to diverge and become unavailable for the cooperative binding of a carbonyl compound. By eliminating these flaws systematically, we hope to create bidentate Lewis acids that can accomplish the double electrophilic activation of carbonyl compounds and can therefore provide powerful new capabilities in organic synthesis.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. A Varian VXR-300 spectrometer was used to obtain ^{1}H nuclear magnetic resonance (NMR) spectra at 300 MHz, ^{13}C NMR spectra at 75.4 MHz, and ^{51}V NMR spectra at 78.9 MHz. In addition, a Bruker WH-400 instrument was used to record ^{1}H NMR spectra at low temperature. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ), and ^{51}V chemical shifts are relative to external neat $VOCl_3$. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. CH_2Cl_2 and CD_2Cl_2 were dried by distillation from CaH_2, $CDCl_3$ was dried by distillation from P_2O_5, CHF_2Cl was dried by passage over 3-Å molecular sieves and then P_2O_5, acetone was dried over 3-Å molecular sieves and distilled, and pinacolone was dried over anhydrous $MgSO_4$ and 3-Å molecular sieves and was then distilled. $VOCl_2OCH(CH_3)_2$ (**4**) was prepared from 2-propanol by the standard method[8d,12] and purified by distillation in vacuo. Vanadyl chloro alkoxides were handled under dry Ar in Schlenk tubes or in a Vacuum Atmospheres HE-43-2 glovebox. All vanadyl chlorides were mixed with potential ligands at low temperature, and the resulting solutions were protected from light.[8c,9c]

Reaction of the Bis(trimethylsilyl) Ether of *trans*-1,2-Cyclohexanediol with $VOCl_3$ (2 equiv). A solution of the bis(trimethylsilyl) ether[17a] of racemic *trans*-1,2-cyclohexanediol (1.39 g, 5.34 mmol) in CH_2Cl_2 (5 mL) was stirred at −78 °C in the dark under dry Ar and was treated dropwise with $VOCl_3$ (1.85 g, 10.7 mmol). The resulting mixture was then brought to 25 °C. After 24 h, volatiles were removed by evaporation in vacuo. This yielded bidentate vanadyl dichloride alkoxide **6** as a yellow solid of analytical purity (2.06 g, 5.28 mmol, 99%): IR (Nujol mull, CsI) 1000–1050, 450–500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.59 (t, 2 H), 1.90 (d, 2 H), 1.98 (m, 2 H), 2.63 (d, 2 H), 5.81 (bs, 2 H); ^{13}C NMR (75.4 MHz, CD_2Cl_2, −100 °C) δ 22.9, 33.3, 103.5; ^{51}V NMR (78.9 MHz, 4:1 CH_2Cl_2/CD_2Cl_2, −118 °C) δ −293 ($w_{1/2}$ = 250 Hz). Anal. Calcd for $C_6H_{10}Cl_4O_4V_2$: C, 18.49; H, 2.59. Found: C, 19.25; H, 3.06.

Reaction of the Bis(trimethysilyl) Ether of *trans*-1,2-Cyclohexanediol with $VOCl_3$ (1 equiv). A solution of the bis(trimethylsilyl) ether[17a] of racemic *trans*-1,2-cyclohexanediol (0.847 g, 3.25 mmol) in CH_2Cl_2 (6 mL) was stirred at −78 °C in the dark under dry Ar and was treated dropwise with $VOCl_3$ (0.564 g, 3.25 mmol). The resulting mixture was then brought to 25 °C. After 24 h, volatiles were removed by evaporation in vacuo. This yielded the vanadyl chloride dialkoxide assigned structure **7** as a beige solid of analytical purity (0.649 g, 3.00 mmol, 92%): IR (Nujol mull, CsI) 1055, 1035, 1005, 475, 425, 390 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.4–1.6 (m, 4 H), 1.85 (d, 2 H), 2.33 (d, 2 H), 5.78 (m, 2 H); ^{51}V NMR (78.9 MHz, 4:1 CH_2Cl_2/CD_2Cl_2, −100 °C) δ −474 ($w_{1/2}$ = 900 Hz). Anal. Calcd for $C_6H_{10}ClO_3V$: C, 33.28; H, 4.66. Found: C, 33.55; H, 4.84.

