(OC)$_4$Fe$^-$. This was done in the following way. Dissociative attachment of thermal energy electrons to Fe(CO)$_5$ occurs readily to yield (OC)$_4$Fe$^-$; $\Delta H^\circ = -14.3 \pm 10.5$ kcal mol^{-1}.[34] We assume that the vibrationally excited doublet ground state is initially produced. The reactions of the collisionally thermalized (OC)$_4$Fe$^-$ ions in the FA include halogen-atom transfer with certain haloalkanes, which occur by initial electron transfer followed by X$^-$ transfer from RX$^{\bullet-}$ to Fe(CO)$_4$.[9] For example, the bimolecular reaction of (OC)$_4$Fe$^-$ with CCl$_3$Br produces the 18-electron complex (OC)$_4$FeBr$^-$ ($k_{total} = 2.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). When CCl$_3$Br was added to the flow of (OC)$_4$Fe$^-$ produced by reaction 1 (~40%) and those (OC)$_4$Fe$^-$ ions initially formed by dissociative electron attachment (~60%),[12,35] the sole ionic product was (OC)$_4$FeBr$^-$. More significant was the observed linear decay in the plot of log [(OC)$_4$Fe$^-$] vs Cl$_3$CBr concentration through >95% loss of the (OC$_4$)Fe$^-$ ion signal yielding the same rate constant given above. Thus, all of the (OC)$_4$Fe$^{\bullet-}$ ions are in their doublet electronic ground state. *These kinetic and product results are consistent with formation of the doublet electronic ground state of* (OC)$_4$Fe$^-$ *from the addition of CO to the doublet electronic ground state of* (OC)$_3$Fe$^-$.

Summary and Conclusions

The fast reaction of (OC)$_3$Fe$^-$ with ^{13}CO ($k_{total} = (2.4 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) occurs by competitive collisional stabilization (65%) and unimolecular dissociation (35%) of the excited adduct [(OC)$_3$(O^{13}C)Fe$^-$]* (1). The absence of an observable P_{He} effect on k_{total} or the branching fractions suggests that the slopes of the plots of these parameters vs helium concentration are small in the P_{He} regime (0.5-1.1 Torr) investigated. Only 75% of the dissociation of 1 appears as product ions of ligand substitution with the rate constant $k_d'' \geq 7.8 \times 10^{-6}$ s^{-1}, while the remaining 25% of 1 returns to the unlabelled starting ions and ^{13}CO with $k_d' \geq 2.6 \times 10^{-6}$ s^{-1}. These lower limits of the unimolecular rate constants k_d'' and k_d' are arrived at by calculation of the collision frequency, k_s[He] = 1.9×10^{-7} s^{-1}, for stabilizing the adduct [(OC)$_3$(O^{13}C)Fe$^-$]*.

The high efficiency of the reaction of (OC)$_3$Fe$^-$ with CO to give (OC)$_4$Fe$^-$ ($k_{app}/k_{LAN} = 0.24$) suggests that both the starting and product ions are doublet electronic ground state species.

Acknowledgment. The authors thank the National Science Foundation for support of this research, and Professor D. W. Setser for helpful discussions and suggestions.

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[34] McDonald, R. N. *Tetrahedron* **1989**, *45*, 3993, ref 90.

[35] To the helium flow containing the $(OC)_{4,3}Fe^-$ mixture, sufficient CO was added via a gas inlet to convert >95% of the (OC)$_3$Fe$^-$ ions into (OC)$_4$Fe$^-$ within a 10-cm distance of the flow tube. CCl$_3$Br was then added via another inlet located 20 cm downstream of the CO inlet.

Clusters Containing Ynamine Ligands. 3. Syntheses and Structural Characterizations of Re$_2$(CO)$_8$(μ-MeC$_2$NMe$_2$) and Re$_2$(CO)$_7$[μ-C(Me)C(NMe$_2$)C(NMe$_2$)C(Me)]

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The reaction of Re$_2$(CO)$_8$[μ-C(H)=C(H)Bu](μ-H) with MeC$_2$NMe$_2$ at 25 °C yielded the product Re$_2$(CO)$_8$(μ-MeC$_2$NMe$_2$) (1; 25%). Compound 1 was characterized by single-crystal X-ray diffraction analysis and was found to contain an unsymmetric bridging ynamine ligand in which the amine-substituted carbon atom is coordinated to only one metal atom. Compound 1 reacts with additional MeC$_2$NMe$_2$ at 68 °C to yield the three isomeric products Re$_2$(CO)$_7$[μ-C(Me)C(NMe$_2$)C(NMe$_2$)C(Me)] (2; 54%), Re$_2$(CO)$_7$[μ-C(Me)C(NMe$_2$)C(Me)C(NMe$_2$)] (3; 9.5%), and Re$_2$(CO)$_7$[μ-C(NMe$_2$)C(Me)C(Me)C(NMe$_2$)] (4; 17%). Compound 2 was analyzed crystallographically and was found to contain a metallacyclic ring formed by the head-to-head coupling of two ynamine ligands. This ring is π-bonded to a Re(CO)$_3$ grouping. On the basis of IR, ^{1}H NMR, and mass spectrometry compounds 3 and 4 were proposed to have similar structures formed by the head-to-tail and tail-to-tail coupling of two ynamine ligands, respectively. Crystal data: for 1, space group $P2_1/c$, $a = 9.776$ (2) Å, $b = 11.315$ (4) Å, $c = 15.695$ (4) Å, $\beta = 97.56$ (1)°, $Z = 4$, $R = 0.034$, and $R_w = 0.040$ for 1800 reflections; for 2, space group $Pca2_1$, $a = 17.668$ (4) Å, $b = 8.510$ (2) Å, $c = 14.058$ (4) Å, $Z = 4$, $R = 0.018$, and $R_w = 0.021$ for 1429 reflections.

