Table IV. Correlation of Calculated MO Energies with Observed Ionization Potentials for $C_7H_7Mn(CO)_3$

Calcd MO energy, eV	Predicted IP, eV	Obsd IP, eV	Type
−8.72	−7.71	−7.7	M
−9.31	−7.97	−7.9	M
−10.06	−8.30	−8.3	M
−10.20	−8.36		π
−15.01	−10.47	−10.3	π
−15.67	−10.76		π
−17.47	−11.45	~−11.8	π
−17.58	−11.60		CO
−17.70	−11.65		σ

sented by the same line for these molecules. The agreement between calculated and observed values for $C_7H_7Mn(CO)_3$ is shown in Table IV. The agreement is considered quite satisfactory, since the experimental values are estimated to be uncertain by about 0.1 eV. Thus we feel that violations of Koopman's theorem are sufficiently close to constant in the series to allow PES to be useful as a probe of electronic structure. The consistent explanation of the spectra allowed by our calculations indicates that they adequately account for the principal interactions and thus allow a more detailed understanding of the bonding in these molecules.

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Synthesis and Characterization of Dithiolene Complexes of the Early Transition Metals

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The synthesis of tris(dithiolene) complexes of the type $[R_4E]_xM(S_2C_6H_3Y)_3$ (where R_4E is a tetraphenylarsonium or tetraalkylammonium ion; M is Ti, Zr, or Hf and $x = 2$ or M is Ta or Nb and $x = 1$; and Y is H or CH₃) has been accomplished by reaction of the appropriate metal amide with a mixture of the dithiol and its sodium salt in THF. The results of ir, visible, and uv spectra, conductivity, ¹H and limited ¹³C nmr studies are presented. The electronic spectra are dominated by ligand-to-metal charge-transfer bands. The band positions change in the expected order Ti < Zr ~ Hf, Nb < Ta, Nb < Zr, and Ta < Hf. The variety of coordination geometries within the reported complexes is noted and the importance of matching ligand and metal d orbital energies for the stabilization of trigonal prismatic geometry is discussed.

The chemistry of 1,2-dithiolene complexes of the transition metals has been the subject of considerable study over the past decade.[1-7] It is noteworthy, however, that during this period of great activity, few complexes of the early transition metals[8-10] have been reported aside from those of vanadium. The inability to synthesize these complexes can be traced to the lack of a suitable preparative method. Indeed, attempts to obtain dithiolene complexes of the early transition metals by known synthetic procedures, e.g., the reaction of anhydrous metal chlorides with dithiols or their sodium salts, have invariably led to failures except in the cases noted above, both in our laboratories and elsewhere.[9] It seemed to us that the difficulties presented by the known methods could be overcome by using starting materials with more readily displaceable ligands. In this context, the extensive investigations of Bradley,[11,12] Thomas,[13] and Lappert[14] into the reactivity of transition metal amido derivatives, $M(NR_2)_x$, seemed par-

ticularly relevant. Indeed, these authors have amply demonstrated the usefulness of these complexes both in insertion reactions and in reactions with protic ligands. However, the reaction of these metal amides with 1,2-dithiols seems to have been overlooked.

In this article, we report the detailed synthesis of benzene-1,2-dithiol and toluene-3,4-dithiol complexes of Ti, Zr, Hf, Nb, and Ta utilizing the corresponding metal amides as starting materials. Further, we discuss the results of physical studies carried out on these complexes. Comparison of our results with previous investigations has clarified several trends and greatly assisted our understanding of the behavior of dithiolene complexes.

Experimental Section

All operations were performed in Schlenk type apparatus under an atmosphere of nitrogen dried by passing through a column of

Aquasorb purchased from Mallinckrodt Chemical Works. Tetrahydrofuran, toluene, and ether were purified by distillation from flasks containing Na–K alloy. Acetonitrile was distilled from P_2O_5, as was CH_2Cl_2 after preliminary washing with concentrated H_2SO_4 and water, and drying over $CaSO_4$. Tetraalkylammonium and tetraphenylarsonium salts were dried overnight at 100° (0.01 mm) prior to use.

