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Synthesis and Characterization of Cluster Complexes Containing Iminium Ion Ligands. The Crystal and Molecular Structures of Two Isomers of $Os_3(CO)_7(\mu\text{-}CNMe_2)(H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$

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The reaction of $CH_2(NMe_2)_2$ with the cluster complex $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (**3**) in refluxing heptane has yielded two isomeric products with the formula $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (**4**, 37% yield, and **5**, 27% yield). Both products were characterized by IR and ^1H NMR spectroscopies and by single-crystal X-ray diffraction analyses. For **4**: space group $P2_1/c$, $a = 9.986$ (1) Å, $b = 24.909$ (5) Å, $c = 10.027$ (1) Å; $\beta = 97.81$ (1)°; $Z = 4$. The structure of **4** was solved by direct methods (MULTAN) and was refined with 3030 reflections to the final values of the residuals $R = 0.038$ and $R_w = 0.042$. The structure consists of a triangular cluster of three metal atoms and is very similar to the parent compound **3** except that it contains an iminium $H_2CNMe_2^+$ ligand bridging one edge of the cluster with the carbon and nitrogen atoms bonded to different metal atoms. The C–N distance at 1.50 (2) Å is slightly longer than a C–N single bond distance. For **5**: space group $P\bar{1}$, $a = 13.509$ (2) Å, $b = 12.075$ (3) Å, $c = 9.925$ (2) Å; $\alpha = 102.18$ (2)°, $\beta = 103.39$ (1)°, $\gamma = 94.89$ (2)°; $Z = 2$. The structure was solved by a combination of Patterson and difference Fourier methods and was refined with 3581 reflections to the final values of the residuals $R = 0.049$ and $R_w = 0.058$. The structure of **5** is similar to **4** except that the η^2-iminium ligand is coordinated to only one metal atom. In this case the C–N distance (1.42 (2) Å) is slightly shorter than a C–N single bond distance. When refluxed in an octane solution, **5** was converted to **4** in 86% yield. A mechanism for the transformation is proposed and discussed.

Introduction

Evidence that supports the ability of transition-metal cluster compounds to produce catalysis continues to accumulate.[1-5] We have recently reported that the carbene containing cluster $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ serves as a precursor to an osmium cluster catalyst system that produces the exchange of alkyl groups in tertiary amines (eq 1).[4]

$$NR_3 + NR'_3 \rightleftharpoons NR_2R' + NR'_2R \qquad (1)$$

Although the carbene ligand appears to play a central role in the catalysis in this system, intermediates that contain iminium ligands, $R_2C{=}NR'_2{}^+$, have been widely discussed for other systems that also produce this exchange reaction.[6,7] However, to date, there have been few reports of complexes that contain iminium ligands and no examples of them in cluster complexes.[7-10]

In recent studies we have found that the (arenethiolato)osmium cluster complexes $Os_3(CO)_{10}(\mu\text{-}SAr)(\mu\text{-}H)$ (**1**) react with tertiary diaminomethanes, $CH_2(NR_2)_2$, to yield the new aminocarbene and aminocarbyne cluster complexes $Os_3(CO)_9[C(H)NR_2](\mu\text{-}SAr)(\mu\text{-}H)$ (**2**) and $Os_3(CO)_8(\mu\text{-}CNR_2)(\mu\text{-}SAr)(\mu\text{-}H)_2$ (**3**), respectively.[11] Minor products that were also obtained from this reaction have now been established to have been formed by the reaction of the carbyne cluster **3** with an additional amount of the diaminomethane. These products that have been found to contain the first examples of iminium ligands in cluster complexes have now been fully characterized. Their syntheses and characterizations are described in this report.

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere, unless otherwise specified. Reagent grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen prior to use. The compound $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (**3**) was prepared by published procedures.[11] $CH_2[N(CH_3)_2]_2$ was purchased from Aldrich and was used without further purification. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. A Brüker AM300 FT-NMR was used to obtain ^1H NMR spectra. Elemental analyses were performed by MICANAL, Tuczon, AZ.

Reaction of $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (3) with $CH_2(NMe_2)_2$. An excess of $CH_2(NMe_2)_2$ (0.5 mL) was added to a heptane solution (50 mL) of **3** (30 mg, 0.0312 mmol). This mixture was refluxed for 2 h. After the mixture was cooled, the solvent was removed in vacuo, and the residue was extracted with a minimum of CH_2Cl_2 and applied to silica gel TLC plates. The products were separated by using a 25:75 CH_2Cl_2/hexane solvent mixture. Two products that were found to be isomers with the formula $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ were obtained. In order of elution they were **4** (11 mg, 37% yield) and **5** (8 mg, 27% yield). IR (ν(CO) in hexane solvent (cm^{-1}): for **4**, 2062 (m), 2012 (s), 2002 (vs), 1990 (m), 1970 (w), 1946 (s); for **5**, 2066 (m), 2032 (vs), 1992 (s), 1975 (m), 1959 (w), 1954 (m), 1932 (w). ^1H NMR (δ in CD_2Cl_2 solvent): for **4**, 7.30 (m, 5 H), 4.55 (d, $J_{H-H} = 11.5$ Hz, 1 H), 3.84 (s, 3 H), 3.79 (s, 3 H), 3.04 (s, 3 H), 2.83 (s, 3 H), 2.05 (d, $J_{H-H} = 11.5$ Hz, 1 H), −10.25 (s, 1 H); for **5**, 7.33 (m, 5 H), 3.82 (t, $J_{H-H} = 1.8$ Hz, 1 H), 3.75 (s, 3 H), 3.64 (s, 3 H), 3.51 (s, 3 H), 3.23 (s, 3 H), 2.35 (t, $J_{H-H} = 1.8$ Hz, 1 H), −15.99 (t, $J_{H-H} = 1.6$ Hz, 1 H). ^1H NMR (δ in CD_2Cl_2 solvent) with hydride irradiation for **5**: 3.82 (d, $J_{H-H} = 1.95$ Hz, 1 H), 3.75

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Table I. Crystallographic Data for X-ray Diffraction Studies

