Appendix

All calculations have been carried out within the extended Hückel formalism[17] with use of the weighted H_{ij} formula.[18] The atomic parameters utilized are listed in Table II. The parameters for Os come from earlier work.[19] In all models one axial and two equatorial carbonyls were terminally bonded to each Os atom and the following bond distances (Å) were used: Os–Os = 2.85, Os–C(O) = 1.92, C–O = 1.15, C–C = 1.43, C–N = 1.33, C–H = 1.09, N–H = 1.01. All the C(O)–Os–C(O) angles were set at 90°. In the closo models, Os–C(1) and Os(2,3)–C(2) distances were set equal to 2.15 and 2.10 Å, respectively, whereas in the basketlike models Os(1)–C(1) = 2.10 Å and Os(2,3)–C(2) = 2.15 Å. Finally, in the nido complexes, Os(1)–C(1,2) and Os(2,3)–C(1,2) distances of 2.15 and 2.10 Å, respectively, were used.

Registry No. 3, 105286-41-7.

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Cluster Complexes Containing Ynamine Ligands. 2. Reactions of $MeC{\equiv}CNMe_2$ with $M_3(CO)_{10}(\mu_3\text{-}S)$ (M = Fe, Ru, Os) and Structural Characterizations of $Ru_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$, $Ru_2(CO)_6[\mu\text{-}SCMeC(NMe_2)]$, and $Os_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu_3\text{-}S)$

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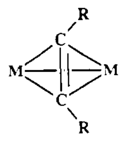
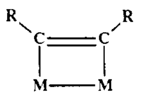
The reactions of the compounds $M_3(CO)_{10}(\mu_3\text{-}S)$ (**1a**, M = Fe; **1b**, M = Ru) with MeC_2NMe_2 yielded the products $M_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$ (**2a**, M = Fe, 3%; **2b**, M = Ru, 36%) and $M_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu_3\text{-}S)$ (**3a**, M = Fe, 30%; **3b**, M = Ru, 14%). The reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ (**1c**) with MeC_2NMe_2 yielded only the trinuclear product $Os_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu_3\text{-}S)$ (**3c**, 87%). Compounds **2b** and **3c** were characterized by single-crystal X-ray diffraction analyses. Compound **2b** consists of a metal–metal-bonded $Ru_2(CO)_6$ grouping bridged by a $SC(NMe_2)CMe$ ligand. The sulfur and *C*-methyl carbon atom are strongly bonded to both metal atoms. The NMe_2-substituted carbon atom is weakly bonded to one metal atom and not bonded to the other. Compound **3c** consists of an open triosmium cluster with a triply bridging sulfido ligand and a triply bridging MeC_2NMe_2 ligand. The *C*-methyl carbon atom is bonded to two metal atoms. The NMe_2-substituted carbon atom is coordinated only to the one remaining metal atom. Structurally, this grouping resembles an NMe_2-substituted carbene ligand. This is also supported by the ^{13}C NMR spectrum, which shows a very low field resonance, +251.92 ppm for **3a** and +243.50 ppm for **3c**. It is proposed that the ynamine ligands in the compounds **3a–c** should be formulated as (α,α-dimetallioethyl)(dimethylamino)carbene ligands. Compound **2b** isomerizes when heated to form the compound $Ru_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$ (**2b′**) in 38% yield. Compound **2b′** was characterized structurally. The structure is similar to that of **2b** except that the methyl-substituted carbon atom is bonded to the sulfur atom and the NMe_2-substituted carbon atom is not a bridging atom but is terminally coordinated to one of the metal atoms. The iron homologue of **2b′**, $Fe_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$ (**2a′**), was obtained (55% yield) by pyrolysis of **3a** at 100 °C. Crystal data: for **2b**, space group $P\bar{1}$, a = 9.189 (1) Å, b = 11.705 (3) Å, c = 8.213 (1) Å, α = 106.18 (1)°, β = 110.06 (1)°, γ = 79.60 (2)°, V = 793.3 (3) Å^3, Z = 2, R = 0.020, and R_w = 0.023 for 2373 reflections; for **2b′**, space group $P2_1/n$, a = 10.531 (2) Å, b = 10.799 (2) Å, c = 14.336 (3) Å, β = 98.07 (2)°, V = 1614 (1) Å^3, Z = 4, R = 0.025, and R_w = 0.026 for 1615 reflections; for **3c**, space group $P\bar{1}$, a = 9.397 (4) Å, b = 13.406 (7) Å, c = 8.914 (3) Å, α = 92.84 (4)°, β = 115.20 (3)°, γ = 97.54 (4)°, V = 1000.3 (8) Å^3, Z = 2, R = 0.030, and R_w = 0.035 for 2814 reflections.

Introduction

Recent studies of the ligand behavior of unsymmetrical ynamines, $RC{\equiv}CNR'_2$, have shown that these molecules exhibit unusual bridging coordinations.[1-5] In binuclear coordination, simple alkynes usually exhibit either the perpendicular (A) or parallel (B) bonding modes,[6] but unsymmetrical ynamines have been found to exhibit the skewed bridging form C that lies approximately halfway



A



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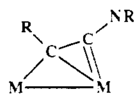

C

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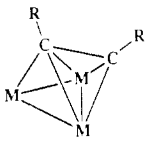
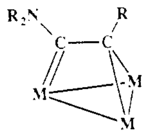
Table I. IR and NMR Spectra of 2a,a′,b,b′ and 3a–c