Metal amides were prepared by previously published procedures,[11,15] and sodium cyclopentadienide was prepared by standard methods. Hexane solutions of *n*-butyllithium were purchased from Foote Chemical Co., while toluene-3,4-dithiol was obtained from Eastman Kodak or Matheson Coleman and Bell. All other chemicals used were readily available reagent grade chemicals, except for benzene-1,2-dithiol which was prepared according to the following modification of the method of Hünig and Fleckenstein.[16]

1,2,3-Benzothiadiazole was prepared as follows. In a 1-l. three-neck flask fitted with a dropping funnel, thermometer, and mechanical stirrer, 100 ml of *o*-aminothiophenol[17] was dissolved in 400 ml of glacial acetic acid and 40 ml of water. This mixture was cooled in an ice–methanol bath and kept at 0–5° throughout the addition of a solution of 65 g of $NaNO_2$ in 200 ml of water. Addition was stopped as soon as a persistent brown color was observed. The mixture was then stirred overnight followed by extraction with three 200-ml portions of CH_2Cl_2. The extract was washed with an aqueous 5% $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed with the assistance of a water aspirator and the product was distilled at 56° (0.1 mm) to yield 103 g (43%) of 1,2,3-benzothiadiazole as a low-melting solid.

From this point the synthesis of benzene-1,2-dithiol proceeded without difficulty.

Preparation of the Complexes. Method I. Direct Reaction. $[(C_2H_5)_2NH_2]_2[Ti(S_2C_6H_3CH_3)_3]$. Toluene-3,4-dithiol, 0.762 g (0.00486 mol), was dissolved in 25 ml of dry toluene in a three-neck flask fitted with a nitrogen inlet, dropping funnel, and magnetic stirrer. A solution of $Ti[N(C_2H_5)_2]_4$, 0.407 g (0.00121 mol) in 50 ml of toluene was transferred to the dropping funnel. Dropwise addition of the Ti solution was accompanied by the formation of a dark red-brown solution and a black solid. The reaction mixture was stirred for 24 hr with no apparent change and then refluxed for 2 hr which resulted in increased amounts of the precipitate. The black solid was collected by filtration to give 0.765 g, 96% yield based on Ti. The product may be recrystallized from acetone–light petroleum ether in about 60% yield; mp 261–263° uncorrected. *Anal.* Calcd: C, 52.86; H, 6.43; N, 4.25; Ti, 7.27. Found:[18] C, 53.07; H, 6.48; N, 4.11; Ti, 7.24.

The same product has also been isolated by reaction of 3 mol of toluene-3,4-dithiol with 1 mol of the Ti amide and has been identified by its ir and melting point.

Method II. Use of *n*-Butyllithium. $[(C_2H_5)_4N]_2[Ti(S_2C_6H_3CH_3)_3]$. A solution prepared by adding 2.5 ml of a 1.67 *N* hexane solution of *n*-butyllithium to 10 ml of THF was added dropwise to 0.646 g (0.00415 mol) of toluene-3,4-dithiol in 25 ml of THF. After 0.5 hr, 16 ml of a solution of 0.428 g (0.00127 mol) of $Ti[N(C_2H_5)_2]_4$ in 20 ml of THF was added dropwise to the reaction mixture. (Part of the Ti solution was discarded as a convenient way to control the stoichiometry of the reaction.) The resulting mixture was stirred overnight and then 1.099 g of $(C_2H_5)_4NI$ was added directly. The resulting suspension was stirred for several days and then the solvent was removed under vacuum and was replaced by 25 ml of methanol. After stirring for 1 hr, the reaction mixture was allowed to settle for 3 hr and the resulting black, microcrystalline solid was collected by filtration in the open. After drying under vacuum the yield was 0.257 g (33%); mp 229–230° uncorrected. *Anal.* Calcd: C, 57.63; H, 7.58; N, 3.64; S, 24.95. Found: C, 57.18, 57.43; H, 7.50, 7.39; N, 4.11, 4.05; S, 25.19, 25.62.

$[(C_4H_9)_4N][Nb(S_2C_6H_3CH_3)_3]$. The procedure used here was essentially the same as for Ti except that methanol was not used for the exchange. Instead, 10 ml of CH_2Cl_2 was added to dissolve the crude product, then 190 ml of ether was added and, after brief stirring, a violet solid was filtered off. The product was recrystallized by dissolving it in 100 ml of CH_2Cl_2 and adding 100 ml of ether. After standing for 4 days, violet crystals were collected. Two further crystallizations gave violet hexagons in 13% yield, 160° dec. *Anal.* Calcd: C, 55.68; H, 6.82; N, 1.75; S, 24.10; Nb, 11.64. Found:[19] C, 55.92, 55.82; H, 6.58, 6.57; N, 1.79, 1.72; S, 24.11, 24.10; Nb, 11.50, 11.79.