	4	5
	(A) Crystal Data	
formula	$Os_3SO_7N_2C_{19}H_{20}$	$Os_3SO_7N_2C_{19}H_{20}\cdot C_6H_6$
temp, ±3 °C	23	23
space group	$P2_1/c$, No. 14	$P\bar{1}$, No. 2
a, Å	9.986 (1)	13.509 (2)
b, Å	24.909 (5)	12.075 (3)
c, Å	10.027 (1)	9.925 (2)
α, deg	90.0	102.18 (2)
β, deg	97.81 (1)	103.39 (1)
γ, deg	90.0	94.89 (2)
V, Å^3	2471.1 (5)	1524.1 (6)
M_r	990.9	990.9
Z	4	2
ρ_{calcd}, g/cm^3	2.66	2.33
	(B) Measurement of Intensity Data	
radiation	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
monochromator	graphite	graphite
detector aperture, mm		
horizontal	2.0	2.0
vertical	2.0	2.0
cryst faces	100, $\bar{1}00$, $0\bar{1}1$, 010, $0\bar{1}\bar{1}$	110, $\bar{1}\bar{1}0$, $1\bar{1}0$, $\bar{1}10$, $0\bar{1}2$, $10\bar{1}$
cryst size, mm	0.11 × 0.19 × 0.19	0.15 × 0.15 × 0.05
cryst orientatn: directn; deg from ϕ axis	[100]; 1.0	[110]; 0.7
reflctns measd	$+h,+k,\pm l$	$+h,\pm k,\pm l$
max 2θ, deg	50	50
scan type	moving crystal–stationary counter	moving crystal–stationary counter
ω-scan width (A + 0.347 tan θ)°, A =	1.1	1.1
ω-scan rate, deg/min	4	4
no. of reflctns measd	4717	5037
data used ($F^2 \geq 3.0\sigma(F^2)$)	3030	3581
	(C) Treatment of Data	
abs correctn	applied	applied
coeff, cm^{-1}	164.3	133.3
grid	6 × 12 × 12	10 × 8 × 12
transmissn coeff		
max	0.25	0.25
min	0.15	0.16
P factor	0.03	0.04
final residuals		
R_F	0.038	0.049
R_{wF}	0.042	0.058
esd of unit wt observn	1.396	1.794
largest shift/error value of final cycle	0.07	0.18
largest peak in final diff Fourier, e/Å^3	1.01	1.35

(s, 3 H), 3.64 (s, 3 H), 3.51 (s, 3 H), 3.23 (s, 3 H) 2.35 (d, J_{H-H} = 1.95 Hz). Anal. Calcd for 4: C, 23.02; H, 2.00; N, 2.83. Found: C, 23.11; H, 2.01; N, 2.86. Calcd for 5: C, 23.02; H, 2.00; N, 2.83. Found: C, 23.28; H, 2.26; N, 2.67.

Compounds 4 and 5 were also obtained as minor products (17% and 11% yields) from the reaction of $Os_3(CO)_{10}(\mu\text{-SPh})(\mu\text{-H})$ (1) with excess $CH_2(NMe_2)_2$.[11]

Pyrolysis of 5 under CO Atmosphere. An octane solution (60 mL) of 5 (25 mg, 0.0252 mmol) was refluxed for 3 h under a continuous CO purge. The solvent was removed in vacuo, and the residue was transferred to silica gel TLC plates in a CH_2Cl_2 solution. Elution with 40:60 CH_2Cl_2/hexane solvent mixture separated 4 (18 mg, 86% yield) from unreacted 5 (4 mg).

Pyrolysis of 5 in the Presence of $CH_2(NMe_2)_2$. An octane solution (40 mL) of 5 (25 mg, 0.0252 mmol) and an excess of $CH_2(NMe_2)_2$ (0.5 mL) were refluxed for 1 h. The solvent was removed in vacuo and the residue placed on silica gel TLC plates. Elution with a 40:60 CH_2Cl_2/hexane solvent mixture separated 4 (4.5 mg, (18%)) and a trace amount of 5 (<1 mg).

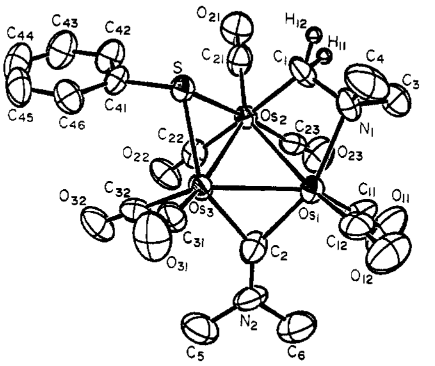

Figure 1. An ORTEP diagram of $Os_3(CO)_7(\mu\text{-CNMe}_2)(\mu\text{-H}_2\text{CNMe}_2)(\mu\text{-SPh})(\mu\text{-H})$ (4) showing 50% probability thermal ellipsoids. The ellipsoids on the hydrogen atoms have been reduced for clarity.

Crystallographic Analyses. Yellow crystals of 4 and 5 were grown by slow evaporation of solvent from CH_2Cl_2/hexane solutions at −20 °C and from benzene at 23 °C, respectively. Data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer using Mo Kα radiation. Unit cells were determined from 25 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 data processing was performed on a Digital Equipment Corp. MICROVAX I computer, by using the TEXSAN structure solving program library obtained from Molecular Structure Corp., College Station, TX. Absorption corrections of a Gaussian integration type were performed for each structure. Neutral atom scattering factors were calculated by the standard procedures.[12a] Anamolous dispersion corrections were applied to all non-hydrogen atoms.[12b] Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o - F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound 4 crystallizes in the monoclinic crystal system. The space group $P2_1/c$ was determined from systematic absences observed in the data. The positions of the metal atoms were determined by direct methods (MULTAN). The remaining non-hydrogen atoms were located by a series of difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms of the iminium ligand were determined by difference Fourier techniques. The remaining hydrogen atom positions were calculated by assuming idealized geometries. The contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 5 crystallizes 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 Patterson and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated by assuming idealized geometry, and these positions were not refined. In the final stages of solution the crystal was found to contain 1 mol of benzene solvent that had cocrystallized with each mole of 5. This was added to the calculations and was refined also.