compd	IR (ν(CO) in hexane), cm^{-1}	NMR (in $CDCl_3$ at 25 °C), δ	
2a	2066 (m), 2023 (vs), 1994 (s), 1977 (m), 1964 (w)	^1H	2.79 (s, NMe_2), 2.22 (s, CMe)
2a′	2065 (m), 2023 (vs), 1993 (s), 1979 (s), 1972 (m), 1958 (w)	^1H	3.08 (s, NMe_2), 1.94 (s, CMe)
		^{13}C	32.6 (NMe_2), 75.1 (C*Me*), 199.2 (*C*Me), 208.5 (1, CO), 209.5 (1, CO), 211.4 (*C*NMe_2), 212.3 (3, CO), 214.6 (1, CO)
2b	2075 (s), 2042 (vs), 2004 (vs), (m) 1987 (s), 1975	^1H	2.76 (s, NMe_2), 2.26 (s, CMe)
		^{13}C	196.5 (6, CO), 153.1 (*C*NMe_2), 104.9 (*C*Me), 40.56 (NMe_2), 23.1 (C*Me*)
2b′	2076 (s), 2043 (vs), 2005 (s), 1989 (s), 1984 (s), 1968 (m)	^1H	3.03 (s, NMe_2), 2.20 (s, CMe)
		^{13}C	34.5 (NMe_2), 75.8 (C*Me*), 191.1 (*C*Me), 196.7 (*C*NMe_2), 198.8 (3, CO), 200.9 (3, CO)
3a	2076 (w), 2046 (vs), 2020 (s), 2005 (s), 1988 (s), 1978 (w)	^1H	3.52 (s, NMe), 3.23 (s, NMe), 2.03 (s, CMe)
		^{13}C	251.92 (*C*NMe_2), 212.37 (3, CO), 210.96 (CO), 209.30 (br, 3, CO), 208.19 (CO), 205.80 (CO), 127.84 (*C*Me), 49.17 (NMe), 47.26 (NMe), 37.40 (C*Me*)
3b	2087 (w), 2067 (vs), 2039 (s), 2016 (vs), C, 1996 (s), 1986 (m), 1978 (w)	^1H	3.45 (s, NMe), 3.15 (s, NMe), 2.02 (s, CMe)
3c	2088 (w), 2066 (vs), 2039 (s), 2008 (vs), 2004 (m, sh), 1988 (m), 1971 (m), 1962 (vw)	^1H	3.39 (s, NMe), 3.10 (s, NMe), 2.28 (s, CMe)
		^{13}C	243.50 (*C*NMe), 178.93 (CO), 177.70 (3, CO), 177.55 (CO), 176.41 (CO), 176.10 (CO), 173.14 (CO), 172.40 (CO), 85.92 (*C*Me), 51.17 (N*Me*), 46.40 (N*Me*), 38.63 (C*Me*)

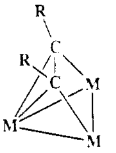
between the A and B modes.[1-3] In trinuclear coordination, some unsymmetrical ynamines have been found to adopt the "slipped" perpendicular triply bridging mode D[4,5] that distinguishes it from both the normal perpendicular mode E and the parallel mode F.[7] For both of the modes C and D, it has been proposed that the amine-substituted carbon atom may contain a significant amount of carbene-like character.[1,2,4] Short C–N distances and the planar geometry of the amino groups imply the existence of significant interactions between the lone pair of electrons on the nitrogen atom and the adjacent alkynyl carbon atom. Support for this has been obtained recently from molecular orbital calculations.[8]



E



D



F

In this report, the reactions of the series of cluster complexes $M_3(CO)_{10}(\mu_3\text{-}S)$ (M = Fe (**1a**), Ru (**1b**), Os (**1c**)) with MeC_2NMe_2 are described. The products $M_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$ (M = Fe (**2a**), Ru (**2b**)) and $M_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (M = Fe (**3a**), Ru (**3b**), Os (**3c**)) have been obtained and characterized, including crystallographic structural characterizations of **2b** and **3c**.

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 Kieselgel 60 F_{254}, E. Merck, West Germany). 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. Carbon NMR spectra were run on a Bruker AM-500 spectrometer at the ^{13}C natural abundance. Variable-temperature ^1H NMR spectra were run on an IBM NR-80 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were run on a VG Model 70SQ mass spectrometer. The starting materials $M_3(CO)_{10}(\mu_3\text{-}S)$ (**1a**, M = Fe;[9] **1b**, M = Ru;[10] **1c**, M = Os[9]) and MeC_2NMe_2[11] were prepared by previously reported procedures. UV irradiation were performed in Pyrex glassware by using an externally positioned high-pressure mercury lamp.

Reaction of 1a with MeC_2NMe_2. A 40-mg (0.083-mmol) amount of **1a** was dissolved in 80 mL of hexane at 0 °C. A 20-μL portion of MeC_2NMe_2 was added, and the solution was irradiated with stirring for 2 h at 0 °C. The resulting solution was subsequently stirred for 10 h at 25 °C without irradiation. The solvent was evaporated in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with a mixture of hexane/CH_2Cl_2 (10/1) yielded the following bands in order of elution: 2.5 mg of $Fe_3(CO)_9(\mu_3\text{-}S)_2$, a trace of $Fe_3(CO)_{12}$, 0.9 mg of orange $Fe_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$ (**2a**, 3%), and 13.3 mg of brown $Fe_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**3a**, 30%). IR and NMR spectra are listed in Table I. Mass spectra showed the following ions (*m/e*): for **2a**, $395 - 28x$, $x = 0\text{-}6$ ($M^+ - xCO$); for **3a**, $535 - 28x$, $x = 0\text{-}9$ ($M^+ - xCO$). Anal. Calcd (found) for **2a**: C, 33.46 (33.54); H 2.30 (2.16); N, 3.55 (3.70). Calcd (found) for **3a**: C, 31.44 (31.46); H, 1.70 (1.63); N, 2.62 (2.54).

Reaction of 1b with MeC_2NMe_2. A 75-mg (0.12-mmol) amount of **1b** was dissolved in 100 mL of hexane. A 70-μL portion of MeC_2NMe_2 was added, and the solution was irradiated for 7 h at room temperature. The solvent was evaporated, and the residue was chromatographed with hexane/CH_2Cl_2 (4/1) to give the following compounds in order of elution: 22.0 mg of yellow $Ru_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$ (**2b**, 36%) and 11.0 mg of orange-red $Ru_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**3b**, 14%). IR and NMR spectra are listed in Table I. Mass spectra showed the following ions (*m/e*): for **2b**, $485 - 28x$, $x = 0\text{-}6$ ($M^+ - xCO$); for **3b**, $670 - 28x$, $x = 1, 4\text{-}9$ ($M^+ - xCO$). Anal. Calcd (found) for **2b**: C, 27.22 (27.16); H, 1.87 (1.77); N, 2.88 (2.99). Calcd (found) for **3b**: C, 25.08 (24.93); H, 1.35 (1.26); N, 2.09 (2.01).

Reaction of 1c with MeC_2NMe_2. A 20.0-mg (0.023-mmol) amount of **1c** was dissolved in 50 mL of hexane, and the solution was heated to reflux. At this temperature, 1.5 μL of MeC_2NMe_2 was added and the reflux was continued for 1 h. The solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and was chromatographed on silica TLC plates by using a hexane/CH_2Cl_2 (7/3) solvent mixture. This yielded 18.5 mg of $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**3c**, 87%) as an orange-yellow band. Anal. Calcd (found) for **3c**: C, 17.94 (17.82); H, 0.96 (0.93); N, 1.50 (1.48).

