 (2)	N(1A)–C(5A)	1.48 (2)
Re(1B)–C(12B)	1.75 (3)	N(1B)–C(3B)	1.32 (2)
Re(1B)–C(13B)	1.97 (2)	N(1B)–C(4B)	1.46 (2)
Re(1B)–C(14B)	1.97 (2)	N(1B)–C(5B)	1.47 (2)
Re(2A)–C(1A)	2.32 (2)	C(1A)–C(2A)	1.41 (2)
Re(2A)–C(2A)	2.32 (2)	C(1B)–C(2B)	1.41 (3)
Re(2A)–C(3A)	2.92 (2)	C(2A)–C(3A)	1.45 (2)
Re(2A)–C(21A)	1.95 (2)	C(2B)–C(3B)	1.43 (2)
Re(2A)–C(22A)	1.94 (2)	O–C (av)	1.19 (3)
Re(2A)–C(23A)	1.93 (2)		

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

Table XI. Intramolecular Bond Angles for 3[a]

Re(2A)–Re(1A)–C(3A)	65.6 (4)	Re(1B)–Re(2B)–C(22B)	88.6 (5)
Re(2A)–Re(1A)–C(11A)	168.0 (7)	Re(1B)–Re(2B)–C(23B)	178.4 (6)
Re(2A)–Re(1A)–C(12A)	92.8 (5)	Re(1B)–Re(2B)–C(24B)	82.5 (8)
Re(2A)–Re(1A)–C(13A)	98.1 (5)	C(3A)–N(1A)–C(4A)	123 (2)
Re(2A)–Re(1A)–C(14A)	87.0 (5)	C(3A)–N(1A)–C(5A)	124 (2)
Re(2B)–Re(1B)–C(3B)	65.4 (4)	C(4A)–N(1A)–C(5A)	113 (2)
Re(2B)–Re(1B)–C(11B)	169.4 (6)	C(3B)–N(1B)–C(4B)	124 (2)
Re(2B)–Re(1B)–C(12B)	86 (1)	C(3B)–N(1B)–C(5B)	124 (1)
Re(2B)–Re(1B)–C(13B)	96.1 (5)	C(4B)–N(1B)–C(5B)	112 (1)
Re(2B)–Re(1B)–C(14B)	90.7 (5)	C(1A)–C(2A)–C(3A)	127 (2)
Re(1A)–Re(2A)–C(1A)	98.3 (5)	C(1B)–C(2B)–C(3B)	130 (2)
Re(1A)–Re(2A)–C(2A)	64.9 (4)	Re(1A)–C(3A)–N(1A)	131 (1)
Re(1A)–Re(2A)–C(21A)	80.2 (4)	Re(1A)–C(3A)–C(2A)	108 (1)
Re(1A)–Re(2A)–C(22A)	94.5 (5)	N(1A)–C(3A)–C(2A)	121 (2)
Re(1A)–Re(2A)–C(23A)	172.1 (5)	Re(1B)–C(3B)–N(1B)	131 (1)
Re(1A)–Re(2A)–C(24A)	83.5 (5)	Re(1B)–C(3B)–C(2B)	107 (1)
Re(1B)–Re(2B)–C(1B)	98.0 (6)	N(1B)–C(3B)–C(2B)	121 (2)
Re(1B)–Re(2B)–C(2B)	64.0 (5)	Re–C–O (av)	177 (1)
Re(1B)–Re(2B)–C(21B)	83.2 (7)		

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

δ 229.5, which we attribute to the amine-substituted carbon atom. We feel that this also supports the formulation of carbene-like character at that carbon atom in 1. The hydride ligand in 2 was located and refined crystallographically (Re(1)–H = 1.97 (8) Å and Re(2)–H = 1.92 (8) Å, δ −15.66 ppm). The molecule contains seven linear terminal carbonyl ligands.