Error analyses for both structures were calculated from the inverse matrix obtained in the final cycle of refinement. See supplementary materials for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters.

Results

Reaction of the aminocarbyne cluster $Os_3(CO)_8(\mu\text{-CNMe}_2)(\mu\text{-SPh})(\mu\text{-H})_2$ (3) with $CH_2(NMe_2)_2$ yielded the two isomeric products $Os_3(CO)_7(\mu\text{-CNMe}_2)(\mu\text{-H}_2\text{CNMe}_2)(\mu\text{-SPh})(\mu\text{-H})$ [4 (37% yield) and 5 (27% yield)].

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

Table II. Positional Parameters and B_{eq} (Å^2) for $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (4)

atom	x	y	z	B_{eq}
Os(1)	0.298828 (60)	0.098499 (23)	0.138533 (58)	3.1
Os(2)	0.007736 (56)	0.125972 (23)	0.128717 (54)	2.8
Os(3)	0.199910 (58)	0.112346 (23)	0.375619 (55)	2.9
S	0.04709 (38)	0.18671 (14)	0.32215 (35)	3.1
O(11)	0.3023 (16)	0.01810 (67)	−0.0875 (16)	7.5
O(12)	0.6008 (13)	0.09915 (52)	0.1623 (15)	6.9
O(21)	−0.2492 (12)	0.17714 (58)	−0.0153 (12)	6.5
O(22)	−0.1423 (12)	0.04530 (45)	0.2886 (11)	4.3
O(23)	−0.0053 (13)	0.04822 (53)	−0.1039 (12)	5.1
O(31)	0.4105 (12)	0.13835 (58)	0.6109 (12)	5.2
O(32)	0.0352 (12)	0.05843 (51)	0.5723 (12)	6.4
N(1)	0.2599 (12)	0.17100 (52)	0.0099 (11)	3.7
N(2)	0.3258 (13)	0.00152 (51)	0.3314 (15)	5.3
C(1)	0.1218 (16)	0.18721 (65)	0.0387 (16)	4.8
C(2)	0.2890 (16)	0.04910 (62)	0.2957 (16)	4.1
C(3)	0.2544 (22)	0.15907 (92)	−0.1349 (17)	9.7
C(4)	0.3585 (20)	0.21402 (75)	0.0390 (23)	6.9
C(5)	0.3038 (20)	−0.02177 (73)	0.4590 (20)	6.6
C(6)	0.3841 (21)	−0.03530 (79)	0.2399 (23)	8.3
C(11)	0.2990 (18)	0.04906 (74)	−0.0026 (21)	5.8
C(12)	0.4803 (18)	0.09923 (58)	0.1510 (17)	4.2
C(21)	−0.1543 (16)	0.15792 (73)	0.0404 (17)	4.5
C(22)	−0.0853 (15)	0.07553 (65)	0.2291 (15)	2.8
C(23)	0.0064 (17)	0.07587 (64)	−0.0130 (17)	4.8
C(31)	0.3297 (14)	0.12726 (68)	0.5216 (15)	4.5
C(32)	0.0937 (15)	0.07787 (62)	0.4967 (15)	3.4
C(41)	−0.0850 (14)	0.18567 (55)	0.4264 (14)	2.9
C(42)	−0.2199 (15)	0.18604 (70)	0.3752 (18)	4.6
C(43)	−0.3153 (17)	0.18808 (82)	0.4625 (21)	5.3
C(44)	−0.2825 (22)	0.19080 (80)	0.5948 (22)	6.3
C(45)	−0.1501 (21)	0.19092 (77)	0.6474 (17)	4.9
C(46)	−0.0508 (17)	0.18815 (67)	0.5656 (15)	3.7

Table III. Intramolecular Distances (Å) for $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (4)[a]

Os(1)–C(12)	1.80 (2)	O(12)–C(12)	1.19 (2)
Os(1)–C(11)	1.88 (2)	O(21)–C(21)	1.14 (2)
Os(1)–C(2)	2.01 (2)	O(22)–C(22)	1.16 (2)
Os(1)–N(1)	2.22 (1)	O(23)–C(23)	1.14 (2)
Os(1)–Os(3)	2.7174 (8)	O(31)–C(31)	1.15 (2)
Os(1)–Os(2)	2.9750 (8)	O(32)–C(32)	1.13 (2)
Os(2)–C(23)	1.89 (2)	N(1)–C(4)	1.46 (2)
Os(2)–C(21)	1.91 (2)	N(1)–C(3)	1.48 (2)
Os(2)–C(22)	1.93 (2)	N(1)–C(1)	1.50 (2)
Os(2)–C(1)	2.17 (1)	N(2)–C(2)	1.28 (2)
Os(2)–S	2.449 (4)	N(2)–C(5)	1.45 (2)
Os(2)–Os(3)	2.9388 (8)	N(2)–C(6)	1.47 (2)
Os(3)–C(31)	1.86 (2)	C(41)–C(42)	1.37 (2)
Os(3)–C(32)	1.92 (2)	C(41)–C(46)	1.39 (2)
Os(3)–C(2)	2.03 (1)	C(42)–C(43)	1.38 (2)
Os(3)–S	2.414 (4)	C(43)–C(44)	1.32 (3)
S–C(41)	1.79 (1)	C(44)–C(45)	1.36 (3)
O(11)–C(11)	1.15 (2)	C(45)–C(46)	1.37 (2)

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

Table IV. Intramolecular Bond Angles (deg) for $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (4)[a]