Synthesis of $Fe_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$ (2a′). A 17-mg (0.032-mmol) amount of **3a** was dissolved in 2 mL of toluene. The solution was heated to 100 °C for 80 min in a oil bath. After the solution was cooled, the solvent was then evaporated and the residue was chromatographed by TLC with a mixture of hexane/CH_2Cl_2 (5/1) as the solvent. This yielded, in order of elution, reddish brown $Fe_3(CO)_9(\mu_3\text{-}S)_2$ (1.5 mg), orange $Fe_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$ (**2a′**, 6.0 mg (55%)), and 2.1 mg of unreacted **2a**.

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Table II. Crystal Data for the Structural Analyses

	2b	2b′	3c
empirical formula	$Ru_2SO_6NC_{11}H_9$	$Ru_2SO_6NC_{11}H_9$	$Os_3SO_9NC_{14}H_9$
fw	485.40	485.40	937.89
cryst syst	triclinic	monoclinic	triclinic
lattice params			
a, Å	9.189 (1)	10.531 (2)	9.397 (4)
b, Å	11.705 (3)	10.799 (2)	13.406 (7)
c, Å	8.213 (1)	14.336 (3)	8.914 (3)
α, deg	106.18 (1)		92.84 (4)
β, deg	110.06 (1)	98.97 (2)	115.20 (3)
γ, deg	79.60 (2)		97.54 (4)
V, Å^3	793.3 (3)	1614 (1)	1000.3 (8)
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	2	4	2
D_{calc}, g/cm^3	2.03	2.00	3.11
μ(Mo Kα), cm^{-1}	20.16	19.81	191.72
temp, °C	23	23	23
$2\theta_{max}$, deg	50.0	45.0	48.0
no. of observns ($I > 3\sigma(I)$)	2373	1615	2814
no. of variables	226	190	253
residuals: R; R_w	0.020; 0.023	0.025; 0.026	0.030; 0.035
goodness of fit indicator	1.39	1.27	2.06
max shift in final cycle	0.34	0.01	0.01
largest peak in final diff map, e/Å^3	0.27	0.31	1.79

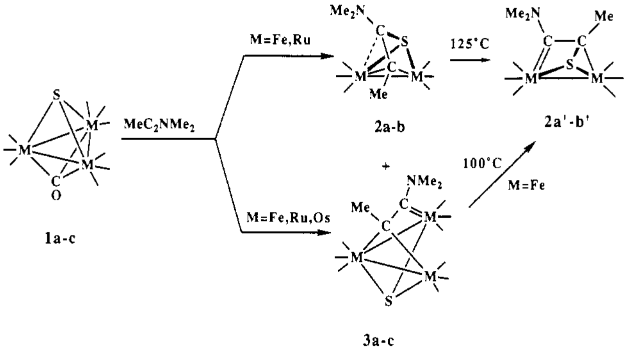
IR and NMR spectra of **2a′** are given in Table I. Anal. Calcd (found) for **2a′**: C, 33.46 (33.80); H, 2.30 (2.19); N, 3.55 (3.40).

Isomerization of 2b to $Ru_2(CO)_6[\mu\text{-}SC(Me)NMe_2]$ (2b′). A 45-mg (0.093-mmol) amount of **2b** was dissolved in 40 mL of octane. The solution was heated to reflux for 70 min. The solvent was evaporated and the residue chromatographed by TLC with hexane to give 17.1 mg (38%) of yellow **2b′** as the only carbonyl-containing product. IR and NMR spectra of **2b** are given in Table I. Anal. Calcd (found): C, 27.22 (27.48); H, 1.87 (1.70); N, 2.88 (3.16).

Crystallographic Analyses. Crystals of **2b** suitable for diffraction analysis were grown from a solution in hexane solvent at −15 °C. Yellow crystals of **2b′** were grown from a hexane solution at 25 °C, and yellow crystals of **3c** were grown from solutions in a CH_2Cl_2/hexane (7/3) solvent mixture at −10 °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. 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 II. All intensity measurements were made by using the standard ω-scan (moving-crystal–stationary-counter) technique. Background measurements were made by a one-fourth additional scan at each end of the scan. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library (version 2.0) obtained from 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] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compounds **2b** and **3c** both 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 in each case. Compound **2b′** 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. All of the structures were solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined by using anisotropic thermal parameters. For **2b**, the positions of all hydrogen atoms were located and refined with isotropic thermal parameters. For **2b′** and **3c**, 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.

Scheme I



Error analyses for all three structures were calculated from the inverse matrix obtained on the final cycle of refinement. See the supplementary material for tables of structure factor amplitudes, tables of hydrogen atom positional parameters, and the values of the anisotropic thermal parameters for all three of the structural analyses.

Results and Discussion

A summary of the results of the reactions reported here is given in Scheme I. The reactions of **1a** and **1b** with MeC_2NMe_2 both yielded two products in moderate to low yields. These were identified as the dinuclear species $M_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$ (M = Fe (**2a**), Ru (**2b**)) and the trinuclear species $M_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (M = Fe (**3a**), Ru (**3b**)). The reaction of **1c** with MeC_2NMe_2 yielded only the trinuclear product $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**3c**). These products were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction analyses of **2b** and **3c**.

An ORTEP drawing of the molecular structure of **2b** is shown in Figure 1. Final atomic positional parameters are listed in Table III. Selected interatomic bond distances and angles are listed in Table IV and V, respectively. The molecule consists of a metal–metal-bonded $Ru_2(CO)_6$ grouping with the metal atoms bridged by a $SC(NMe_2)CMe$ ligand. The Ru–Ru bond distance, 2.6636 (6) Å, is similar to the lengths found in other bridged

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

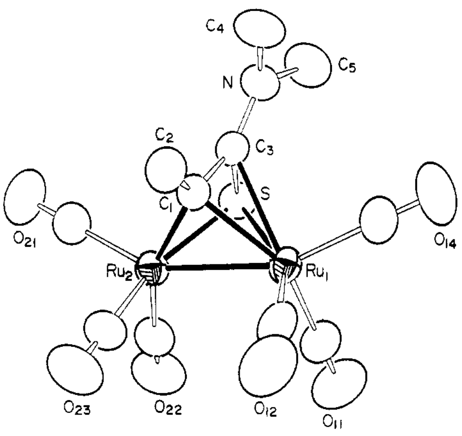


Figure 1. ORTEP drawing of $Ru_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$ (**2b**) showing 50% probability thermal ellipsoids.