Introduction

Recent investigations of the coordination of unsymmetric ynamines, RC≡CNR$_2$, in polynuclear metal complexes have revealed a structural pattern that strongly suggests the existence of a carbene-like character at the amine-substituted carbon atom.[1-5] In both di- and trinuclear metal complexes the amine-substituted carbon atom is bonded to only one metal atom as in A and B. The spectroscopic and reactivity properties of these ligands also support the existence of carbene-like character.[5-7]

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[1] Cabrera, E.; Daran, J. C.; Jeannin, Y.; Kristiansson, O. *J. Organomet. Chem.* **1986**, *310*, 367.

[2] Muller, F.; van Koten, G.; Kraakman, M. J.; Vrieze, K.; Heijdenrijk, D.; Zoutberg, M. C. *Organometallics* **1989**, *8*, 1331.

[3] Adams, R. D.; Tanner, J. T. *Organometallics* **1989**, *8*, 563.

[4] Adams, R. D.; Tanner, J. T. *Organometallics* **1988**, *7*, 2241.

[5] Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics* **1990**, *9*, 595.

[6] (a) Cabrera, E.; Daran, J. C.; Jeannin, Y. *Organometallics* **1988**, *7*, 2010. (b) Cabrera, E.; Daran, J. C.; Jeannin, Y. *Organometallics* **1989**, *8*, 1811.

[7] Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, Y. *Organometallics* **1990**, *9*, 1523.

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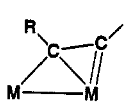
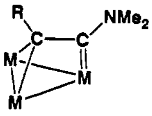
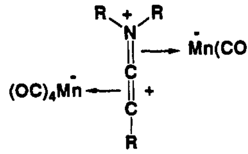


A



B



C

We have now extended our studies of the coordination of ynamines to rhenium. The only previous report of ynamine complexes of the manganese subgroup was made by King et al., who prepared the complexes $Mn_2(CO)_8(RC_2NR'_2)$ (C; R = Me, R′ = Et; R = Ph, R′ = Me; R = NEt_2, R′ = Et).[8] The proposed structure for these complexes was based on spectroscopic evidence alone and contained no metal–metal bonding. We have now prepared the related rhenium complex $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ (1) and the three new complexes $Re_2(CO)_7[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)CMe]$ (2), $Re_2(CO)_7[\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)]$ (3), and $Re_2(CO)_7[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)]$ (4), which are isomers and were formed by the head-to-head, head-to-tail, and tail-to-tail coupling of two ynamine molecules at the dirhenium center. Compounds 1 and 2 have been characterized structurally by X-ray diffraction methods. The structure of 1 contains a bridging ynamine ligand of the established form A.

Experimental Section

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. Mass spectra were run on a VG Model 70SQ mass spectrometer. MeC_2NMe_2[9] and $Re_2(CO)_8[\mu\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$[10] were prepared by previously reported procedures.

Reaction of $Re_2(CO)_8[\mu\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ with $CH_3C_2NMe_2$. A. At 25 °C. To a solution of 150 mg (0.22 mmol) of $Re_2(CO)_8[\mu\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ in 50 mL of hexane was added 95 μL (1.14 mmol) of MeC_2NMe_2. The solution was stirred at 25 °C for 24 h. The solvent was evaporated and the residue chromatographed by TLC with hexane/CH_2Cl_2 (5:1) solvent to give the following compounds in order of elution: 9.0 mg of starting material and 35.0 mg of orange $Re_2(CO)_8(\mu\text{-}MeC_2NMe)$ (1), 25% yield. IR (ν(CO) in hexane, cm^{-1}): for 1, 2086 (w), 2046 (m), 1994 (m, sh), 1988 (vs), 1961 (s), 1950 (w), 1933 (m). ^1H NMR (δ in $CDCl_3$): for 1, 3.53 (s, 3 H), 3.48 (s, 3 H), 3.30 (s, 3 H). Anal. Calcd (found): C, 22.97 (22.80); H, 1.33 (1.19); N, 2.06 (2.14). The mass spectrum of 1 showed the parent ion m/e = 679 and ions corresponding to the loss of each of the eight carbonyl ligands.