C(12)–Os(1)–C(11)	87.4 (7)	C(32)–Os(3)–C(2)	102.3 (6)
C(12)–Os(1)–C(2)	96.2 (7)	C(32)–Os(3)–S	95.5 (4)
C(12)–Os(1)–N(1)	97.3 (6)	C(32)–Os(3)–Os(1)	142.6 (5)
C(12)–Os(1)–Os(3)	114.8 (5)	C(32)–Os(3)–Os(2)	103.3 (4)
C(12)–Os(1)–Os(2)	166.0 (5)	C(2)–Os(3)–S	143.8 (5)
C(11)–Os(1)–C(2)	101.2 (7)	C(2)–Os(3)–Os(1)	47.5 (4)
C(11)–Os(1)–N(1)	96.5 (7)	C(2)–Os(3)–Os(2)	91.6 (5)
C(11)–Os(1)–Os(3)	141.4 (6)	S–Os(3)–Os(1)	101.37 (8)
C(11)–Os(1)–Os(2)	103.1 (5)	S–Os(3)–Os(2)	53.37 (8)
C(2)–Os(1)–N(1)	158.1 (5)	Os(1)–Os(3)–Os(2)	63.32 (2)
C(2)–Os(1)–Os(3)	48.0 (4)	C(41)–S–Os(3)	110.7 (5)
C(2)–Os(1)–Os(2)	90.9 (4)	C(41)–S–Os(2)	113.7 (5)
N(1)–Os(1)–Os(3)	110.4 (3)	Os(3)–S–Os(2)	74.4 (1)
N(1)–Os(1)–Os(2)	72.6 (3)	C(4)–N(1)–C(3)	106 (2)
Os(3)–Os(1)–Os(2)	61.97 (2)	C(4)–N(1)–C(1)	112 (1)
C(23)–Os(2)–C(21)	90.4 (7)	C(4)–N(1)–Os(1)	115 (1)
C(23)–Os(2)–C(22)	90.4 (6)	C(3)–N(1)–C(1)	109 (1)
C(23)–Os(2)–C(1)	95.8 (7)	C(3)–N(1)–Os(1)	113 (1)
C(23)–Os(2)–S	170.9 (5)	C(1)–N(1)–Os(1)	101.5 (8)
C(23)–Os(2)–Os(3)	119.6 (5)	C(2)–N(2)–C(5)	123 (1)
C(23)–Os(2)–Os(1)	77.3 (5)	C(2)–N(2)–C(6)	122 (2)
C(21)–Os(2)–C(22)	94.3 (7)	C(5)–N(2)–C(6)	115 (1)
C(21)–Os(2)–C(1)	88.5 (7)	N(1)–C(1)–Os(2)	116 (1)
C(21)–Os(2)–S	98.3 (5)	N(2)–C(2)–Os(1)	138 (1)
C(21)–Os(2)–Os(3)	148.7 (5)	N(2)–C(2)–Os(3)	137 (1)
C(21)–Os(2)–Os(1)	150.9 (5)	Os(1)–C(2)–Os(3)	84.6 (6)
C(22)–Os(2)–C(1)	173.1 (6)	O(11)–C(11)–Os(1)	178 (2)
C(22)–Os(2)–S	91.5 (4)	O(12)–C(12)–Os(1)	178 (2)
C(22)–Os(2)–Os(3)	77.9 (4)	O(21)–C(21)–Os(2)	178 (1)
C(22)–Os(2)–Os(1)	111.8 (4)	O(22)–C(22)–Os(2)	179 (1)
C(1)–Os(2)–S	81.9 (5)	O(23)–C(23)–Os(2)	173 (1)
C(1)–Os(2)–Os(3)	96.4 (4)	O(31)–C(31)–Os(3)	178 (2)
C(1)–Os(2)–Os(1)	67.1 (4)	O(32)–C(32)–Os(3)	177 (1)
S–Os(2)–Os(3)	52.26 (9)	C(42)–C(41)–C(46)	118 (1)
S–Os(2)–Os(1)	93.72 (9)	C(42)–C(41)–S	123 (1)
Os(3)–Os(2)–Os(1)	54.71 (2)	C(46)–C(41)–S	119 (1)
C(31)–Os(3)–C(32)	88.7 (6)	C(41)–C(42)–C(43)	119 (2)
C(31)–Os(3)–C(2)	99.8 (7)	C(44)–C(43)–C(42)	123 (2)
C(31)–Os(3)–S	112.0 (5)	C(43)–C(44)–C(45)	119 (2)
C(31)–Os(3)–Os(1)	114.7 (4)	C(44)–C(45)–C(46)	121 (2)
C(31)–Os(3)–Os(2)	161.3 (5)	C(45)–C(46)–C(41)	120 (2)

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

Both products were characterized by IR, ^{1}H NMR, and X-ray crystallographic analyses.

An ORTEP drawing of 4 is shown in Figure 1. Final positional parameters are listed in Table II. Interatomic distances and angles are listed in Tables III and IV, respectively. The structure of 4 consists of a triangular cluster of three osmium atoms. One bond, Os(1)–Os(3) = 2.7174 (8) Å, is significantly shorter than the other two, Os(1)–Os(2) = 2.9750 (8) Å and Os(2)–Os(3) = 2.9388 (8) Å. The short bond is bridged by a (dimethylamino)carbyne ligand, $CNMe_2$, C(2)–N(2) = 1.28 (2) Å. This ligand is structurally similar to those found in 3[11] and in the cluster $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (6).[13] A benzenethiolato ligand bridges the Os(2)–Os(3) distance, Os(2)–S = 2.449 (4) Å and Os(3)–S = 2.414 (4) Å, but the most interesting ligand in the cluster is an *N*,*N*-dimethyliminium group that bridges the Os(1)–Os(2) bond, Os(1)–N(1) = 2.22 (1) Å and Os(2)–C(1) = 2.17 (1) Å. To the best of our knowledge this is the first example of an iminium ligand bridging two metal atoms. The C–N distance of the iminium ligand is significantly longer than that of the carbyne ligand, C(1)–N(1) = 1.50 (2) Å, and is slightly longer than a C–N single bond distance of 1.47 Å.[14] The presence of a metal–hydride ligand (not observed crystallographically) was indicated by a resonance with its characteristically high-field ^{1}H NMR shift, δ −10.25. The long lengths of the Os(1)–Os(2) and Os(2)–Os(3) bonds could be an indication that it bridges one of these bonds. The positions of the methylene protons in the iminium ligand were obtained from a difference Fourier synthesis. They were observed as a pair of AB doublets centered at 4.55 and 2.05 ppm (J_{H-H} = 11.5 Hz) in the ^{1}H NMR spectrum.