Table III. Positional Parameters and *B*(eq) Values for $Ru_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$ (2b)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru(1)	0.78264 (03)	0.31062 (02)	0.03619 (03)	3.24 (1)
Ru(2)	0.88201 (03)	0.23429 (02)	0.33627 (03)	3.31 (1)
S	0.83064 (10)	0.10337 (07)	0.04367 (12)	3.95 (3)
O(11)	1.0864 (04)	0.3518 (03)	−0.0015 (05)	7.7 (2)
O(12)	0.7184 (04)	0.5693 (02)	0.2133 (04)	6.8 (1)
O(14)	0.5791 (04)	0.3213 (03)	−0.3434 (04)	7.6 (2)
O(21)	0.8499 (04)	0.0809 (03)	0.5647 (04)	7.1 (2)
O(22)	1.2382 (03)	0.2122 (03)	0.4244 (05)	7.8 (2)
O(23)	0.8627 (04)	0.4690 (03)	0.6033 (04)	6.9 (1)
N	0.5146 (03)	0.1045 (02)	−0.0939 (04)	4.1 (1)
C(1)	0.6476 (03)	0.2590 (02)	0.1803 (04)	3.0 (1)
C(2)	0.5155 (04)	0.3367 (04)	0.2377 (05)	4.0 (1)
C(3)	0.6332 (04)	0.1597 (03)	0.0341 (04)	3.3 (1)
C(4)	0.3537 (05)	0.1490 (04)	−0.1073 (07)	5.3 (2)
C(5)	0.5367 (08)	0.0217 (05)	−0.2534 (07)	6.4 (2)
C(11)	0.9732 (04)	0.3363 (03)	0.0108 (05)	4.8 (2)
C(12)	0.7421 (04)	0.4728 (03)	0.1426 (05)	4.3 (1)
C(14)	0.6541 (04)	0.3155 (03)	−0.2037 (05)	4.7 (2)
C(21)	0.8633 (04)	0.1370 (03)	0.4782 (05)	4.5 (1)
C(22)	1.1087 (05)	0.2202 (03)	0.3968 (05)	4.9 (2)
C(23)	0.8738 (04)	0.3806 (03)	0.5058 (05)	4.3 (1)

Table IV. Intramolecular Distances for 2b[a]

Ru(1)–C(12)	1.884 (4)	Ru(2)–C(1)	2.110 (3)
Ru(1)–C(11)	1.917 (4)	Ru(2)–S	2.403 (1)
Ru(1)–C(14)	1.929 (4)	Ru(2)–C(3)	2.787 (3)
Ru(1)–C(1)	2.232 (3)	S–C(3)	1.797 (3)
Ru(1)–S	2.400 (1)	N–C(3)	1.342 (4)
Ru(1)–C(3)	2.419 (3)	N–C(5)	1.449 (5)
Ru(1)–Ru(2)	2.6636 (6)	N–C(4)	1.453 (5)
Ru(2)–C(23)	1.891 (4)	C(1)–C(3)	1.407 (4)
Ru(2)–C(21)	1.906 (4)	C(1)–C(2)	1.509 (4)
Ru(2)–C(22)	1.956 (4)	O–C (av)	1.132 (4)
		S···C(1)	2.541 (3)

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

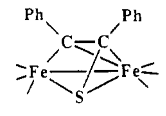
diruthenium complexes[13] and to that of its isomer **2b′** described below. The sulfur atom is equally bonded to the two ruthenium atoms; Ru(1)–S = 2.400 (1) Å and Ru(2)–S = 2.403 (1) Å. C(1) is bonded strongly but not equally to the ruthenium atoms; Ru(1)–C(1) = 2.232 (3) Å and Ru(2)–C(1) = 2.110 (3) Å. C(3) may be weakly bonded to Ru(1), Ru(1)–C(3) = 2.419 (3) Å, but is probably not bonded to Ru(2), Ru(2)···C(3) = 2.787 (3) Å. Compound

Table V. Intramolecular Bond Angles for 2b[a]

C(12)–Ru(1)–C(1)	89.9 (1)	C(22)–Ru(2)–S	97.2 (1)
C(12)–Ru(1)–S	151.3 (1)	C(22)–Ru(2)–Ru(1)	103.7 (1)
C(12)–Ru(1)–C(3)	121.2 (1)	C(1)–Ru(2)–S	68.17 (8)
C(12)–Ru(1)–Ru(2)	96.3 (1)	C(1)–Ru(2)–Ru(1)	54.27 (7)
C(11)–Ru(1)–C(1)	152.4 (1)	S–Ru(2)–Ru(1)	56.27 (3)
C(11)–Ru(1)–S	100.8 (1)	C(3)–S–Ru(1)	68.6 (1)
C(11)–Ru(1)–C(3)	144.0 (1)	C(3)–S–Ru(2)	81.8 (1)
C(11)–Ru(1)–Ru(2)	102.3 (1)	Ru(1)–S–Ru(2)	67.35 (3)
C(14)–Ru(1)–C(1)	110.3 (1)	C(3)–N–C(5)	121.4 (3)
C(14)–Ru(1)–S	105.9 (1)	C(3)–N–C(4)	121.5 (3)
C(14)–Ru(1)–C(3)	89.9 (1)	C(5)–N–C(4)	114.7 (4)
C(14)–Ru(1)–Ru(2)	156.1 (1)	C(3)–C(1)–C(2)	126.1 (3)
C(1)–Ru(1)–S	66.42 (8)	C(3)–C(1)–Ru(2)	103.0 (2)
C(1)–Ru(1)–C(3)	34.9 (1)	C(3)–C(1)–Ru(1)	79.8 (2)
C(1)–Ru(1)–Ru(2)	50.13 (7)	C(2)–C(1)–Ru(2)	128.0 (2)
S–Ru(1)–C(3)	43.80 (7)	C(2)–C(1)–Ru(1)	124.7 (2)
S–Ru(1)–Ru(2)	56.38 (3)	Ru(2)–C(1)–Ru(1)	75.6 (1)
C(3)–Ru(1)–Ru(2)	66.31 (7)	N–C(3)–C(1)	135.6 (3)
C(23)–Ru(2)–C(1)	94.3 (1)	N–C(3)–S	120.2 (2)
C(23)–Ru(2)–S	156.1 (1)	N–C(3)–Ru(1)	131.3 (2)
C(23)–Ru(2)–Ru(1)	100.6 (1)	C(1)–C(3)–S	104.3 (2)
C(21)–Ru(2)–C(1)	100.5 (1)	C(1)–C(3)–Ru(1)	65.3 (2)
C(21)–Ru(2)–S	103.2 (1)	S–C(3)–Ru(1)	67.6 (1)
C(21)–Ru(2)–Ru(1)	150.7 (1)	O–C–Ru (av)	177.7 (4)
C(22)–Ru(2)–C(1)	157.6 (1)		