B. At 50 °C. An 80-mg (0.12-mmol) amount of $Re_2(CO)_8[\mu\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ and 60 μL (0.72 mmol) of MeC_2NMe_2 in 50 mL of hexane were heated to 50 °C for 1.5 h. After the mixture was cooled, the solvent was evaporated and the residue chromatographed in the same way as described above to give the following compounds in order of elution: 5.5 mg of yellow $Re_2(CO)_7[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)C(Me)]$ (2), 6% yield; 1.2 mg of yellow $Re_2(CO)_7[\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)]$ (3), 1% yield; 3.1 mg of orange $Re_2(CO)_7[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)]$ (4), 3% yield; 26 mg of orange $Re_2(CO)_8(MeC_2NMe_2)$ (1), 32% yield. IR (ν(CO) in hexane, cm^{-1}): for 2, 2082 (m), 2028 (s), 2004 (m), 1996 (vs), 1925 (m); for 3, 2078 (w), 2024 (vs), 2000 (m), 1966 (m), 1959 (s), 1930 (m); for 4, 2073 (w), 2022 (vs), 1994 (s), 1964 (m), 1955 (s), 1930 (m). ^1H NMR (δ in $CDCl_3$): for 2, 2.89 (s, 12 H), 2.73 (s, 6 H); for 3, 2.90 (s, 6 H), 2.79 (s, 3 H), 2.57 (s, 6 H), 2.38 (s, 3 H); for 4, 2.47 (s, 12 H), 2.40 (s, 6 H). Anal. Calcd (found) for 2: C, 27.79 (27.77); H, 2.47 (2.32); N, 3.81 (3.87). Calcd (found) for 3: C, 27.79 (28.07); H, 2.47 (2.62); N, 3.81 (3.87). Calcd (found) for 4: C, 27.79 (27.64); H, 2.47 (2.23); N, 3.81 (4.02). Mass spectra of all three compounds were similar and showed the following ions (m/e): for 2–4, $m/e = 734 - 28x$, x = 0–7 ($M^+ - x$CO).

Table I. Crystal Data for Structural Analyses of Compounds 1 and 2

	1	2
empirical formula	$Re_2O_8NC_{13}H_9$	$Re_2O_7N_2C_{17}H_{18}$
fw	679.63	734.75
cryst syst	monoclinic	orthorhombic
lattice params		
a, Å	9.776 (2)	17.668 (4)
b, Å	11.315 (4)	8.510 (2)
c, Å	15.695 (4)	14.058 (4)
β, deg	97.56 (2)	
V, Å^3	1721.0 (9)	2114 (2)
space group	$P2_1/c$ (No. 14)	$Pca2_1$ (No. 29)
Z	4	4
D_{calc}, g/cm^3	2.62	2.31
μ(Mo Kα), cm^{-1}	142.85	116.37
abs cor	analytical	empirical
temp, °C	23	23
$2\theta_{max}$, deg	44.0	46.0
no. of observns ($I > 3\sigma(I)$)	1800	1429
no. of variables	217	252
residuals: R; R_w	0.034; 0.040	0.018; 0.021
goodness of fit indicator	2.45	1.35
max shift in final cycle	0.01	0.00
largest peak in final diff map, e/Å^3	1.07	0.44

Reaction of 1 with MeC_2NMe_2. A 43-mg (0.063-mmol) amount of 1 and 40 μL (0.48 mmol) of MeC_2NMe_2 were dissolved in 50 mL of hexane. The solution was heated to a slow reflux for 80 min. After the solution was cooled, the solvent was evaporated to dryness and the residue was chromatographed by TLC with hexane/CH_2Cl_2 (5/1) as solvent to give the following bands in order of elution: yellow 2 (25.1 mg, 54%); yellow 3 (4.4 mg, 9.5%); orange 4 (7.0 mg, 17%); 4.4 mg of unreacted 1.

Crystallographic Analyses. Crystals of 1 suitable for diffraction analysis were grown from a solution in a hexane/CH_2Cl_2 solvent mixture at 25 °C. Crystals of 2 were grown from a hexane/CH_2Cl_2 solution at −15 °C. 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 AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All intensity measurements were made by using the standard ω-scan (moving-crystal–stationary-counter) technique. Background measurements were made by an additional one-fourth scan at each end of the scan. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[11a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[11b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02F_o^2)^2]^{1/2}/Lp$.

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(8) King, R. B.; Harmon, C. A. *Inorg. Chem.* **1976**, *15*, 879.

(9) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971; p 146.

(10) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4955.

(11) (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.