An ORTEP drawing of 5 is shown in Figure 2. Final positional parameters are listed in Table V. Interatomic distances and angles are listed in Table VI and VII, respectively. The structure of 5 consists of a triangular cluster of osmium atoms with the metal–metal distances Os(1)–Os(2) = 2.837 (1) Å, Os(1)–Os(3) = 2.854 (1) Å, and

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(13) Churchill, M. R.; DeBoer, B. G.; Rotella, F. *J. Inorg. Chem.* **1976**, *15*, 1843.

(14) See ref 12, Vol. III, Table 4.2.4, p 276.

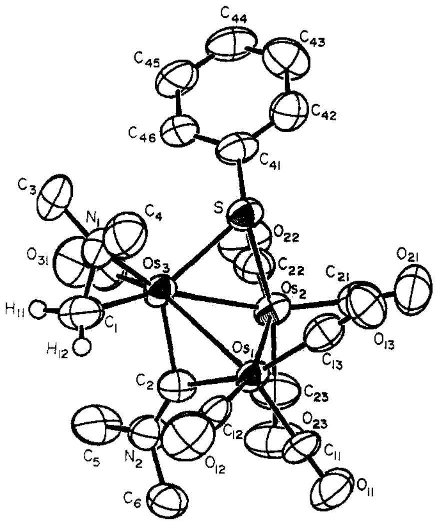


Figure 2. An ORTEP diagram of $Os_3(CO)_7(\mu\text{-}CNMe_2)(H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (5) showing 50% probability thermal ellipsoids. The hydrogen atoms are shown in idealized positions.

Table V. Positional Parameters and B_{eq} (Å^2) for $Os_3(CO)_7(\mu\text{-}CNMe_2)(H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (5)

atom	x	y	z	B_{eq}
Os(1)	−0.276267 (51)	−0.118201 (56)	0.017969 (67)	4.3
Os(2)	−0.168668 (54)	−0.310178 (59)	−0.007425 (74)	5.3
Os(3)	−0.220489 (52)	−0.215407 (59)	−0.237289 (67)	4.2
S	−0.04901 (33)	−0.19012 (37)	−0.08526 (45)	4.8
O(11)	−0.3855 (12)	−0.1903 (14)	0.2257 (16)	9.1
O(12)	−0.4078 (14)	0.0625 (14)	−0.0575 (18)	11.7
O(13)	−0.0945 (11)	0.0248 (12)	0.2589 (15)	5.5
O(21)	−0.0405 (13)	−0.2759 (16)	0.2934 (17)	10.6
O(22)	−0.0900 (12)	−0.5261 (12)	−0.1403 (17)	9.0
O(23)	−0.3550 (12)	−0.4501 (14)	0.0303 (21)	13.6
O(31)	−0.2377 (13)	−0.4245 (14)	−0.4679 (16)	7.5
N(1)	−0.2006 (12)	−0.0914 (13)	−0.3621 (15)	5.9
N(2)	−0.4341 (11)	−0.3089 (13)	−0.2161 (16)	5.0
C(1)	−0.3063 (15)	−0.1293 (19)	−0.3791 (23)	8.3
C(2)	−0.3453 (12)	−0.2449 (13)	−0.1638 (18)	4.8
C(3)	−0.1579 (18)	−0.1250 (23)	−0.4866 (21)	8.8
C(4)	−0.1627 (19)	0.0285 (21)	−0.2884 (24)	8.8
C(5)	−0.4590 (16)	−0.3975 (18)	−0.3474 (24)	5.3
C(6)	−0.5188 (13)	−0.2992 (16)	−0.1439 (20)	5.6
C(11)	−0.3453 (14)	−0.1632 (19)	0.1470 (19)	6.8
C(12)	−0.3572 (15)	−0.0080 (17)	−0.0261 (18)	6.1
C(13)	−0.1638 (15)	−0.0255 (16)	0.1694 (20)	6.4
C(21)	−0.0927 (16)	−0.2915 (19)	0.1795 (26)	8.1
C(22)	−0.1184 (15)	−0.4459 (18)	−0.0929 (21)	5.9
C(23)	−0.2845 (16)	−0.3937 (18)	0.0201 (25)	8.4
C(31)	−0.2305 (14)	−0.3461 (19)	−0.3821 (20)	6.5
C(41)	0.0398 (14)	−0.2758 (14)	−0.1493 (20)	5.1
C(42)	0.1304 (16)	−0.2815 (16)	−0.0558 (19)	5.6
C(43)	0.2041 (16)	−0.3416 (18)	−0.0974 (25)	7.1
C(44)	0.1869 (16)	−0.4021 (17)	−0.2339 (25)	8.1
C(45)	0.0973 (17)	−0.3953 (21)	−0.3317 (22)	7.7
C(46)	0.0240 (15)	−0.3308 (23)	−0.2903 (21)	7.8
C(91)	−0.4219 (29)	0.1291 (33)	0.4868 (43)	11.7
C(92)	−0.4048 (33)	0.2068 (38)	0.6110 (46)	13.6
C(93)	−0.3161 (27)	0.2907 (29)	0.6436 (36)	10.6
C(94)	−0.2543 (24)	0.2842 (27)	0.5567 (34)	9.5
C(95)	−0.2807 (28)	0.2008 (33)	0.4403 (40)	11.5
C(96)	−0.3639 (28)	0.1251 (31)	0.3992 (37)	11.0

Table VI. Intramolecular Distances (Å) for $Os_3(CO)_7(\mu\text{-}CNMe_2)(H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (5)[a]