Compound 3 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 2. Final atomic positional parameters are listed in Table IX. Selected interatomic distances and angles are listed in Tables X and XI, respectively. The two rhenium atoms are joined by a metal–metal bond and a bridging vinyl(dimethylamino)carbene ligand. The rhenium–rhenium distance of 3.052 (1) Å (3.044 (1) Å) is very similar to that in $Re_2(CO)_{10}$ (3.041 (1) Å).[15] The carbene center is located at atom C(3). The Re(1)–C(3) distance of 2.15 (2) Å (2.14 (2) Å) is slightly longer than the Re–carbene distances observed in the dirhenium carbene complexes $Re_2(CO)_9[C(OR)SiPh_3]$ (R = Me, 2.09 (2) Å; R = Et, 2.09 (4) Å), which contain equatorially positioned, terminally coordinated alkoxycarbene ligands.[16] The nitrogen atom is planar, the C(3)–N bond is short (1.30 (2) Å (1.32 (2) Å)), and there is hindered rotation about the C(3)–N bond in solution as

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(15) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

(16) Schubert, U.; Ackermann, K.; Rustenmeyer, P. *J. Organomet. Chem.* **1982**, *231*, 323.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	0.15522 (05)	0.05329 (02)	0.24992 (05)	2.27 (2)
Re(2)	0.17386 (05)	0.19939 (02)	0.41715 (05)	2.20 (2)
O(11)	0.2710 (13)	−0.0818 (06)	0.1319 (10)	5.9 (6)
O(12)	0.1163 (12)	0.1394 (05)	−0.0142 (10)	5.0 (5)
O(13)	0.1738 (12)	−0.0280 (05)	0.5186 (10)	5.0 (5)
O(14)	−0.1707 (11)	0.0077 (05)	0.1621 (10)	4.5 (5)
O(21)	0.2824 (13)	0.2718 (06)	0.1827 (11)	5.6 (6)
O(22)	0.3374 (11)	0.3156 (05)	0.5992 (09)	4.3 (5)
O(23)	0.0791 (12)	0.1284 (06)	0.6627 (11)	5.5 (6)
O(24)	−0.1182 (12)	0.2849 (06)	0.3576 (11)	5.4 (5)
N	0.4795 (11)	0.1145 (05)	0.2673 (11)	3.4 (5)
C(1)	0.4492 (15)	0.1054 (08)	0.5709 (14)	4.2 (7)
C(2)	0.3707 (13)	0.1292 (06)	0.4590 (13)	2.8 (6)
C(3)	0.3710 (14)	0.0992 (06)	0.3278 (13)	3.1 (6)
C(4)	0.4868 (16)	0.0923 (09)	0.1369 (15)	5.2 (8)
C(5)	0.6067 (16)	0.1624 (09)	0.3280 (17)	5.5 (8)
C(11)	0.2278 (16)	−0.0316 (07)	0.1751 (13)	3.6 (6)
C(12)	0.1344 (14)	0.1086 (06)	0.0807 (13)	2.8 (6)
C(13)	0.1686 (14)	0.0016 (07)	0.4234 (14)	3.1 (6)
C(14)	−0.0504 (16)	0.0242 (07)	0.1979 (13)	3.1 (6)
C(21)	0.2424 (16)	0.2451 (06)	0.2673 (14)	3.5 (6)
C(22)	0.2753 (13)	0.2719 (06)	0.5309 (12)	2.5 (5)
C(23)	0.1126 (14)	0.1526 (06)	0.5720 (14)	3.1 (6)
C(24)	−0.0098 (16)	0.2532 (07)	0.3781 (12)	3.1 (6)

Table XIII. Intramolecular Distances for 4[a]

Re(1)–Re(2)	3.2083 (8)	Re(2)–C(22)	1.91 (1)
Re(1)–C(2)	2.99 (1)	Re(2)–C(23)	1.99 (1)
Re(1)–C(3)	2.18 (1)	Re(2)–C(24)	1.95 (1)
Re(1)–C(11)	1.94 (1)	Re(2)–H(1)	1.9 (1)
Re(1)–C(12)	2.00 (1)	N–C(3)	1.31 (1)
Re(1)–C(13)	2.01 (1)	N–C(4)	1.42 (2)
Re(1)–C(14)	1.95 (1)	N–C(5)	1.51 (2)
Re(1)–H(1)	1.6 (1)	C(1)–C(2)	1.31 (2)
Re(2)–C(2)	2.22 (1)	C(2)–C(3)	1.46 (2)
Re(2)–C(3)	2.89 (1)	O–C (av)	1.14 (1)
Re(2)–C(21)	1.97 (1)		