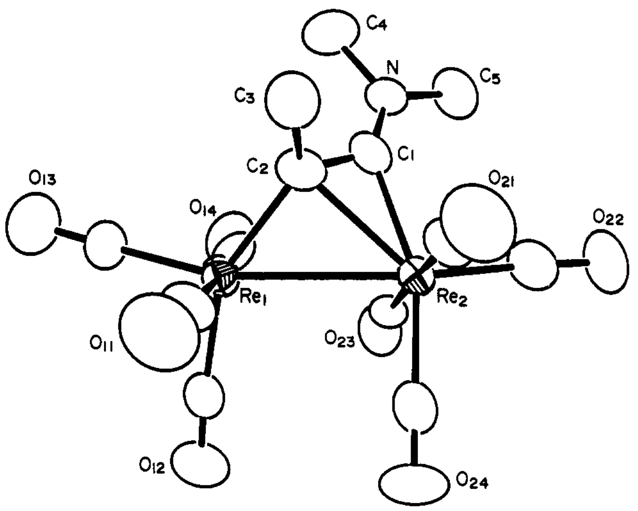

Figure 1. ORTEP drawing of $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ (1) showing 50% probability thermal ellipsoids.

Compound 1 crystallized in the monoclinic crystal system. The space group $P2_1/c$ 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 techniques. All non-hydrogen atoms were refined by using anisotropic thermal parameters. The hydrogen atom positions were calculated by assuming idealized geometries and employing observed positions whenever possible. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 2 crystallized in the orthorhombic crystal system with four molecules in the unit cell. The systematic absences were consistent with either of the space groups $Pca2_1$ (noncentric) or *Pbcm* (centric). Efforts to refine the structure in the centric space group were unsuccessful. As was found later, the molecule did not contain a rigorous plane of symmetry as was required by this space group. The noncentric space group yielded a reasonable solution with an excellent refinement and was thus deemed to be correct. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated with use of idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. See the supplementary material for the tables of structure factor amplitudes, tables of hydrogen atom positional parameters, and the values of the anisotropic thermal parameters for both of the structural analyses.

Results and Discussion

In 1976, King reported that $Mn_2(CO)_{10}$ reacted with ynamines when exposed to UV irradiation to yield the ynamine substitution products C.[8] Similar reactions with $Re_2(CO)_{10}$ instead of $Mn_2(CO)_{10}$ failed to yield the corresponding rhenium analogues.[8] In 1982, Nubel and Brown prepared the complexes $Re_2(CO)_8[\mu\text{-}C(H){=}CRR'](\mu\text{-}H)$ from the reaction of $Re_2(CO)_{10}$ with terminal alkenes induced by UV irradiation. They also showed that these complexes readily released alkene and were good reagents for the preparation of a variety of $Re_2(CO)_8(\text{ligand})_2$ complexes.[10]

We have now found that $Re_2(CO)_8[\mu\text{-}CH{=}C(H)Bu^n](\mu\text{-}H)$ reacts with $MeC{\equiv}CNMe_2$ at 25 °C to yield $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$ (1; 25%). The structure of this complex was established by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of 1 is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic bond distances and angles are listed in Tables III and IV, respectively. The molecule consists of two $Re(CO)_4$ groups joined by a rhenium–rhenium bond and a bridging MeC_2NMe_2 ligand. The Re(1)–Re(2) distance of 3.023 (1) Å is slightly shorter than that in $Re_2(CO)_{10}$ (3.041 (1) Å).[12] The ynamine ligand bridges the Re–Re bond in the "twisted" fashion A that has been observed for ynamines in other dinuclear bridging modes.[1-3] The methyl-substituted carbon atom is bonded asymmetrically to both metal atoms (Re(1)–C(2) = 2.09 (1) Å, Re(2)–C(2) = 2.40 (1) Å), while the amine-substituted carbon atom is coordinated solely to Re(2) (Re(2)–C(1) = 2.13 (1) Å). The

Table II. Positional Parameters and *B*(eq) Values for $Re_2(CO)_8[\mu\text{-}C(Me)C(NMe_2)]$ (1)