Os(1)–C(12)	1.85 (2)	O(12)–C(12)	1.18 (2)
Os(1)–C(11)	1.89 (2)	O(13)–C(13)	1.15 (2)
Os(1)–C(13)	1.94 (2)	O(21)–C(21)	1.15 (2)
Os(1)–C(2)	2.07 (2)	O(22)–C(22)	1.12 (2)
Os(1)–Os(2)	2.837 (1)	O(23)–C(23)	1.16 (2)
Os(1)–Os(3)	2.854 (1)	O(31)–C(31)	1.11 (2)
Os(2)–C(21)	1.86 (2)	N(1)–C(1)	1.42 (2)
Os(2)–C(23)	1.89 (2)	N(1)–C(4)	1.46 (3)
Os(2)–C(22)	1.93 (2)	N(1)–C(3)	1.48 (2)
Os(2)–S	2.442 (4)	N(2)–C(2)	1.30 (2)
Os(2)–Os(3)	2.739 (1)	N(2)–C(5)	1.45 (2)
Os(3)–C(31)	1.87 (2)	N(2)–C(6)	1.49 (2)
Os(3)–C(2)	2.02 (2)	C(41)–C(42)	1.37 (3)
Os(3)–C(1)	2.11 (2)	C(41)–C(46)	1.37 (2)
Os(3)–N(1)	2.17 (1)	C(42)–C(43)	1.37 (3)
Os(3)–S	2.409 (5)	C(43)–C(44)	1.35 (3)
S–C(41)	1.79 (2)	C(44)–C(45)	1.39 (3)
O(11)–C(11)	1.13 (2)	C(45)–C(46)	1.39 (3)

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

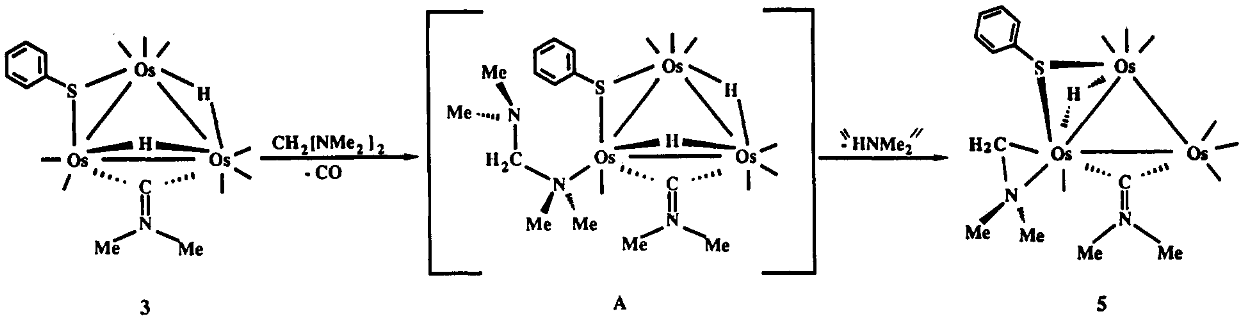
Table VII. Intramolecular Bond Angles (deg) for Compound 5[a]

C(12)–Os(1)–C(11)	96.4 (8)	C(1)–Os(3)–N(1)	38.7 (6)
C(12)–Os(1)–C(13)	100.9 (8)	C(1)–Os(3)–S	137.4 (6)
C(12)–Os(1)–C(2)	96.8 (7)	C(1)–Os(3)–Os(2)	158.4 (5)
C(12)–Os(1)–Os(2)	162.3 (5)	C(1)–Os(3)–Os(1)	100.1 (6)
C(12)–Os(1)–Os(3)	105.7 (5)	N(1)–Os(3)–S	100.1 (4)
C(11)–Os(1)–C(13)	93.1 (8)	N(1)–Os(3)–Os(2)	154.6 (4)
C(11)–Os(1)–C(2)	100.0 (7)	N(1)–Os(3)–Os(1)	112.6 (4)
C(11)–Os(1)–Os(2)	94.5 (6)	S–Os(3)–Os(2)	56.2 (1)
C(11)–Os(1)–Os(3)	139.7 (6)	S–Os(3)–Os(1)	85.1 (1)
C(13)–Os(1)–C(2)	156.6 (7)	Os(2)–Os(3)–Os(1)	60.92 (3)
C(13)–Os(1)–Os(2)	92.3 (5)	C(41)–S–Os(3)	117.2 (6)
C(13)–Os(1)–Os(3)	114.5 (5)	C(41)–S–Os(2)	108.7 (6)
C(2)–Os(1)–Os(2)	67.5 (4)	Os(3)—S–Os(2)	68.8 (1)
C(2)–Os(1)–Os(3)	45.0 (4)	C(1)–N(1)–C(4)	117 (2)
Os(2)–Os(1)–Os(3)	57.54 (3)	C(1)–N(1)–C(3)	118 (2)
C(21)–Os(2)–C(23)	94 (1)	C(1)–N(1)–Os(3)	68 (1)
C(21)–Os(2)–C(22)	98.4 (9)	C(4)–N(1)–C(3)	111 (2)
C(21)–Os(2)–S	98.2 (7)	C(4)–N(1)–Os(3)	119 (1)
C(21)–Os(2)–Os(3)	147.2 (7)	C(3)–N(1)–Os(3)	119 (1)
C(21)–Os(2)–Os(1)	101.3 (7)	C(2)–N(2)–C(5)	124 (2)
C(23)–Os(2)–C(22)	93.7 (8)	C(2)–N(2)–C(6)	123 (1)
C(23)–Os(2)–S	166.7 (7)	C(5)–N(2)–C(6)	114 (1)
C(23)–Os(2)–Os(3)	111.8 (7)	N(1)–C(1)–Os(3)	73 (1)
C(23)–Os(2)–Os(1)	86.9 (6)	N(2)–C(2)–Os(3)	135 (1)
C(22)–Os(2)–S	90.6 (6)	N(2)–C(2)–Os(1)	136 (1)
C(22)–Os(2)–Os(3)	100.2 (6)	Os(3)–C(2)–Os(1)	88.6 (6)
C(22)–Os(2)–Os(1)	160.2 (6)	O(11)–C(11)–Os(1)	179 (2)
S–Os(2)–Os(3)	55.0 (1)	O(12)–C(12)–Os(1)	178 (2)
S–Os(2)–Os(1)	84.8 (1)	O(13)–C(13)–Os(1)	177 (2)
Os(3)–Os(2)–Os(1)	61.54 (3)	O(21)–C(21)–Os(2)	176 (2)
C(31)–Os(3)–C(2)	103.7 (7)	O(22)–C(22)–Os(2)	178 (2)
C(31)–Os(3)–C(1)	92.7 (9)	O(23)–C(23)–Os(2)	176 (2)
C(31)–Os(3)–N(1)	96.7 (7)	O(31)–C(31)–Os(3)	179 (2)
C(31)–Os(3)–S	105.9 (6)	C(42)–C(41)–C(46)	118 (2)
C(31)–Os(3)–Os(2)	98.7 (6)	C(42)–C(41)–S	119 (1)
C(31)–Os(3)–Os(1)	146.6 (6)	C(46)–C(41)–S	123 (2)
C(2)–Os(3)–C(1)	89.3 (7)	C(43)–C(42)–C(41)	122 (2)
C(2)–Os(3)–N(1)	125.1 (6)	C(44)–C(43)–C(42)	120 (2)
C(2)–Os(3)–S	121.4 (5)	C(43)–C(44)–C(45)	119 (2)
C(2)–Os(3)–Os(2)	70.2 (5)	C(44)–C(45)–C(46)	121 (2)
C(2)–Os(3)–Os(1)	46.4 (5)	C(41)–C(46)–C(45)	119 (2)