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

Table XIV. Intramolecular Bond Angles for 4[a]

C(3)–N–C(4)	125 (1)	Re(1)–C(3)–N	130 (1)
C(3)–N–C(5)	123 (1)	Re(1)–C(3)–C(2)	108.8 (8)
C(4)–N–C(5)	113 (1)	N–C(3)–C(2)	120 (1)
Re(2)–C(2)–C(1)	132 (1)	Re(1)–H(1)–Re(2)	131 (6)
Re(2)–C(2)–C(3)	101.3 (8)	Re–C–O (av)	178 (1)
C(1)–C(2)–C(3)	125 (1)		

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

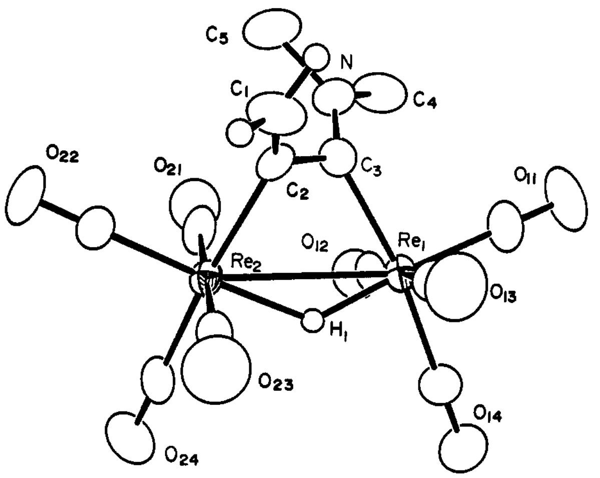
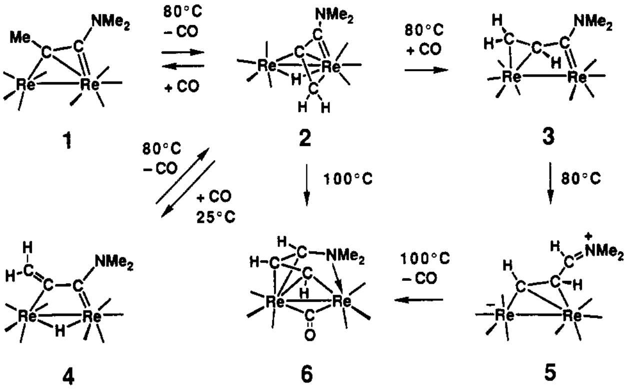


Figure 3. ORTEP diagram of $Re_2(CO)_8[\mu\text{-}H_2C{=}CCNMe_2](\mu\text{-}H)$ (4) showing 50% probability thermal ellipsoids.

Scheme I



indicated by the separate resonances for the *N*-methyl groups in the ^{1}H NMR spectrum. The vinyl grouping (C(1)–C(2) = 1.41 (2) Å (1.41 (3) Å)) is π-bonded to the second rhenium atom (Re(2)–C(1) = 2.32 (2) Å (2.36 (2) Å) and Re(2)–C(2) = 2.32 (2) Å (2.30 (2) Å)). Each metal atom contains four linear terminal carbonyl ligands.