atom	*x*	*y*	*z*	*B*(eq), Å²
Re(1)	0.82536 (05)	0.12265 (05)	0.69431 (04)	2.94 (3)
Re(2)	0.71775 (05)	0.29347 (05)	0.55312 (04)	2.93 (3)
O(11)	1.0539 (12)	0.2913 (11)	0.7821 (09)	6.5 (7)
O(12)	1.0507 (12)	0.0059 (12)	0.6026 (09)	6.8 (7)
O(13)	0.8711 (12)	−0.0190 (11)	0.8597 (08)	5.9 (6)
O(14)	0.6244 (12)	−0.0806 (12)	0.6321 (08)	6.1 (6)
O(21)	0.7951 (13)	0.5425 (12)	0.6339 (09)	6.8 (7)
O(22)	0.5563 (12)	0.4206 (11)	0.3984 (08)	6.3 (6)
O(23)	0.6624 (12)	0.0495 (11)	0.4589 (07)	5.2 (6)
O(24)	1.0035 (11)	0.2842 (14)	0.4862 (08)	6.6 (7)
N	0.4290 (11)	0.2367 (10)	0.6255 (07)	3.3 (5)
C(1)	0.5586 (14)	0.2540 (11)	0.6293 (09)	3.3 (7)
C(2)	0.6717 (13)	0.2505 (13)	0.6961 (09)	3.5 (7)
C(3)	0.6705 (15)	0.3475 (16)	0.7626 (10)	4.8 (8)
C(4)	0.3647 (15)	0.1934 (18)	0.6982 (11)	6 (1)
C(5)	0.3318 (14)	0.2532 (16)	0.5506 (11)	5.0 (8)
C(11)	0.9656 (15)	0.2328 (15)	0.7480 (11)	4.2 (8)
C(12)	0.9693 (15)	0.0458 (15)	0.6390 (10)	4.2 (7)
C(13)	0.8538 (14)	0.0343 (14)	0.7945 (10)	3.9 (7)
C(14)	0.6950 (15)	−0.0013 (16)	0.6492 (09)	4.0 (7)
C(21)	0.7671 (15)	0.4504 (16)	0.6078 (11)	4.3 (8)
C(22)	0.6131 (16)	0.3675 (16)	0.4577 (11)	4.7 (8)
C(23)	0.6848 (14)	0.1359 (14)	0.4964 (10)	3.4 (7)
C(24)	0.9027 (15)	0.2904 (14)	0.5113 (10)	3.7 (7)

Table III. Intramolecular Distances for 1[a]

Re(1)–Re(2)	3.023 (1)	Re(2)–C(22)	1.89 (2)
Re(1)–C(2)	2.09 (1)	Re(2)–C(23)	2.00 (2)
Re(1)–C(11)	1.96 (2)	Re(2)–C(24)	2.00 (2)
Re(1)–C(12)	1.95 (2)	N–C(1)	1.28 (2)
Re(1)–C(13)	1.85 (2)	N–C(4)	1.46 (2)
Re(1)–C(14)	1.96 (2)	N–C(5)	1.42 (2)
Re(2)–C(1)	2.13 (1)	C(1)–C(2)	1.42 (2)
Re(2)–C(2)	2.40 (1)	C(2)–C(3)	1.51 (2)
Re(2)–C(21)	2.00 (2)	O–C (av)	1.15 (2)

[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]

Re(2)–Re(1)–C(2)	52.1 (4)	C(1)–Re(2)–C(24)	159.6 (6)
Re(2)–Re(1)–C(11)	93.7 (5)	C(2)–Re(2)–C(21)	81.0 (6)
Re(2)–Re(1)–C(12)	99.2 (4)	C(2)–Re(2)–C(22)	133.0 (6)
Re(2)–Re(1)–C(13)	164.9 (5)	C(2)–Re(2)–C(23)	101.4 (5)
Re(2)–Re(1)–C(14)	92.6 (5)	C(2)–Re(2)–C(24)	126.3 (5)
C(2)–Re(1)–C(11)	91.0 (6)	C(1)–N–C(4)	123 (1)
C(2)–Re(1)–C(12)	151.2 (6)	C(1)–N–C(5)	125 (1)
C(2)–Re(1)–C(13)	113.0 (6)	C(4)–N–C(5)	112 (1)
C(2)–Re(1)–C(14)	93.8 (6)	Re(2)–C(1)–N	143 (1)
Re(1)–Re(2)–C(1)	70.4 (4)	Re(2)–C(1)–C(2)	82.3 (8)
Re(1)–Re(2)–C(2)	43.5 (3)	N–C(1)–C(2)	135 (1)
Re(1)–Re(2)–C(21)	102.2 (5)	Re(1)–C(2)–Re(2)	84.5 (5)
Re(1)–Re(2)–C(22)	164.1 (5)	Re(1)–C(2)–C(1)	120 (1)
Re(1)–Re(2)–C(23)	77.1 (4)	Re(1)–C(2)–C(3)	126 (1)
Re(1)–Re(2)–C(24)	89.3 (4)	Re(2)–C(2)–C(1)	61.8 (8)
C(1)–Re(2)–C(2)	36.0 (5)	Re(2)–C(2)–C(3)	121 (1)
C(1)–Re(2)–C(21)	95.6 (5)	C(1)–C(2)–C(3)	114 (1)
C(1)–Re(2)–C(22)	100.3 (6)	Os–C–O (av)	176 (1)
C(1)–Re(2)–C(23)	88.6 (5)		

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

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[12] Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* 1981, *20*, 1609.