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

2b is structurally similar to the compound $Fe_2(CO)_6(\mu\text{-}SCPhCPh)$ (4), except that the sulfur-bonded carbon atom is more asymmetrically bonded to the iron atoms than is found in **2b**; Fe–C = 2.061 (6) Å and Fe···C = 2.654 (6) Å.[14b] The C(3)–N bond distance in **2b** is short, 1.342 (4) Å, and indicative of a partial multiple bonding formed by donation of the lone pair of electrons on the nitrogen atom to C(3). In accord with this formulation, the nitrogen atom exhibits a planar geometry. However, this C–N multiple bonding did not produce a spectroscopically observable hindered rotation about the C–N bond. Even at −70 °C, only a single resonance was observed in the ^1H NMR spectrum for the *N*-methyl groups. It is believed that the lone-pair donation to atom C(3) causes a weakening of the metal–carbon bonding and this could account for the greater length of the Ru(1)–C(3) bond compared to that found in 4. The ^{13}C NMR spectrum of **2b** showed a single carbonyl resonance, indicating a dynamic averaging of the CO ligands at 25 °C. This could occur by a combination of a "windshield wiper"-like flip-flop of the $SC(NMe_2)CMe$ ligand, in which the long and short metal–carbon bonds to C(3) are interchanged, and a 3-fold rotation of the CO ligands on the $Ru(CO)_3$ groups. The resonance of the N-bonded carbon atom C(3) was observed at a low-field shift value of +153.11 ppm.



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On the basis of its similar IR and ^1H NMR spectra, compound **2a** is believed to be structurally similar to **2b**. The addition of alkynes to sulfido ligands in cluster complexes has been observed in other systems.[15]

An ORTEP drawing of the molecular structure of **3c** is shown in Figure 2. Final atomic positional parameters are listed in Table VI. Selected interatomic distances and

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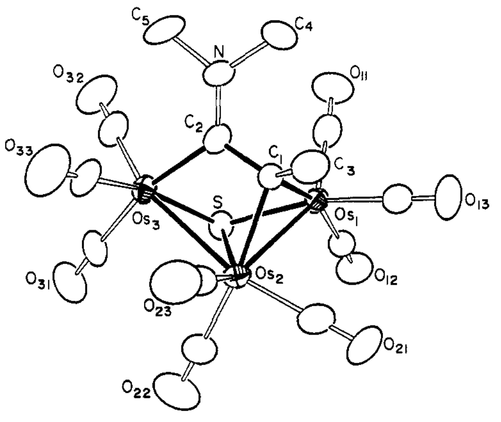


Figure 2. ORTEP drawing of $Os_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu_3\text{-}S)$ (**3c**) showing 50% probability thermal ellipsoids.

Table VI. Positional Parameters and *B*(eq) Values for $Os_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu_3\text{-}S)$ (3c)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.43633 (05)	0.19029 (03)	0.22262 (05)	2.43 (1)
Os(2)	0.24733 (05)	0.24210 (03)	0.37336 (05)	2.32 (1)
Os(3)	−0.01471 (05)	0.21443 (03)	0.05519 (05)	2.45 (1)
S	0.1759 (03)	0.1038 (02)	0.1589 (03)	2.63 (8)
O(11)	0.4624 (12)	0.1559 (09)	−0.1011 (11)	5.8 (4)
O(12)	0.5636 (11)	−0.0026 (07)	0.3636 (11)	4.8 (4)
O(13)	0.7670 (11)	0.3208 (09)	0.3907 (12)	6.3 (4)
O(21)	0.5753 (11)	0.2970 (08)	0.6712 (10)	5.3 (4)
O(22)	0.1018 (14)	0.1135 (10)	0.5659 (14)	7.4 (5)
O(23)	0.1366 (12)	0.4372 (07)	0.4273 (11)	5.2 (4)
O(31)	−0.2252 (11)	0.0646 (08)	0.1606 (13)	5.7 (4)
O(32)	−0.1968 (12)	0.1309 (08)	−0.3111 (11)	5.7 (4)
O(33)	−0.1906 (12)	0.3899 (08)	0.0459 (13)	6.1 (4)
N	0.1722 (10)	0.3544 (07)	−0.0911 (10)	2.8 (3)
C(1)	0.3185 (11)	0.3186 (08)	0.1908 (11)	2.5 (3)
C(2)	0.1756 (12)	0.3083 (08)	0.0402 (12)	2.5 (3)
C(3)	0.4153 (14)	0.4263 (09)	0.2588 (14)	3.6 (4)
C(4)	0.3167 (14)	0.3947 (10)	−0.1085 (14)	3.7 (4)
C(5)	0.0282 (16)	0.3581 (10)	−0.2421 (14)	4.4 (5)
C(11)	0.4534 (13)	0.1662 (10)	0.0219 (14)	3.7 (4)
C(12)	0.5182 (13)	0.0676 (11)	0.3093 (14)	3.4 (4)
C(13)	0.6446 (15)	0.2720 (11)	0.3291 (14)	3.9 (5)
C(21)	0.4547 (15)	0.2724 (10)	0.5601 (14)	3.6 (4)
C(22)	0.1577 (16)	0.1603 (12)	0.4948 (15)	4.6 (5)
C(23)	0.1742 (14)	0.3633 (10)	0.4075 (13)	3.4 (4)
C(31)	−0.1518 (13)	0.1194 (11)	0.1183 (16)	3.9 (5)
C(32)	−0.1303 (13)	0.1617 (09)	−0.1759 (15)	3.4 (4)
C(33)	−0.1271 (13)	0.3226 (11)	0.0478 (14)	3.8 (4)

Table VII. Intramolecular Distances for 3c[a]

Os(1)–C(11)	1.88 (1)	Os(2)–Os(3)	2.820 (2)
Os(1)–C(13)	1.92 (1)	Os(3)–C(33)	1.89 (1)
Os(1)–C(12)	1.96 (1)	Os(3)–C(32)	1.92 (1)
Os(1)–C(1)	2.13 (1)	Os(3)–C(31)	1.96 (1)
Os(1)–S	2.380 (3)	Os(3)–C(2)	2.10 (1)
Os(1)–Os(2)	2.776 (1)	Os(3)–S	2.384 (3)
Os(1)–Os(3)	3.941 (1)	N–C(2)	1.34 (1)
Os(2)–C(23)	1.90 (1)	N–C(5)	1.46 (1)
Os(2)–C(21)	1.92 (1)	N–C(4)	1.47 (1)
Os(2)–C(22)	1.93 (1)	C(1)–C(2)	1.42 (1)
Os(2)–C(1)	2.25 (1)	C(1)–C(3)	1.54 (1)
Os(2)–S	2.402 (3)	O–C (av)	1.13 (1)
Os(2)–C(2)	2.96 (1)		