An ORTEP drawing of compound 4 is shown in Figure 3. Final atomic positional parameters are listed in Table XII. Selected interatomic distances and angles are listed in Tables XIII and XIV. The molecule contains two rhenium atoms joined by a very long hydride-bridged metal–metal bond (Re(1)–Re(2) = 3.2083 (8) Å) and a μ-η^2-(dimethylamino)allenyl ligand. Atom C(2) is coordinated only to Re(2) (Re(2)–C(2) = 2.22 (1) Å, Re(1)···C(2) = 2.99 (1) Å), and C(3) is coordinated only to Re(1) (Re(1)–C(3) = 2.18 (1) Å and Re(2)···C(3) = 2.89 (1) Å). There appears to be substantial carbene-like character at the amine-substituted carbon atom C(3) (Re(2)–C(3) = 2.18 (1) Å). This is supported by the low-field resonance of the amine-substituted carbon atom (+212.7 ppm). The C(3)–N distance is short (1.31 (1) Å), and there is hindered rotation about the bond in solution, as indicated by the separate resonances for the *N*-methyl groups in the ^{1}H NMR spectrum. As expected by electron counting, there is a double bond between atoms C(1) and C(2) (C(1)–C(2) = 1.31 (2) Å). It might be expected that the ligand would be planar in order to delocalize the π-electron density between the C–C double bond and the carbene center, but in fact it has substantial nonplanarity. The C(1)–C(2)–C(3)–N torsion angle is 78 (2)°. The hydride ligand was located and refined crystallographically (Re(1)–H(1) = 1.6 (1) Å and Re(2)–H(1) = 1.9 (1) Å, δ −15.80 ppm). Each metal atom contains four linear terminal carbonyl ligands.

When heated to 100 °C for 35 h, compound 3 was transformed to two new compounds, $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}C_3H_3NMe_2)$ (5) and $Re_2(CO)_7(\mu\text{-}\eta^4\text{-}C_3H_3NMe_2)$ (6), in a molar ratio of 0.58/1. We are unable to purify complex 5, since it decomposed rapidly when placed in contact with silica gel TLC plates, but compound 6 was isolated in 53% yield. The structure of 5 was deduced from the characteristic features of its ^{1}H NMR spectrum, which contains three hydrogen resonances with three large trans-vicinal coupling constants (δ 7.11 (d, 1 H, $J_{H\text{-}H}$ = 11.6 Hz), 5.12 (d, 1 H, $J_{H\text{-}H}$ = 10.8 Hz), 3.13 (dd, 1 H, $J_{H\text{-}H}$ = 10.8 and 11.6 Hz)), and comparison with the corresponding manganese complex $Mn_2(CO)_8(\mu\text{-}\eta^2\text{-}C_3H_3NEt_2)$, which has been structurally characterized.[12] The structure of 6 was determined by a comparison of its IR and ^{1}H NMR spectra with those of the known manganese complex $Mn_2(CO)_7(\mu\text{-}\eta^4\text{-}C_3H_3NEt_2)$.[12]

Discussion

A summary of the results of this study are shown in Scheme I. The transformations of compound 1 were initiated by decarbonylation, which occurs at a significant rate at 80 °C. The product 2 was the first of several that were formed. It was formed by decarbonylation and the activation of one of the CH bonds on the *C*-methyl group. The ynamine ligand was transformed into a μ-η^3-aminoallenyl ligand and a bridging hydride ligand. A triply bridging aminoallenyl ligand was formed by a decarbonylation and CH activation at the *C*-methyl group of the ynamine ligand in the osmium complex $Os_3(CO)_{10}(\mu$-$MeC_2NMe_2)$ to yield the complex $Os_3(CO)_{10}(\mu$-$H_2CCNMe_2)(\mu$-H) (eq 2).[2c] Compound 2 was found to add CO at room temperature to form compound 4 by converting the μ-η^3-aminoallenyl ligand to a μ-η^2-aminoallenyl ligand. At 75 °C, 4 lost CO to re-form 2. However, at 75 °C in a closed system, compound 4 was slowly converted to 3. This is believed to occur by decarbonylation to 2 and a slow readdition of CO to yield 3, which is simply a more stable isomer of 4. With prolonged heating 3 was converted to the even more stable isomer 5, which can be decarbonylated to yield 6. However, we also found that substantial amounts of 6 were formed by heating 2 to 100 °C for 10 min in the absence of CO. Since compound 5 was not significantly converted to 6 and 6 does not add CO to yield 5 under these conditions, we believe that 2 can probably also be converted to 6 without the intermediacy of 5.