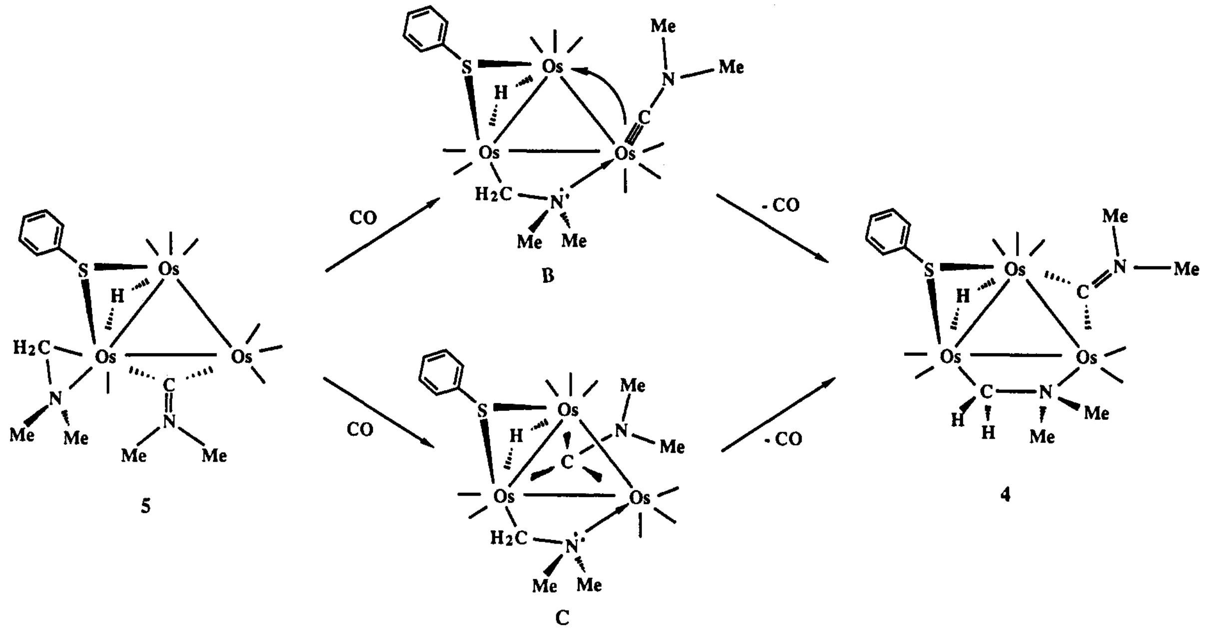
[a] Estimated standard deviations in the least significant figure are given in parentheses.

Os(2)–Os(3) = 2.739 (1) Å. As in **4**, (dimethylamino)carbyne and benzenethiolato ligands bridge the Os(1)–Os(3) and Os(2)–Os(3) bonds, respectively. This compound contains an *N*,*N*-dimethyliminium ligand, but in this case, the carbon and nitrogen atoms are both bonded to one metal atom, Os(3), Os(3)–C(1) = 2.11 (2) Å and Os(3)–N(1) = 2.17 (1) Å. This bonding mode of the iminium ligand has been observed previously in mononuclear metal complexes.[7-9] The C–N bonding distance in **5**, C(1)–N(1) = 1.42 (2) Å, is significantly shorter than the distance observed in **4** and indicates that there is an important contribution of C–N multiple bonding in the mononuclear coordination form in **5**. The C–N bond distances in mononuclear metal iminium ligand complexes are as follows: 1.450 (15) Å in $Mn(CO)_4[H_2C{=}N(CH_2)_2]$;[7] 1.392 (6) Å in

Scheme I



Scheme II



$[Ni(PPh_3)(H_2C{=}NMe_2)]Cl$;[8] and 1.42 (1) Å in $CpFe[C_5H_4CH_2(Me)N{=}CH_2]Mn(CO)_4$.[9] The presence of a bridging hydride ligand in 5 was indicated by a resonance at −15.99 ppm in the ^1H NMR spectrum. The hydride resonance appears as a triplet due to equal coupling to the two hydrogen atoms of the methylene group of the iminium ligand. The hydride ligand and the hydrogen atoms on the methylene group were not observed crystallographically. The latter are shown in Figure 2 in idealized positions. The inequivalent hydrogen atoms of the methylene group appear as a pair of triplets δ 3.82 and 2.35 in the ^1H NMR spectrum. The multiplet character is due to their coupling to each other, J_{H-H} = 1.8 Hz, and a nearly equal coupling to the hydride ligand, J_{H-H} = 1.6 Hz. Compound 5 was converted to 4 (86% yield) when refluxed in octane solvent under an atmosphere of carbon monoxide. This conversion also takes place under nitrogen in the presence of $CH_2(NMe_2)_2$, but the yield (18%) is lower.