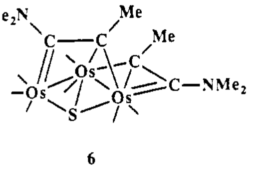
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table VIII. Intramolecular Bond Angles for 3c[a]

C(11)–Os(1)–C(1)	104.2 (5)	Os(1)–Os(2)–Os(3)	88.75 (4)
C(11)–Os(1)–S	103.2 (4)	C(33)–Os(3)–C(2)	93.2 (5)
C(11)–Os(1)–Os(2)	146.8 (4)	C(33)–Os(3)–S	160.7 (3)
C(13)–Os(1)–C(1)	93.0 (5)	C(33)–Os(3)–Os(2)	106.6 (3)
C(13)–Os(1)–S	164.5 (3)	C(32)–Os(3)–C(2)	98.3 (4)
C(13)–Os(1)–Os(2)	110.5 (4)	C(32)–Os(3)–S	102.2 (4)
C(12)–Os(1)–C(1)	160.6 (4)	C(32)–Os(3)–Os(2)	154.8 (3)
C(12)–Os(1)–S	88.0 (3)	C(31)–Os(3)–C(2)	166.3 (4)
C(12)–Os(1)–Os(2)	108.2 (3)	C(31)–Os(3)–S	86.0 (4)
C(1)–Os(1)–S	81.7 (3)	C(31)–Os(3)–Os(2)	94.5 (4)
C(1)–Os(1)–Os(2)	52.6 (3)	C(2)–Os(3)–S	83.2 (3)
S–Os(1)–Os(2)	54.89 (7)	C(2)–Os(3)–Os(2)	72.3 (3)
C(23)–Os(2)–C(1)	87.1 (4)	S–Os(3)–Os(2)	54.20 (7)
C(23)–Os(2)–S	138.9 (4)	Os(1)–S–Os(3)	110.5 (1)
C(23)–Os(2)–Os(1)	134.5 (3)	Os(1)–S–Os(2)	70.97 (9)
C(23)–Os(2)–Os(3)	85.3 (3)	Os(3)–S–Os(2)	72.20 (9)
C(21)–Os(2)–C(1)	96.1 (4)	C(2)–N–C(5)	125 (1)
C(21)–Os(2)–S	122.5 (4)	C(2)–N–C(4)	123.1 (9)
C(21)–Os(2)–Os(1)	79.6 (3)	C(5)–N–C(4)	111.7 (8)
C(21)–Os(2)–Os(3)	165.9 (3)	C(2)–C(1)–C(3)	117 (1)
C(22)–Os(2)–C(1)	169.6 (5)	C(2)–C(1)–Os(1)	113.9 (7)
C(22)–Os(2)–S	91.9 (4)	C(2)–C(1)–Os(2)	105.3 (7)
C(22)–Os(2)–Os(1)	128.6 (4)	C(3)–C(1)–Os(1)	120.6 (7)
C(22)–Os(2)–Os(3)	100.6 (4)	C(3)–C(1)–Os(2)	113.8 (6)
C(1)–Os(2)–S	78.9 (3)	Os(1)–C(1)–Os(2)	78.6 (4)
C(1)–Os(2)–Os(1)	48.8 (3)	N–C(2)–C(1)	121 (1)
C(1)–Os(2)–Os(3)	70.0 (2)	N–C(2)–Os(3)	127.1 (7)
S–Os(2)–Os(1)	54.14 (7)	C(1)–C(2)–Os(3)	111.8 (7)
S–Os(2)–Os(3)	53.60 (7)	O–C–Os (av)	177 (1)

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

angles are listed in Tables VII and VIII. The molecule consists of an open triangular cluster of three osmium atoms containing a triply bridging sulfido ligand and a triply bridging MeC_2NMe_2 ligand. The Os–Os and Os–S bond distances, Os(1)–Os(2) = 2.776 (1) Å, Os(2)–Os(3) = 2.820 (2) Å, Os(1)–S = 2.380 (3) Å, Os(2)–S = 2.402 (3) Å, and Os(3)–S = 2.384 (3) Å, are very similar to those in the open triosmium cluster complexes $Os_3(CO)_9(\mu_3\text{-}S)_2$,[16] $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)_2$,[16] and $Os_3(CO)_8(CS)(\mu_3\text{-}S)_2$,[17] each of which contains two triply bridging sulfido ligands. The coordination of the ynamine ligand is related to the unusual structural type D first observed in the complex $Os_3(CO)_9(\mu_3\text{-}Et_2NC_2H)(\mu\text{-}H)_2$ (**5**),[4,5] since the amine-substituted carbon atom is bonded to only one metal atom Os(3); Os(3)–C(2) = 2.10 (1) Å. The Os(2)···C(2) distance of 2.96 (1) Å is nonbonding. Carbon C(1) bridges the Os(1)–Os(2) bond; Os(1)–C(1) = 2.13 (1) Å and Os(2)–C(1) = 2.25 (1) Å. Since the C(1)–C(2) vector is nearly perpendicular to the Os(1)–Os(2) vector, this coordination could also be described as a μ-perpendicular bridging mode.[7] A similarly coordinated $\mu_3\text{-}MeC_2NMe_2$ was observed in the complex $Os_3(CO)_7(\mu_3\text{-}Me_2NC_2Me)(\mu\text{-}Me_2NC_2Me)(\mu_3\text{-}S)$ (**6**), which also contains an edge-bridging



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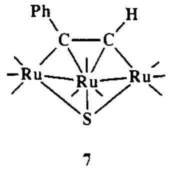

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MeC_2NMe_2 ligand coordinated in the structural type C.[18] In contrast, in the open cluster complex $Ru_3(CO)_9(\mu\text{-}HC_2Ph)(\mu_3\text{-}S)$ (**7**), both carbon atoms of the alkyne ligand are bonded to two metal atoms and the C–C vector is nearly parallel to the vector between the two nonbonded ruthenium atoms (i.e. a $\mu_{\parallel}$ bridge).[19] There is a strong C–N

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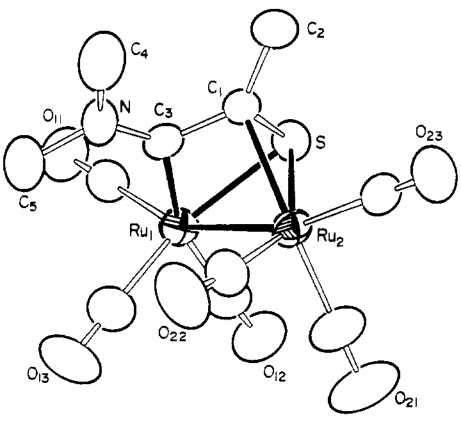

Figure 3. ORTEP drawing of $Ru_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$ (**2b′**) showing 50% probability thermal ellipsoids.

bond in **3c**, C(2)–N = 1.34 (1) Å, and the nitrogen atom has a planar geometry. Similarly, short C–N distances were observed in **5**, 1.33 (2) Å,[4] and **6**, 1.31 (2) Å.[18] Both factors can be attributed to the importance of donation of the lone pair of electrons on the nitrogen atom to an empty π^* orbital on C(2).