Table V. Positional Parameters and B(eq) Values for $Re_2(CO)_7[MeC_2(NMe_2)(Me_2N)C_2Me]$ (2)

atom	x	y	z	B(eq), Å^2
Re(1)	0.15730 (02)	0.09764 (05)	0.1502	3.10 (2)
Re(2)	0.11171 (02)	0.41074 (05)	0.09584 (05)	2.71 (2)
O(11)	0.2492 (08)	0.0173 (14)	0.3351 (10)	9.1 (7)
O(12)	0.3061 (05)	0.2623 (11)	0.0925 (12)	8.9 (7)
O(13)	0.0278 (07)	−0.1180 (11)	0.2330 (08)	7.0 (6)
O(14)	0.2088 (05)	−0.1747 (10)	0.0196 (08)	5.5 (5)
O(21)	0.2080 (07)	0.6245 (11)	0.2263 (09)	7.6 (6)
O(22)	0.2123 (05)	0.4608 (14)	−0.0782 (07)	6.5 (6)
O(23)	0.0232 (05)	0.7028 (10)	0.0376 (07)	5.3 (5)
N(1)	−0.0597 (05)	0.2445 (12)	0.0343 (08)	4.4 (5)
N(2)	−0.0519 (05)	0.3603 (12)	0.2270 (08)	4.4 (5)
C(1)	0.0743 (06)	0.1717 (11)	0.0475 (08)	2.6 (4)
C(2)	0.0072 (05)	0.2357 (11)	0.0832 (07)	2.3 (4)
C(3)	0.0146 (06)	0.2924 (11)	0.1852 (07)	2.5 (5)
C(4)	0.0852 (06)	0.2681 (12)	0.2283 (07)	3.3 (5)
C(5)	−0.0928 (08)	0.1009 (18)	0.0012 (15)	8 (1)
C(6)	−0.1118 (08)	0.3804 (16)	0.0362 (13)	5.7 (7)
C(7)	−0.0999 (08)	0.2482 (16)	0.2718 (11)	6.0 (8)
C(8)	−0.0513 (09)	0.5135 (18)	0.2746 (11)	6.2 (8)
C(9)	0.0768 (08)	0.1230 (15)	−0.0557 (09)	4.7 (7)
C(10)	0.0973 (08)	0.3104 (15)	0.3314 (08)	4.7 (6)
C(11)	0.2144 (09)	0.0450 (18)	0.2683 (13)	6.6 (9)
C(12)	0.2489 (08)	0.2120 (14)	0.1122 (12)	5.3 (7)
C(13)	0.0755 (08)	−0.0394 (14)	0.2031 (09)	4.4 (6)
C(14)	0.1935 (07)	−0.0763 (14)	0.0712 (09)	4.0 (6)
C(21)	0.1734 (07)	0.5449 (14)	0.1755 (10)	4.3 (6)
C(22)	0.1748 (07)	0.4467 (13)	−0.0126 (10)	3.7 (6)
C(23)	0.0566 (07)	0.5920 (14)	0.0609 (08)	3.6 (6)

Table VI. Intramolecular Distances for 2[a]

Re(1)–C(14)	1.96 (1)	Re(2)–C(3)	2.35 (1)
Re(1)–C(12)	1.96 (1)	Re(2)–C(2)	2.379 (9)
Re(1)–C(11)	1.99 (2)	N(1)–C(2)	1.37 (1)
Re(1)–C(13)	2.00 (2)	N(2)–C(3)	1.44 (1)
Re(1)–C(1)	2.15 (1)	C(1)–C(2)	1.40 (1)
Re(1)–C(4)	2.22 (1)	C(1)–C(9)	1.51 (2)
Re(1)–Re(2)	2.8868 (7)	C(2)–C(3)	1.52 (1)
Re(2)–C(23)	1.89 (1)	C(3)–C(4)	1.40 (1)
Re(2)–C(22)	1.91 (1)	C(4)–C(10)	1.51 (2)
Re(2)–C(21)	1.94 (1)	O–C (av)	1.14 (2)
Re(2)–C(1)	2.24 (1)	C(Me)–N (av)	1.45 (2)
Re(2)–C(4)	2.27 (1)		

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

C(1)–C(2) length of 1.42 (2) Å is similar to that found for other bridging ynamine ligands. The C(1)–N bond is characteristically short (1.28 (2) Å), and the nitrogen atom has a planar geometry. Both features indicate the existence of multiple bonding between these atoms. This is further supported by the observation of separate ^1H NMR resonances for the N-methyl groups, indicating hindered rotation about the C(1)–N bond.

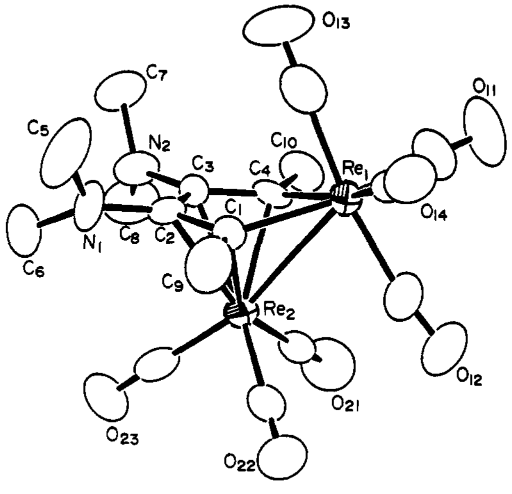


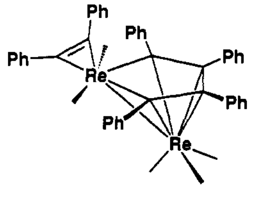
Figure 2. ORTEP drawing of $Re_2(CO)_7[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)C(Me)]$ (2) showing 50% probability thermal ellipsoids.