Discussion

The two isomeric clusters $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (4 and 5) have been synthesized by the reaction of $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (3) with *N,N,N′,N′*-tetramethyldiaminomethane. The reaction results in the introduction of a *N,N*-dimethyliminium ion into the cluster complex and must occur by the removal of one dimethylamino group from the diaminomethane molecule. The fate of this group has not been ascertained, but the fact that one hydride ligand was also eliminated from 3 could indicate that dimethylamine was formed. It is believed that the transformation of the diaminomethane molecule was induced by complexation to the cluster. Thus, the first step in the reaction probably involves the substitution of one of the amino groups of the diaminomethane for a carbonyl ligand in 3. The fact that the nitrogen is bonded to atom Os(3) in compound 5 would strongly suggest that the initial site of attachment was atom Os(3). This is shown schematically in intermediate A (Scheme I). A cleavage of the carbon–nitrogen bond at this stage would be similar in form to that of the well-known β-hydrogen elimination reaction.[15] Subsequent, elimination of Me_2NH would lead to 5 directly.

Compound 4 is believed to have been derived from 5, and this transformation was demonstrated independently. It was observed that 5 was converted into 4 when its solutions in octane solvent were heated to reflux under an atmosphere of CO. In 5 the carbon atoms of the iminium ligand and the carbyne ligand are attached to the same metal atom, Os(3), while in 4 these carbon atoms do not share a common metal atom. Therefore a key step in the transformation of 5 into 4 is one in which these carbon atoms are separated. Scheme II shows two processes in which this separation is achieved by a shifting of the bridging aminocarbyne ligand. Intermediate B involves a terminally coordinated aminocarbyne ligand. Terminally coordinated aminocarbyne ligands have been observed previously.[16] Intermediate C involves a triply bridging

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[15] Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985; Chapter 9.

[16] Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *J. Am. Chem. Soc.* 1983, *105*, 6162.

aminocarbyne ligand. Examples of triply bridging aminocarbyne ligands have also been reported.[17] We cannot distinguish between these processes at this time. Another important step in the transformation is the conversion of the iminium ligand into a bridging ligand. It is proposed that this occurs by a cleavage of the osmium-nitrogen bond to produce an aminomethyl ligand. Such a transformation has been reported previously.[8] In the present case, the transformation would be assisted by the addition of a mole of CO from the environment. Nucleophilic attack of the amino group on the appropriate neighboring metal atom could induce loss of a CO ligand and complete the formation of the bridge. The transformation would occur similarly via either of the proposed intermediates B or C. To complete the formation of **4** an additional CO ligand must be acquired at atom Os(3) and one must be eliminated from Os(2). This could be accomplished most easily by an intramolecular shift involving a bridging CO ligand but could have occurred alternatively by a dissociation/addition process.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Johnson Matthey Inc. for a loan of osmium tetraoxide. The Brüker AM-300 NMR spectrometer was purchased with funds from the National Science Foundation under Grant No. CHE-8411172.

Registry No. **3**, 106906-16-5; **4**, 106906-17-6; **5**, 106906-15-4; $CH_2(NMe_2)_2$, 51-80-9.

Supplementary Material Available: Tables of anisotropic thermal parameters for **4** and **5** (4 pages); structure factor amplitudes for compounds **4** and **5** (46 pages). Ordering information is given on any current masthead page.

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Linear Chain Organometallic Donor-Acceptor Complexes and One-Dimensional Alloys. Synthesis and Structure of $[(\eta^6\text{-}C_6Me_3H_3)_2M][C_6(CN)_6]$ (M = Fe, Ru)

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Organometallic linear chain complexes $[(\eta^6\text{-}C_6Me_3H_3)_2M][C_6(CN)_6]$ (M = Fe, **1a**; M = Ru, **2a**) and $[(\eta^6\text{-}C_6Me_6)_2M][C_6(CN)_6]$ (M = Fe, **1b**; M = Ru, **2b**) prepared from $[(\eta^6\text{-arene})_2M]^{2+}$ cations and $[C_6(CN)_6]^{2-}$ are described. Single-crystal X-ray studies show that **1a** crystallizes in the space group $R\bar{3}$, with a = 14.875 (5) Å, c = 9.858 (4) Å, V = 1889 (2) Å^3, ρ = 1.38 g cm^{-3}, Z = 3, R_u = 0.047, and R_w = 0.056. The ruthenium analogue **2a** also crystallizes in the space group $R\bar{3}$, with a = 14.825 (5) Å, c = 10.093 (3) Å, V = 1921 (2) Å^3, ρ = 1.48 g cm^{-3}, Z = 3, R_u = 0.026, and R_w = 0.031. Both complexes exhibit mixed stacks of alternating cations and anions with interplanar spacings less than the sum of the van der Waals radii. The complexes exhibit strong charge-transfer bands and are best described as "superionic" donor-acceptor (DA) complexes with nominally doubly charged $(D^{2-}A^{2+})$ ground states and (D^-A^+) excited states. The difference in the charge-transfer absorption energies for a given donor dianion is equivalent to the difference in the reduction potentials of the isostructural $[(\eta^6\text{-arene})_2M]^{2+}$ cations in solution. Since **1a** and **2a** both crystallize in the $R\bar{3}$ space group and exhibit different unit cell lengths along only the linear chain axis, mixed-metal linear chain complexes $[(\eta^6\text{-}C_6Me_3H_3)_2Fe]_x[(\eta^6\text{-}C_6Me_3H_3)_2Ru]_{1-x}[C_6(CN)_6]$ are readily prepared. These mixed-metal phases exhibit optical absorption intensities consistent with Beer's law behavior, and the macroscopic optical properties can be tailored by control of the relative amounts of the iron and ruthenium chromophores.

Introduction

Molecular solids, and particularly quasi-one-dimensional (1-D) materials, have been the subject of intensive investigation owing to their unique and interesting properties,[1] as well as their potential for electronic applications.[2] Design of new molecular solids relies on better understanding of the structure-property relationships as well as new concepts for rational modification of physical properties. Although most studies have focused upon electrical and magnetic behavior, investigation of optical properties can also lend insight into the solid-state properties of 1-D materials. In particular, behavior associated with Mulliken charge-transfer (CT) interactions between π-donors and π-acceptors[3-5] allows one to explore the nature of donor-acceptor (DA) interactions in mixed-stack solids.

In an effort to further understand the properties of low-dimensional solids, we have sought to prepare new materials that incorporate organometallic components. The design of new one-dimensional materials using or-

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