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Contribution from the Department of Chemistry,
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A Tetranuclear Tervalent Platinum Complex with α-Pyrrolidonate and Deprotonated Ammine Bridging Ligands, $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$

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Received February 5, 1991

From the reaction of α-pyrrolidonate-bridged $[Pt^{II}{}_2Pt^{III}{}_2(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$ with excess pyrazine in water were obtained dark green, almost black block crystals of $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$. The crystal is monoclinic ($P2_1/c$) with cell dimensions of a = 10.652 (5) Å, b = 18.512 (7) Å, c = 10.430 (4) Å, β = 102.42 (3)°, Z = 2, and V = 2008 (1) Å^3. The complex consists of two α-pyrrolidonate-bridged Pt(III) dimeric units. The two dimers are bridged by two NH_2^- ligands to form tetranuclear $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2{}^{4+}$. The Pt–Pt distance in the dimeric unit is 2.608 (1) Å, whereas that of the interdimer separation is 3.160 (2) Å.

We have synthesized a series of α-pyrrolidonate-bridged tetranuclear mixed-valent platinum complexes with various platinum oxidation states, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ (n = 5, 6, 8).[1–6] In the course of the study on the solution behavior of the tetranuclear complexes, we recently isolated a very unusual tetranuclear Pt(III) complex from an aqueous solution of $[Pt^{III}{}_2Pt^{II}{}_2(NH_3)_8(C_4H_6NO)_4]^{6+}$ with pyrazine. The tetranuclear Pt(III) complex is composed of two α-pyrrolidonate-bridged Pt(III) dimers, which are bridged by two NH_2^- ligands to form a tetranuclear complex with a formula of $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2{}^{4+}$. The complex is the first example of a structurally elucidated NH_2^--bridged tetranuclear Pt(III) complex.

Experimental Section

The complex was synthesized by adding 8 mg (0.1 mmol) of pyrazine to a solution of 100 mg (0.06 mmol) of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6\cdot 2H_2O$ (**1**)[1] in 4 mL of H_2O. After the solution was left at 5 °C for a few days, dark green, almost black block crystals appeared. The yield was 8%. The formula of the complex is $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$ (**2**).[7]

Table I. Crystallographic Data for $[(NO_3)(NH_3)_2Pt(C_4H_6NO)_2Pt(NH_3)(\mu\text{-}NH_2)]_2(NO_3)_4$ (**2**)

formula	$Pt_4C_{16}H_{46}N_{18}O_{22}$	Z	2
fw	1623.12	T, °C	25
space group	$P2_1/c$ (No. 14)	radiation (λ, Å)	Mo Kα (0.71068)
a, Å	10.652 (5)	ρ_{calcd}, g cm^{-3}	2.68
b, Å	18.512 (7)	μ(Mo Kα), cm^{-1}	147.2
c, Å	10.430 (4)	transm coeff	1.00–0.70
β, deg	102.42 (3)	R^a	0.058
V, Å^3	2008 (1)	$R_w{}^b$	0.041

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

The X-ray analysis of **2** was carried out with a Rigaku AFC-5R automated diffractometer and the programs UNICS-III[8] and ORTEP.[9] Accurate unit cell dimensions were calculated from the setting angles of 20 reflections with 20° < 2θ < 25°. The structure was solved by a standard heavy-atom method. The crystallographic data for **2** are shown in Table I. Three standard reflections were measured every 200 measurements during the data collection. Lorentz and polarization corrections were applied to the data. All the non-hydrogen atoms were located in succeeding Fourier syntheses. An empirical absorption correction was

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(7) Anal. Calcd for $Pt_4C_{16}H_{46}N_{18}O_{22}$: C, 11.84; H, 2.86; N, 15.53. Found: C, 12.07; H, 3.07; N, 15.79.
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(9) Johnson, C. K. Report ORNL-3794 (revised); Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