Method III. Use of Sodium Cyclopentadienide. $[(C_2H_5)_4N]_2[Hf(S_2C_6H_3CH_3)_3]$. Sodium cyclopentadienide, 0.508 g (0.00578 mol), in 20 ml of THF was added to 1.268 g (0.00815 mol) of toluene-3,4-dithiol in 50 ml of THF. Next, 1.230 g (0.00264 mol) of $Hf[N(C_2H_5)_2]_4$ in 20 ml of THF was added dropwise to the reaction mixture and the resulting orange solution was stirred overnight. Tetraethylammonium bromide, 1.23 g (0.00578 mol), was added to the reaction mixture and after about 1 hr of stirring the solvent was removed under vacuum and the residue was thoroughly dried. The residue was stirred with 150 ml of CH_3CN for 0.5 hr and then filtered to remove NaBr. By concentrating the filtrate under vacuum and cooling it in a freezer, 1.324 g (55%) of an orange solid was obtained, mp 232–233° uncorrected. *Anal.* Calcd: C, 49.15; H, 6.47; N, 3.10; S, 21.28. Found: C, 48.58, 48.86; H, 6.36, 6.54; N, 3.00, 3.06; S, 21.41, 21.15.

Using similar synthetic procedures, the following compounds were also obtained.

$[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]$: red crystals, mp 229–230° uncorrected, 46% yield. *Anal.* Calcd: C, 54.56; H, 7.18; N, 3.44; S, 23.62. Found: C, 54.23, 54.15; H, 7.44, 7.47; N, 3.69, 3.70; S, 22.62, 22.87.

$[(C_2H_5)_4N]_2[Zr(S_2C_6H_4)_3]$: red crystals, mp 227° uncorrected, 60% yield. *Anal.* Calcd: C, 52.87; H, 6.78; N, 3.63; S, 24.91. Found: C, 53.59, 53.12; H, 6.95, 7.17; N, 3.68; S, 25.27, 25.45.

$[(C_2H_5)_4N]_2[Ti(S_2C_6H_4)_3]$: black crystalline solid, mp 224–225° uncorrected, 80% yield. *Anal.* Calcd: C, 56.01; H, 7.19; N, 3.84; S, 26.39. Found: C, 55.78; H, 7.00; N, 3.27; S, 25.84.

$[(C_2H_5)_4N][Ta(S_2C_6H_3CH_3)_3]$: dark brown crystals, 206° dec, 27% yield. *Anal.* Calcd: C, 45.00; H, 4.95; N, 1.81; S, 24.86. Found: C, 44.11, 44.18; H, 4.82, 5.03; N, 1.57, 1.92; S, 23.87, 23.46.

$[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$. Instead of treating the residue with CH_3CN, it was transferred to a continuous extractor and extracted with 100 ml of CH_2Cl_2. Concentrating and cooling the extract gave violet crystals in 38% yield, 214° dec uncorrected. *Anal.* Calcd: C, 56.25; H, 3.60; S, 21.45. Found: C, 56.36, 56.17; H, 3.86, 3.80; S, 21.46, 21.19.

$[(C_6H_5)_4As][Ta(S_2C_6H_4)_3]$. Instead of treating the residue with CH_3CN, it was dissolved in CH_2Cl_2 and filtered to remove NaCl. As before a dark-brown solid was obtained, 220° dec, yield 47%. *Anal.* Calcd: C, 51.22; H, 3.28; S, 19.53. Found: C, 50.78, 50.69; H, 3.22, 3.60; S, 20.00, 19.44.

The following compounds were also prepared for purposes of comparison.

$[(C_6H_5)_4As][Sb(S_2C_6H_4)_3]$. This compound was prepared by the method of Gagliardi and Durst.[20] *Anal.* Calcd: C, 54.49; H, 3.48; S, 20.78. Found: C, 53.82; H, 3.62; S, 20.40.

$[Mo(S_2C_6H_4)_3]$ and $[W(S_2C_6H_3CH_3)_3]$. These complexes were prepared by the method of Gray, *et al.*,[21] and were characterized by physical methods.