We have shown previously that the manganese complex $Mn_2(CO)_8(\mu$-$MeC_2NEt_2)$, which is structurally very similar to 1, also undergoes a series of hydrogen-shift transformations to yield an isomer containing a bridging aminoallene ligand, an isomer similar to 5 that contains a bridging η^2-metalated aminoallyl ligand, and a decarbonylated complex containing a bridging η^4-metalated aminoallyl ligand similar to that proposed for 6.[12] In the present study, we have characterized yet another isomeric form of the ynamine ligand, namely, the vinyl(amino)carbene as found in compound 3. In contrast to the manganese study, we have also demonstrated that hydride-containing intermediates are involved in the hydrogen-shift processes.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for 2–4 (11 pages); listings of structure factor amplitudes (47 pages). Ordering information is given on any current masthead page.

Chemistry of Organoindium Hydrides. Synthesis, Characterization, and Crystal Structure of $K\{H[In(CH_2CMe_3)_3]_2\}$

O. T. Beachley, Jr.,* Sun-Hua L. Chao, Melvyn Rowen Churchill,* and Ronald F. See

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

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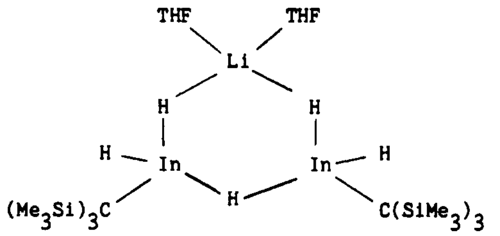
Two new organoindium hydrides $K\{H[In(CH_2CMe_3)_3]_2\}$ and $K[HIn(CH_2CMe_3)_3]$ have been prepared and fully characterized according to their physical properties, partial elemental analyses, molecular weight studies, and IR and ^{1}H and ^{13}C NMR spectral studies. The unique hydrogen atoms bonded to indium in the two compounds provide characteristic infrared bands and ^{1}H NMR resonances, which have been identified by comparative studies with the corresponding deuterium derivatives. The indium hydride $K\{H[In(CH_2CMe_3)_3]_2\}$ crystallizes in the monoclinic space group $C2/c$ (No. 15) with cell parameters of a = 22.243 (5) Å, b = 17.021 (3) Å, c = 21.290 (3) Å, β = 110.350 (10)°, V = 7557 (2) Å^3, and Z = 8. Final discrepancy indicies were R = 6.32% and R_w = 4.97% for all 4947 independent data and R = 2.96% and R_w = 3.67% for those 2924 reflections with $|F_o| > 6\sigma(F_o)$. The crystal is composed of K^+ cations and $(Me_3CCH_2)_3In$-H-$In(CH_2CMe_3)_3^-$ anions, each of which lie on 2-fold axes. In–C(neopentyl) distances range from 2.199 (6) to 2.231 (6) Å (averaging 2.213 Å), while In–(μ-H) distances are 1.933 (15) and 1.950 (23) Å. In–H–In angles are 151 (5) and 161 (5)°.

Introduction

Compounds which contain indium–hydrogen bonds are difficult to prepare, isolate, and fully characterize. Thus, no indium hydride has been fully characterized previously by elemental analyses, molecular weight studies, diagnostic spectroscopic data, and X-ray structural studies. The only compound with indium–hydrogen bonds for which an X-ray structural study has been reported is $[(Me_3Si)_3C]$-$In(H)(\mu$-$H)Li(THF)_2(\mu$-$H)In(\mu$-$H)(H)[C(SiMe_3)_3]$.[1]



However, the unique hydrogen atoms were not located. The presence of indium–hydrogen bonds was inferred from infrared and ^{6}Li{^{1}H} NMR spectral data. This compound was too unstable to permit satisfactory carbon and hydrogen analyses. The closely related compounds M-$[InR_3H]$ (M = Na, K; R = Me[2], Et[2], CH_2SiMe_3[3]) are also unstable and decompose to $MInR_4$, MH, indium metal, and hydrogen. Thus, when $In(CH_2SiMe_3)_3$ and KH were combined in the absence of solvent, $KIn(CH_2SiMe_3)_4$ was isolated and was fully characterized.[3]

In this paper, the syntheses and characterizations of two novel compounds with indium–hydrogen bonds, K{H[In-

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