The presence of two *N*-methyl resonances in each of the compounds **3a–c** indicates hindered rotation about the C–N bond at 25 °C. Compounds **3a** and **3b** underwent significant decomposition when heated, and suitable spectra could not be obtained at high temperatures, but **3c** was relatively stable. At elevated temperatures, the *N*-methyl resonances of **3c** broadened, coalesced (83 °C, ΔG^*_{356} = 17.2 ± 0.2 kcal/mol), and merged to a singlet. Hindered rotation about the C–N bond was also observed in compounds **6** and **7**. These features are similar to those of aminocarbene ligands, and in analogy to our formulation of the ynamine ligand in **5** as a (dimetalliomethyl)(diethylamino)carbene ligand, we propose to formulate the ynamine ligands in **3a–c** as (α,α-dimetallioethyl)(dimethylamino)carbene ligands in order to emphasize the carbene-like character of the amine-containing carbon atom C(2).

This formulation is supported further by the very low-field shift of the resonance of this carbon atom. This resonance was observed at +251.92 ppm for **3a** and +243.50 ppm for **3c**. The ^{13}C NMR resonance of the carbene ligands in $[OsCl(NO)(CN(Me)(CH_2)_2NMe)_3][BF_4]_2$ and the osmium cluster $Os_3(CO)_8[C(H)NMe_2](\mu\text{-}S)(\mu\text{-}H)_2$ even lie upfield from those in **3a** and **3c**, +177.6[20] and +199.2 ppm.[21] The ^{13}C NMR resonance of the carbene carbon atom of aminocarbene ligands in carbonyl complexes of the chromium subgroup lie in the range +250–275 ppm.[22] The resonances in **3a** and **3c** also lie at a much lower field value than the amine-substituted carbon atom in **2b**, +153.11 ppm. We feel that this evidence provides overwhelming support for the proposal of carbene-like character at the amine-substituted carbon atom of ynamine ligands in these metal carbonyl cluster complexes.

Table IX. Positional Parameters and *B*(eq) Values for $Ru_2(CO)_6S(MeCCNMe_2)$ (2b′)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ru(1)	0.05283 (04)	0.13658 (04)	0.74474 (03)	3.62 (2)
Ru(2)	−0.08122 (05)	0.33605 (04)	0.66527 (03)	3.66 (2)
S	−0.16651 (14)	0.13631 (13)	0.67333 (10)	3.88 (7)
O(11)	0.0987 (05)	−0.0935 (04)	0.8677 (03)	6.7 (3)
O(12)	0.1484 (05)	0.0307 (05)	0.5681 (04)	7.3 (3)
O(13)	0.3054 (05)	0.2669 (05)	0.8114 (04)	8.2 (3)
O(21)	0.0635 (06)	0.3447 (06)	0.4960 (04)	10.1 (4)
O(22)	0.0695 (05)	0.5328 (05)	0.7844 (04)	8.6 (3)
O(23)	−0.3032 (04)	0.5029 (04)	0.5839 (03)	5.9 (2)
N	−0.0397 (05)	0.2733 (04)	0.9164 (03)	4.2 (2)
C(1)	−0.1821 (05)	0.2412 (05)	0.7687 (04)	3.3 (2)
C(2)	−0.3183 (06)	0.2701 (05)	0.7843 (04)	4.6 (3)
C(3)	−0.0631 (05)	0.2283 (05)	0.8293 (04)	3.3 (3)
C(4)	−0.1326 (07)	0.3455 (06)	0.9614 (05)	6.4 (4)
C(5)	0.0835 (07)	0.2675 (07)	0.9714 (05)	6.3 (4)
C(11)	0.0812 (06)	−0.0094 (06)	0.8203 (05)	4.6 (3)
C(12)	0.1177 (06)	0.0699 (06)	0.6345 (05)	5.0 (3)
C(13)	0.2103 (07)	0.2165 (06)	0.7863 (05)	5.2 (3)
C(21)	0.0100 (07)	0.3424 (06)	0.5588 (05)	6.3 (4)
C(22)	0.0139 (06)	0.4615 (06)	0.7356 (05)	5.3 (3)
C(23)	−0.2208 (06)	0.4393 (06)	0.6138 (04)	4.1 (3)

Table X. Intramolecular Distances for 2b′[a]

Ru(1)–C(13)	1.890 (7)	Ru(2)–S	2.346 (2)
Ru(1)–C(11)	1.912 (7)	S–C(1)	1.801 (5)
Ru(1)–C(12)	1.946 (7)	N–C(3)	1.330 (6)
Ru(1)–C(3)	2.088 (5)	N–C(5)	1.422 (7)
Ru(1)–S	2.392 (2)	N–C(4)	1.469 (8)
Ru(1)–Ru(2)	2.7348 (8)	C(1)–C(3)	1.428 (7)
Ru(2)–C(22)	1.889 (7)	C(1)–C(2)	1.515 (8)
Ru(2)–C(23)	1.909 (7)	Ru(1)–C(1)	2.785 (5)
Ru(2)–C(21)	1.916 (8)	Ru(2)–C(3)	2.606 (5)
Ru(2)–C(1)	2.195 (5)	O–C (av)	1.14 (1)
		S···C(3)	2.547 (5)

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

Table XI. Intramolecular Bond Angles for 2b′[a]