Physical Measurements. Conductivity measurements were made at 10^{-3} *M* in CH_3CN using a cell designed for work under inert atmosphere and a Philips PR9500 conductivity bridge. Molecular weight measurements were made at 10^{-3} *M* in CH_3CN using a Hewlett-Packard 301A vapor phase osmometer calibrated with benzil. Infrared spectra were recorded in the region of 4000 to 250 cm^{-1} as mineral oil mulls and very thin KBr pellets on a Perkin-Elmer 467 infrared spectrophotometer. Visible and ultraviolet spectra were recorded from 10,000 to 40,000 cm^{-1} on a Cary 14 at 10^{-4} *M* in CH_3CN using various path lengths. ^1H nmr spectra were recorded on a Varian Associates A60 or HA-100 spectrometer and ^{13}C spectra were recorded on a Bruker HFX-10. Polarographic measurements in CH_2Cl_2 were made using conditions and apparatus similar to that described in detail by Holm, *et al.*[22] Measurements in CH_3CN were made at 10^{-3} *M* with 0.1 *M* $(C_3H_7)_4NClO_4$ as supporting electrolyte. The apparatus used for CH_3CN was the same as that used for CH_2Cl_2 except that the bridge was silica gel impregnated with 0.1 *M* (*n*-$C_3H_7)_4NClO_4$ in CH_3CN and the reference electrode was Ag|0.1 *M* AgClO_4, 0.1 *M* (*n*-$C_3H_7)_4NClO_4$. The indicator electrode for all measurements was a platinum microelectrode rotated at a constant speed of 600 rpm. All polarographic measurements were made on a Metrohm Polarecord E261 with ir compensator E446.

Results

In an attempt to synthesize eight-coordinate toluene-3,4-dithiol complexes of the early transition metals, tetrakisdiethylamidotitanium was added to 4 mol of toluene-

Table I. Conductivity and Uv and Visible Spectra

Compd	$\Lambda_M{}^a$	Band maxima, $cm^{-1 b,c}$ (ϵ in parentheses)
$[(C_2H_5)_4N]_2[Ti(S_2C_6H_3CH_3)_3]$	213	12,300 (271); 17,900 (7130); 22,700 (16,000); 30,000 (18,300)
$[(C_2H_5)_2NH_2]_2[Ti(S_2C_6H_3CH_3)_3]$	143 53^d 96^e	12,400; 17,700; 22,700; 30,300
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]$	230	27,800 (11,400); 32,300 sh (21,000)
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_4)_3]$	237	20,000 sh (2,030); 35,800 sh (25,200)
$[(C_2H_5)_4N]_2[Hf(S_2C_6H_3CH_3)_3]$	233	25,600 sh (5420); 33,100 (18,400); 38,600 (46,200)
$[(C_4H_9)_4N][Nb(S_2C_6H_3CH_3)_3]$	104	17,200 (10,700); 26,100 (11,900)
$[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$	85	17,700 (10,700); 27,200 (13,800); 30,700 sh (9120)
$[(C_6H_5)_4As][Ta(S_2C_6H_4)_3]$	95	22,300 (4,900); 28,700 (14,500); 33,900 (18,100)
$[(C_6H_5)_4As][Sb(S_2C_6H_4)_3]$		20,400 (2460); 25,300 (2210); 32,200 (4940)

^{a} Molar conductivity in ohm^{-1} cm^2 mol^{-1}. ^{b} Approximately 10^{-4} M CH_3CN solution. ^{c} Key: sh, shoulder. ^{d} Approximately 10^{-3} M CH_3NO_2 solution. ^{e} Approximately 10^{-3} M acetone solution.

Table II. Concentration Studies of the Conductivity of $[(C_2H_5)_2NH_2]_2Ti(S_2C_6H_3CH_3)_3$

$10^3c_m{}^a$	$\Lambda_m{}^b$	Solvent	$10^3c_m{}^b$	$\Lambda_m{}^b$	Solvent
0.995	53	CH_3NO_2	0.150	198	CH_3CN
0.971	56	CH_3NO_2	0.300	177	CH_3CN
0.194	86	CH_3NO_2	0.600	155	CH_3CN
0.0971	109	CH_3NO_2	0.985	139	CH_3CN
			3.00	108	CH_3CN

^{a} Mol.$^{-1}$. ^{b} Cm^2 ohm^{-1} mol^{-1}.