Table VII. Intramolecular Bond Angles for 2[a]

C(14)–Re(1)–C(12)	87.2 (5)	C(2)–Re(2)–Re(1)	70.0 (2)
C(14)–Re(1)–C(11)	97.9 (6)	C(2)–N(1)–C(5)	118 (1)
C(14)–Re(1)–C(13)	90.3 (5)	C(2)–N(1)–C(6)	125 (1)
C(14)–Re(1)–Re(2)	129.7 (3)	C(7)–N(2)–C(3)	114 (1)
C(12)–Re(1)–C(11)	85.4 (7)	C(3)–N(2)–C(8)	123 (1)
C(12)–Re(1)–C(13)	170.4 (6)	C(2)–C(1)–C(9)	118 (1)
C(12)–Re(1)–Re(2)	72.6 (4)	Re(1)–C(1)–Re(2)	82.0 (4)
C(11)–Re(1)–C(13)	85.7 (6)	N(1)–C(2)–C(1)	125 (1)
C(11)–Re(1)–Re(2)	124.7 (5)	N(1)–C(2)–C(3)	122.1 (9)
C(13)–Re(1)–Re(2)	115.8 (4)	N(1)–C(2)–Re(2)	132.3 (8)
C(1)–Re(1)–Re(2)	50.4 (3)	C(1)–C(2)–C(3)	112.9 (8)
C(4)–Re(1)–Re(2)	50.8 (2)	C(4)–C(3)–N(2)	128 (1)
C(23)–Re(2)–C(22)	87.8 (5)	C(4)–C(3)–C(2)	115.9 (9)
C(23)–Re(2)–C(21)	87.6 (5)	N(2)–C(3)–C(2)	116.4 (9)
C(23)–Re(2)–Re(1)	165.1 (3)	N(2)–C(3)–Re(2)	130.0 (7)
C(22)–Re(2)–C(21)	92.2 (5)	C(3)–C(4)–C(10)	120 (1)
C(22)–Re(2)–Re(1)	101.3 (3)	C(3)–C(4)–Re(1)	113.2 (7)
C(21)–Re(2)–Re(1)	103.5 (3)	Re(1)–C(4)–Re(2)	80.0 (4)
C(1)–Re(2)–Re(1)	47.6 (3)	O(12)–C(12)–Re(1)	172 (1)
C(4)–Re(2)–Re(1)	49.2 (3)	O–C–Re (av)	178 (1)
C(3)–Re(2)–Re(1)	70.5 (2)		

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

At 68 °C, compound 1 reacts further with MeC_2NMe_2 by CO elimination to yield the three new isomeric products $Re_2(CO)_7[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)CMe]$ (2; 54%), $Re_2(CO)_7[\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)]$ (3; 9.5%), and $Re_2(CO)_7[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)]$ (4; 17%). Compound 2 was characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the structure of 2 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 a metallacyclic ring formed by the head-to-head coupling of two ynamine ligands. This group is π-bonded to the second rhenium atom in the well-known ferrole-like structure.[13] There is a rhenium–rhenium bond (2.8868 (7) Å), which is significantly shorter than that in 1 and $Re_2(CO)_{10}$.[12] There are relatively few dirhenium complexes for which the ferrole-like structure has been observed. One is the complex $Re_2(CO)_5(PhC_2Ph)[\mu\text{-}C(PhC(Ph)C(Ph)C(Ph)]$ (5), where the Re–Re distance is 2.849 (1) Å.[14] A similar head-to-head coupling and coordination of two ynamine ligands was observed in the complexes $Fe_2(CO)_6[\mu\text{-}C(Me)C(NEt_2)C(NEt_2)C(Me)]$[15] and $Os_4(CO)_{11}[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)C(Me)](\mu_3\text{-}S)$.[16] The C–N distances to the amino groups are longer than the corresponding distances in 1 (1.37 (1) and 1.44 (1) Å), the nitrogen atoms have developed a slight pyramidal struc-



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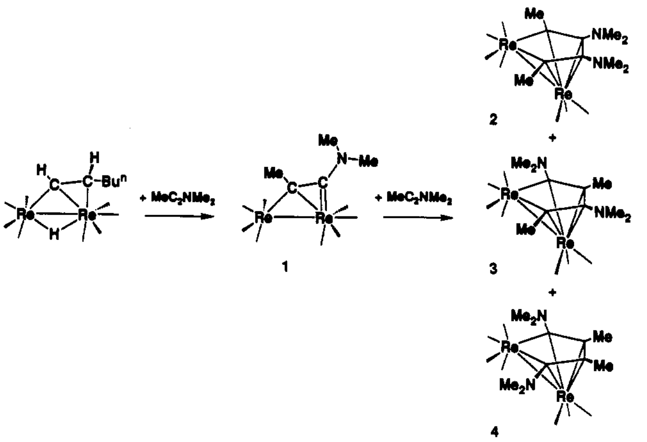
[13] Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 31.4.