0020-1669/91/1330-3032$02.50/0

Table II. Atomic Parameters[a]

atom	x	y	z	B_{eqv}, Å^2
Pt(1)	63945 (7)	2082 (4)	7790 (7)	192 (2)
Pt(2)	76822 (8)	12588 (4)	21220 (7)	221 (2)
N(3)	4604 (13)	552 (6)	566 (12)	23 (4)
N(4)	6112 (14)	−406 (7)	2328 (12)	25 (4)
N(5)	6076 (14)	1872 (7)	2204 (14)	31 (5)
N(6)	7788 (15)	873 (7)	3982 (13)	31 (5)
O(7)	8118 (11)	−262 (6)	840 (10)	31 (4)
N(8)	9243 (14)	677 (8)	2062 (14)	32 (5)
C(9)	9173 (17)	32 (9)	1461 (16)	30 (6)
C(10)	10427 (19)	−355 (11)	1611 (19)	44 (7)
C(11)	11412 (23)	212 (15)	2351 (28)	103 (12)
C(12)	10563 (21)	856 (13)	2657 (22)	63 (9)
O(13)	6518 (12)	742 (6)	−888 (10)	29 (4)
N(14)	7691 (14)	1653 (7)	330 (13)	26 (4)
C(15)	7154 (17)	1367 (10)	−769 (16)	31 (6)
C(16)	7205 (21)	1796 (10)	−1978 (18)	40 (7)
C(17)	8047 (27)	2440 (12)	−1428 (21)	71 (10)
C(18)	8334 (23)	2358 (10)	101 (9)	48 (8)
N(19)	8840 (16)	2576 (7)	3913 (14)	39 (5)
O(20)	9068 (12)	2160 (6)	3012 (11)	37 (4)
O(21)	9647 (13)	3047 (7)	4275 (14)	50 (5)
O(22)	7895 (14)	2495 (7)	4466 (13)	51 (5)
N(23)	909 (16)	1268 (9)	6283 (15)	47 (6)
O(24)	945 (15)	628 (6)	5911 (15)	56 (6)
O(25)	1869 (15)	1541 (7)	6984 (15)	68 (6)
O(26)	−70 (14)	1619 (7)	5910 (14)	63 (6)
N(27)	4551 (17)	857 (9)	4449 (16)	53 (6)
O(28)	4676 (17)	777 (8)	3308 (13)	71 (6)
O(29)	3637 (16)	638 (11)	4868 (15)	102 (8)
O(30)	5411 (18)	1158 (12)	5202 (19)	123 (9)

[a] Positional parameters are multiplied by 10^4, except those for Pt (10^5). Values of $B_{eqv} = {}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$ are multiplied by 10, except those for Pt (10^2).

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Pt(NH_3)_2Pt(NH_3)(\mu\text{-}NH_2)(C_4H_6NO)_2(NO_3)]_2^{4+}$

Pt(1)–Pt(2)	2.608 (1)	Pt(1)–Pt(1)′	3.116 (2)
Pt(1)–N(3)	1.98 (1)	Pt(2)–N(5)	2.07 (1)
–N(4)	2.05 (1)	–N(6)	2.05 (1)
–O(7)	2.02 (1)	–N(8)	1.99 (1)
–O(13)	2.03 (1)	–N(14)	2.01 (1)
–N(3)′	2.11 (1)	–O(20)	2.29 (1)
Pt(2)–Pt(1)–Pt(1)′	141.81 (4)	Pt(1)–N(3)′–Pt(1)′	101.7 (5)
Pt(1)′–Pt(1)–N(3)	40.8 (3)	Pt(1)′–Pt(1)–N(4)	89.1 (4)
–O(7)	131.0 (3)	–O(13)	84.4 (3)
Pt(2)–Pt(1)–N(3)	101.7 (4)	Pt(1)–Pt(2)–N(5)	95.0 (4)
–N(4)	98.1 (3)	–N(6)	99.5 (4)
–O(7)	86.3 (3)	–N(8)	85.8 (4)
–O(13)	88.5 (3)	–N(14)	83.0 (4)
–N(3)	171.1 (4)	–O(20)	168.7 (3)
N(3)′–Pt(1)–N(3)	78.7 (5)	O(20)–Pt(2)–N(5)	92.9 (5)
–N(4)	90.9 (5)	–N(6)	88.3 (5)
–O(7)	93.3 (5)	–N(8)	86.4 (5)
–O(13)	82.6 (5)	–N(14)	88.9 (5)

applied.[10] The structure was refined by the block-diagonal least-squares method with anisotropic temperature factors for all the atoms. The blocks for refinement were chosen so that each block contains coordinates and temperature factors for an atom. Atomic coordinates and equivalent isotropic thermal parameters for **2** are given in Table II. Selected distances and angles for **2** are listed in Table III.