C(13)–Ru(1)–C(3)	99.1 (2)	C(21)–Ru(2)–Ru(1)	94.2 (2)
C(13)–Ru(1)–S	152.5 (2)	C(1)–Ru(2)–S	46.6 (1)
C(13)–Ru(1)–Ru(2)	98.6 (2)	C(1)–Ru(2)–Ru(1)	67.8 (1)
C(11)–Ru(1)–C(3)	96.9 (2)	S–Ru(2)–Ru(1)	55.53 (4)
C(11)–Ru(1)–S	107.8 (2)	C(1)–S–Ru(2)	62.3 (2)
C(11)–Ru(1)–Ru(2)	156.3 (2)	C(1)–S–Ru(1)	82.0 (2)
C(12)–Ru(1)–C(3)	161.4 (2)	Ru(2)–S–Ru(1)	70.51 (4)
C(12)–Ru(1)–S	94.6 (2)	C(3)–N–C(5)	122.7 (5)
C(12)–Ru(1)–Ru(2)	100.0 (2)	C(3)–N–C(4)	123.9 (5)
C(3)–Ru(1)–S	68.9 (2)	C(5)–N–C(4)	113.0 (5)
C(3)–Ru(1)–Ru(2)	63.8 (1)	C(3)–C(1)–C(2)	134.3 (5)
S–Ru(1)–Ru(2)	53.96 (4)	C(3)–C(1)–S	103.6 (4)
C(22)–Ru(2)–C(1)	104.2 (2)	C(3)–C(1)–Ru(2)	89.4 (3)
C(22)–Ru(2)–S	144.2 (2)	C(2)–C(1)–S	115.5 (4)
C(22)–Ru(2)–Ru(1)	98.0 (2)	C(2)–C(1)–Ru(2)	124.2 (4)
C(23)–Ru(2)–C(1)	96.6 (2)	S–C(1)–Ru(2)	71.1 (2)
C(23)–Ru(2)–S	106.1 (2)	N–C(3)–C(1)	124.5 (5)
C(23)–Ru(2)–Ru(1)	161.0 (2)	N–C(3)–Ru(1)	132.2 (4)
C(21)–Ru(2)–C(1)	154.1 (2)	C(1)–C(3)–Ru(1)	103.2 (4)
C(21)–Ru(2)–S	108.1 (2)	O–C–Ru (av)	177 (1)

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

When solutions of **2b** in octane were heated to reflux for 70 min, the new compound $Ru_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$ (**2b′**), an isomer of **2b**, was formed in 38% yield. No other carbonyl-containing products were observed. To establish the finer details of the structure of **2b′**, a single-crystal X-ray diffraction analysis was performed. An ORTEP drawing of the structure of **2b′** is shown in Figure 3. Final atomic positional parameters are listed in Table IX. Selected interatomic distances and angles are listed in Tables X and XI. The molecule contains an $Ru_2(CO)_6$ grouping similar to that in **2b**; Ru(1)–Ru(2) = 2.7349 (8) Å. The Ru–Ru bond is bridged by a $SC(Me)CNMe_2$ ligand. The sulfur atom is more strongly bonded to Ru(2) than Ru(1); Ru(2)–S = 2.346 (2) Å vs Ru(1)–S = 2.392 (2) Å. Unlike the case in **2b**, the sulfur-bonded carbon atom is fairly strongly bonded to one of the metal atoms, Ru(2)–C(1) = 2.195 (5) Å vs Ru(1)···C(1) = 2.787 (5) Å, and the NMe_2-substituted carbon atom C(3) is bonded only to

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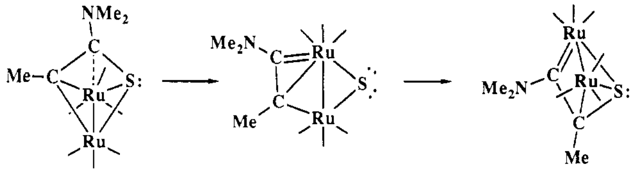
Scheme II



2b G 2b'

one metal atom Ru(1), Ru(1)–C(3) = 2.088 (5) Å vs Ru(2)···C(3) = 2.606 (5) Å. The nitrogen atom has a planar geometry, and the C(3)–N distance of 1.330 (6) Å is very short and indicative of a partial multiple-bonding interaction. Structurally, carbon C(3) appears to contain a significant amount of carbene-like character. This is further supported by the ^{13}C NMR spectrum of **2b′**, which showed a low-field resonance for C(3) at 196.7 ppm. This assignment is somewhat tentative because it lies among the resonances of the CO ligands, which appear as two singlets of equal intensity, presumably due to localized scrambling on each ruthenium atom. The resonance of the methyl-substituted carbon atom also appears at an unusually low-field shift value of 191.1 ppm. At 25 °C, the ^{1}H NMR spectrum of **2b′** showed only one resonance of intensity 6 at 3.03 ppm for the NMe_2 group. However, at lower temperature this resonance broadened and re-formed as two resonances of equal intensity at 3.01 and 2.96 ppm at −53 °C. The coalescence temperature was −43 °C, which implies the energy of activation $\Delta G^*_{230} = 11.5 \pm 0.2$ kcal/mol. These spectral changes can be explained by a hindered rotation about the C–N bond that is rapid on the NMR time scale above −43 °C.

The isomerization of **2b** to **2b′** most likely occurs by an intramolecular homolysis of the carbon–sulfur bond (Scheme II). An intermediate such as G, containing an unsymmetrical MeC_2NMe_2 ligand of the type C serving as a four-electron donor and a bridging sulfido ligand serving as a two-electron donor, is probably traversed. The formation of **2b′** is completed by a carbon–sulfur bond between the methyl-substituted carbon atom and the sulfido ligand.

Compound **2a′** was obtained in 55% yield by heating a toluene solution of **3a** to 100 °C for 80 min. No **2a** was obtained in this transformation. This suggests, as was established for **2b**, that the isomers **2a′** and **2b′** are thermodynamically the more stable of the two in each system. As in **2b′**, the NMe_2 group in **2a′** is rotating rapidly on the NMR time scale at 25 °C, but the rotation is slowed at low temperature. The rotational barrier in **2a′**, $\Delta G^*_{238} = 12.0 \pm 0.2$ kcal/mol, is only slightly higher than that in **2b**. The ^{13}C NMR spectrum of **2a′** is similar to that of **2b′**. The NMe_2-substituted carbon atom also resonates at low field, +211.4 ppm, and the methyl-substituted carbon atom appears at +199.2 ppm. The CO groups are averaged only on one of the iron atoms. The shifts of the CO resonances in **2a′** are very similar to those in $Fe_2(CO)_6(\mu\text{-}SMe)_2$.[23]

In all three structures, there is evidence for significant π-bonding interactions between the lone pair of electrons on the nitrogen atom and the adjacent alkynyl carbon atom. When the amine-substituted carbon atom is bonded to a metal atom, the N–C π-bonding is so strong that the carbon atom begins to develop the character of a metal-coordinated aminocarbene ligand.[8] This carbene-like character of ynamine ligands should have important implications on their reactivity.[24] In one example of this, we have recently shown that **3c** reacts with H_2 by a novel 1,1-dihydrogen addition to the methyl-substituted carbon atom of the ynamine ligand to yield the carbene-containing complex $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$.[25]

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Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of the hydrogen atoms for all three crystal structure analyses (8 pages); tables of structure factor amplitudes (46 pages). Ordering information is given on any current masthead page.

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