[14] Pourreau, D. B.; Whittle, R. R.; Geoffroy, G. L. *J. Organomet. Chem.* **1984**, *273*, 333.

[15] Daran, J. C.; Jeannin, Y. *Organometallics* **1984**, *3*, 1158.

[16] Adams, R. D.; Chen, G.; Sun, S.; Tanner, J. T.; Wolfe, T. A. *Organometallics* **1990**, *9*, 251.

Scheme I



ture, and the observation of a single *N*-methyl resonance in the ^1H NMR spectrum (2.89 ppm) indicates that rotation about the C–N bond is rapid on the NMR time scale at 25 °C.

The infrared spectra of compounds **3** and **4** in the carbonyl region are very similar to that of **2** and indicate that the structural dispositions of the carbonyl ligands in all three complexes are also very similar. The mass spectra of **3** and **4** show parent ions $m/e = 734$ and ions due to the loss of each of seven carbonyl ligands. This supports the notion that **2**–**4** are isomers. The ^1H NMR spectrum of **3** shows two resonances of intensity 6 (2.90 and 2.57 ppm) that we attribute to two inequivalent but rapidly rotating NMe_2 groups and two resonances of intensity 3 that we attribute to inequivalent *C*-methyl groups. On this basis, we propose that the structure of **3** is analogous to that of **2** but contains two ynamine ligands coupled in a head-to-tail fashion. On the other hand, the ^1H NMR spectrum of **4** shows only one *N*-methyl resonance and one *C*-methyl resonance. Accordingly, we propose that the structure of **4** is analogous to that of **2** and **3** but that the ynamine ligands are coupled in a tail-to-tail fashion (see Scheme I). All four products **1**–**4** were obtained when $Re_2(CO)_8[\mu\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ was allowed to react with an excess of MeC_2NMe_2 at 50 °C. As found for the bridging ynamine ligands in other complexes, we believe that further studies will show that the amine-substituted carbon atom in **1** also contains a substantial amount of carbene-like character. The reactivity of **1** is currently being investigated in hopes of finding additional evidence for this.

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Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of the hydrogen atoms for both crystal structure analyses (7 pages); listings of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Synthesis and Structural Characterization of the Sandwichlike Compound $[(12\text{-crown-}4)Li(\eta^5\text{-}C_5H_5)]$ and the η^0-Substituted-Cyclopentadienide Salt $[Li(12\text{-crown-}4)_2][1,2,4\text{-}(Me_3Si)_3C_5H_2]$

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The addition of 12-crown-4, in stoichiometric amounts or in excess, to a solution of LiC_5H_5 in THF affords the complex $[(12\text{-crown-}4)Li(\eta^5\text{-}C_5H_5)]$ (**1**). X-ray structural data demonstrate that it possesses a unique sandwichlike structure in which the Li^+ ion is coordinated on one side by four oxygens from a 12-crown-4 ligand and on the other side by the cyclopentadienide anion, $[C_5H_5]^-$, in an η^5 fashion. In contrast, the addition of 12-crown-4 to THF solutions of $Li(1,2,4\text{-}(Me_3Si)_3C_5H_2)$ gives the ion pair $[Li(12\text{-crown-}4)_2]^+[1,2,4\text{-}(Me_3Si)_3C_5H_2]^-$ (**2**), which has a free (η^0) substituted-cyclopentadienide ion as part of its lattice. The latter complex represents a very rare example of the structure of an η^0 delocalized carbanion, and the structure of **1** is the first of a new class of sandwich structures. Crystal data at 130 K: **1**, $C_{13}H_{21}LiO_4$, $a = 7.729$ (5) Å, $b = 11.268$ (7) Å, $c = 15.618$ (8) Å, orthorhombic, $P2_12_12_1$, $Z = 4$; **2**, $C_{30}H_{61}LiO_8Si_3$, $a = 11.924$ (4) Å, $b = 12.565$ (4) Å, $c = 14.530$ (3) Å, $\alpha = 92.65$ (2)°, $\beta = 90.03$ (2)°, $\gamma = 120.28$ (2)°, triclinic, $P\bar{1}$, $Z = 2$.

Introduction

Although the term π-complex is normally associated with transition-metal species, most notably ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$, numerous compounds that feature π-complexation of a ligand to a main-group element are now known. A recent review[1] of this area cited almost 300 references and showed that complexes which involve gallium[2] and antimony in π-complexation have been known for over a century.

Lithium π-complexes have been studied for a number of years,[3] and they are of importance because, like σ-

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(1) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217.

(2) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

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