The transmittance spectrum was measured with a microcrystalline sample on a Hitachi U-6000 microscopic spectrophotometer.

Results and Discussion

An ORTEP view of the complex is shown in Figure 1. The most striking feature of the complex is that it is a tetranuclear Pt(III) complex, composed of two α-pyrrolidonate-bridged head-to-head Pt(III) dimers,[11] which are further doubly bridged by NH_2^- ligands. The molecule is centrosymmetric at the midpoint of the central Pt(1)···Pt(1)′ vector. One of the ammine ligands formerly coordinated in the equatorial coordination plane to a Pt atom in the starting complex **1** has been deprotonated and acts as an axial ligand to the other Pt(III) dimer unit, thus bridging the two Pt(III) dimeric units. The outer two Pt atoms are axially coordinated by NO_3^- ligands. The geometrical features of the complex are as follows. The tilt angle between the adjacent Pt-coordination planes in the dimer unit is 17.7°, and the average torsion angle about the Pt–Pt vector in the dimer unit is 0.4°. The α-pyrrolidonate-bridged Pt–Pt distance in **2** (2.608 (1) Å) is among the typical Pt(III)–Pt(III) distances.[11-14] The inner Pt(1)···Pt(1)′ distance bridged by two NH_2^- ligands is 3.160 (2) Å and therefore is not metal–metal bonding. The axial distance Pt(1)–N(1)′ (2.11 (1) Å) is the first reported distance of Pt(III)–N(NH_2^-) and is significantly longer than the value of 2.05 (1) Å for Pt(IV)–N(NH_2^-) in $[(H_3N)_4Pt(\mu\text{-}NH_2)_2Pt(NH_3)_4]Cl_6\cdot 2DMSO$.[15] The axial Pt(III)–$NH_2^-$ distance (2.11 (1) Å) is longer than the equatorial Pt(III)–NH_2^- distance (1.97 (1) Å) in compound **2**, which should be contrasted to the almost equal distances of axial and equatorial Pt(IV)–NH_2^- distances in $[(H_3N)_4Pt(\mu\text{-}NH_2)_2Pt(NH_3)_4]Cl_6\cdot$ 2DMSO. It should be noticed that **2** is prepared in an aqueous solution from deprotonation of the coordinated ammine ligands by rather weak base like pyrazine. Although the Pt(IV)–NH_2^- complex $[(H_3N)_4Pt(\mu\text{-}NH_2)_2Pt(NH_3)_4]Cl_6\cdot 2DMSO$[15] is reported to be stable in aqueous solution, it is prepared from the reaction

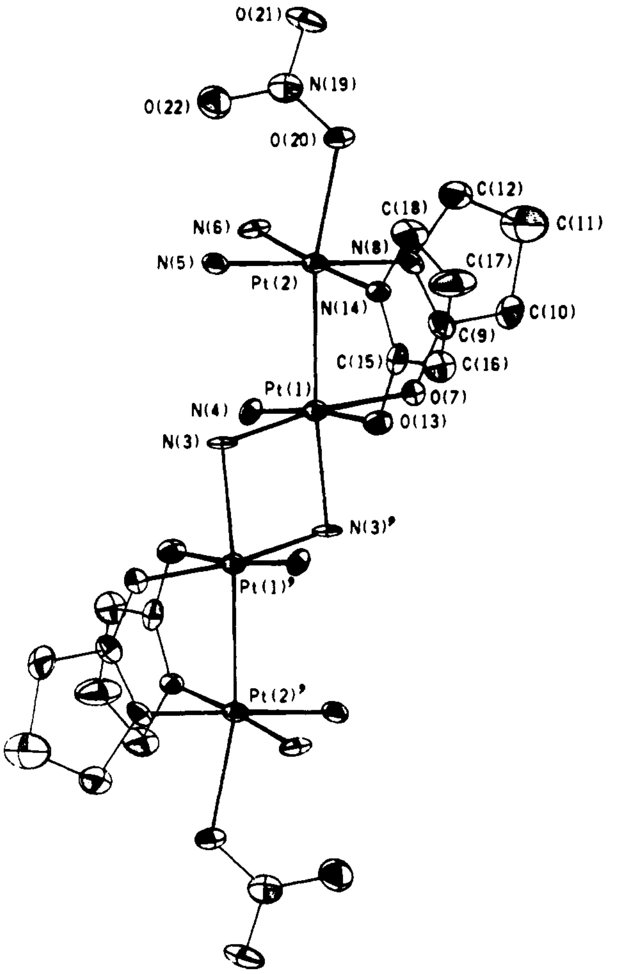

Figure 1. ORTEP drawing of $[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2^{4+}$ shown with 20% probability ellipsoids.

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of liquid ammonia and $(NH_4)_2[PtCl_6]$.[16] The synthetic conditions for **2** are therefore rather unusual for producing NH_2^- and show that the acidity of the coordinated ammine ligands in the parent tetranuclear complex **1** is remarkably increased. The pH of the reaction solution was 2.1 and 2.6 before and after pyrazine addition, respectively. If pyrazine was not added, **2** was not obtained and only the starting material **1** was recovered in 39% yield on gradual evaporation of the solution to ca. two-thirds of the original volume. If the reaction solution plus pyrazine was concentrated to less than two-thirds, **1** and $[Pt^{II}{}_3Pt^{III}(NH_3)_8(C_4H_6NO)_4](NO_3)_5{\cdot}2H_2O$ (**3**)[6,18] were obtained as crystals besides **2**. These complexes were separated microscopically and identified by elemental analyses and UV–vis and ESR spectra.[3,6] No dimeric $[Pt^{II}{}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ [5] or $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2X_2]^{2+}$ [11] (X is an axial ligand) was obtained even when the solution was dried. The products obtained were not affected by the presence or absence of air during the preparation. Recrystallization of **2** from water or diluted H_2SO_4 (pH 2) by gradual evaporation at room temperature gave only **1** and **3**. Complex **2** is diamagnetic[19] and is almost instantaneously reduced to **1** and **3** when dissolved in water, which was confirmed by UV–vis and ESR spectra.[3,6] The visible transmittance spectrum of a microcrystalline sample of **2** shows very broad bands at 450 and 695 nm.

Regarding the formation route of **2**, it is improbable that deprotonation occurs on a coordinated ammine in $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2X_2]^{2+}$, which exists together with $[Pt^{II}{}_2(NH_3)_4(C_4H_6NO)_2]^{2+}$ in equilibrium with **1** in solution as a result of disproportionation reaction,[18] and the deprotonated dimeric Pt(III) complex further dimerizes to form **2** by axially substituting the ligand X with NH_2^-. Actually, addition of pyrazine to either $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2(NO_2)(NO_3)](NO_3)_2{\cdot}H_2O$[11] or $[Pt^{III}{}_4(NH_3)_8(C_4H_6NO)_4](SO_4)(ClO_4)_6$[3] at 0.1–2 times the equivalent amount in water did not give **2**. From the former solution, the dimeric Pt(III) complex with axially coordinated pyrazine was obtained,[20] whereas the latter complex was too unstable in neutral water and is easily reduced to **1** and **3**.[3] Therefore, deprotonation seems to occur only on **1**, which leads to the formation of **2** as follows:

$$\underset{\mathbf{1}}{3[Pt^{II}{}_2Pt^{III}{}_2(NH_3)_8(C_4H_6NO)_2]^{6+}} + 2NO_3^- \rightarrow \underset{\mathbf{2}}{[(NO_3)(NH_3)_2Pt^{III}(C_4H_6NO)_2Pt^{III}(NH_3)(\mu\text{-}NH_2)]_2{}^{4+}} + \underset{\mathbf{3}}{2[Pt^{II}{}_3Pt^{III}(NH_3)_8(C_4H_6NO)_2]^{5+}} + 2H^+ \quad (1)$$

Equation 1 is also supported by the fact that, on addition of pyrazine to **1**, the solution rapidly becomes blue (λ_{max} = 680 nm) due to formation of **3**.

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Supplementary Material Available: Tables of anisotropic thermal parameters (Table S1), detailed crystallographic data (Table S3), bond lengths (Table S4), and bond angles (Table S5) (5 pages); a listing of final structure factors (Table S2) (16 pages). Ordering information is given on any current masthead page.

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[16] Kretschmer, V. M.; Heck, L. *Z. Anorg. Allg. Chem.* **1982**, *490*, 205.

[17] Anal. Calcd for $Pt_4C_{16}H_{52}N_{17}O_{21}$: C, 12.02; H, 3.28; N, 14.89. Found: C, 12.11; H, 3.33; N, 15.02. ESR spectrum of 3 corresponded with that of 3 (see Ref. 3).

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[19] The sample sometimes shows a weak ESR signal; however, this is due to contamination of 3, which was confirmed by the *g* values.

[20] $[Pt^{III}{}_2(NH_3)_4(C_4H_6NO)_2(NO_2)(pyrazine)](NO_3)_3{\cdot}3H_2O$ was obtained. Anal. Calcd for $Pt_2C_{12}H_{34}N_{12}O_{16}$: C, 14.52; H, 3.46; N, 16.93. Found: C, 14.42; H, 3.50; N, 16.78.

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The Dithiocarbonate Route to 1,2-Dithiolene Complexes of Molybdenum and Tungsten

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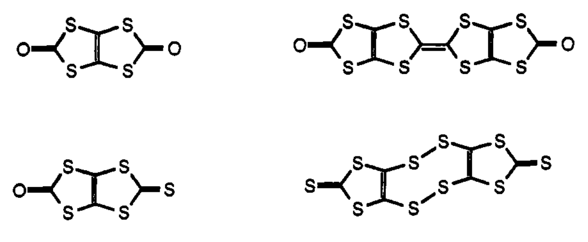
Tetrathiapentalenedione, $C_2S_4(CO)_2$, reacts with MS_4^{2-} (M = Mo, W) to give $M(S_2C_2S_2CO_3)^{2-}$, isolated as PPh_4^+ salts. COS is the major coproduct of this transformation. The new tris(dithiolene) complexes were characterized by spectroscopic methods as well as a crystallographic study of $(PPh_4)_2[W(S_2C_2S_2CO)_3]$. $C_2S_4(CO)(CS)$ and WS_4^{2-} react to give $W(S_2C_2S_2CS)_3^{2-}$ together with $[W_2S_4(S_2C_2S_2CS)_2]^{2-}$. The same compounds can be obtained by the action of WS_4^{2-} on the cyclic bis(disulfide) $(S_2C_2S_2CS)_2$. Electrochemical studies show that $[M(S_2C_2S_2CE)_3]^{2-}$ (M = Mo, W; E = S, O) undergo two one-electron oxidations at mild potentials. $[Mo(S_2C_2S_2CO)_3]^0$ was prepared by the oxidation of the corresponding dianion with nitrosonium and ferrocenium salts. The neutral dithiolenes are soluble in nonpolar organic solvents and were characterized by IR and mass spectrometry. A methanol suspension of $[Mo(S_2C_2S_2CO)_3]^0$ reacts with methoxide followed by methyl or butyl iodide to give the new dithiolenes $[Mo(S_2C_2S_2R_2)_3]^0$. These species are less oxidizing than $[Mo(S_2C_2S_2CO)_3]^0$.

Introduction

The tetrathioanions of V, Mo, W, and Re are the most important molecular chalcogenides of these elements.[1] These MS_4^{n-} species are stoichiometrically simple, easily prepared, and synthetically versatile. They are precursors to low-dimensional materials,[2] and they are the building blocks for a variety of multimetallic inorganic[3-6] and organometallic[7] clusters. In addition to their use as metalloligands, the thiometalates have been shown to be reactive toward oxidants,[8-12] protons,[13-15] and main-group

Chart I



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