3,4-dithiol in toluene. A black solid was isolated which we have tentatively formulated as $[(C_2H_5)_2NH_2]_2[Ti(S_2C_6H_3-CH_3)_3]$ (I). This assignment is based largely upon comparison of uv–visible and ir spectra of I and the analogous tetraethylammonium salt which will be described shortly. In addition to having identical uv–visible spectra, Table I, these two complexes were found to have virtually identical infrared spectra when the difference in cations was taken into account. The ir of I also conclusively shows the presence of the diethylammonium ion. However, a molecular weight measurement in CH_3CN and conductivity data, Table I, were not consistent with the range expected for a 2 to 1 electrolyte. Concentration studies in CH_3NO_2 and CH_3CN yielded nonlinear plots of the molar conductivity vs. $c^{1/2}$ and are consistent with ion pair formation which could conceivably result from hydrogen bonding of the cation to sulfur in the anion. A ^1H nmr of I in CD_3CN showed the presence of all but the N–H protons in approximately the right ratios, although the integration was not very reliable due to the low solubility of the compound. The absence of the N–H protons is not surprising, as they are difficult to locate in $[(C_2-H_5)_2NH_2]Cl$. However, a broad resonance of variable intensity and position was found at $\sim$3–4 ppm from TMS which could possibly be assigned to a S–H group. However, this resonance seems more likely to be an impurity in CD_3CN as distilling the solvent from P_2O_5 greatly reduced its intensity. The distribution of hydrogen between the N and S atoms is nevertheless difficult to resolve and might even be solvent dependent. The somewhat more convincing nature of the uv–visible and infrared evidence, with the concomitant formulation I, led us to attempt the synthesis of six-coordinate dithiolene complexes by an improved route, method II. Method II consists of reacting the metal amide with a mixture of the dithiol and its lithium salt in THF and finally exchanging the lithium for a bulkier cation. However, trace impurities in the n-butyllithium and the conditions necessary to remove lithium halides from the product combined to keep yields very low in all but the Ti and Nb cases. It is noteworthy that the Ti and Nb complexes are more robust than the corresponding Zr, Hf, and Ta complexes. However, sodium cyclopentadienide was found to be a convenient reagent for preparation of sodium salts of the dithiols under totally anhydrous conditions. Also, the sodium ion may be more readily exchanged than the li-

thium ion due to its lower solubility in the solvents that can be utilized to effect the exchange reaction. Method III utilizes this improvement according to the following equation; the desired complexes could then be isolated in good yields as their tetraalkylammonium or tetraphenylarsonium salts by exchange in CH_3CN.

$$M(NR_2)_x + (6-x)NaHS_2C_6H_3CH_3 + (x-3)(HS)_2C_6H_3CH_3 \rightarrow$$
$$Na_{6-x}M(S_2C_6H_3CH_3)_3$$
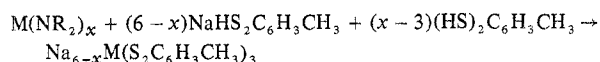
$$M = Ti, Zr, \text{ and } Hf, x = 4; M = Nb, Ta, x = 5$$

The exclusion of water throughout the synthesis is important as is the strict adherence to the stoichiometry of the reaction. Also, the cation exchange should be begun in THF since this seems to add to the stability of the complexes. It was observed that solutions of the complexes are sensitive to moisture in the air and at least one solid compound, Hf, was observed to show significant amounts of decomposition after many weeks of air exposure. The 1:1 electrolytes generally have good solubility in CH_2Cl_2 and modest solubility in CH_3CN. The Ta complexes decompose in DMSO and reactions have also been observed between the Hf and Zr complexes and CH_2Cl_2. Generally, however, the 2:1 electrolytes are well behaved in CH_3CN or DMSO.

Infrared spectra were recorded in the range of 4000 to 250 cm^{-1} and are shown in Table VI.[23] The spectra show strong similarities to the previously reported 2:1 complexes.[24]

Conductivity measurements are shown in Table I, and, although slightly low, are consistent with the expected values.[25]

Visible and ultraviolet spectral maxima are also shown in Table I. The most important feature here is the presence of an intense, low energy absorption in the Ti and Nb cases. This low energy absorption undergoes a shift to higher energy in the following manner: Ti < Zr $\sim$ Hf, Nb < Ta, Mo < Nb < Zr, and W < Ta < Hf.

The ^1H nmr spectra of several complexes were recorded and chemical shifts are given in Table III. These spectra show no important differences from their main group congeners; however, they do further establish the composition of the complexes and the sharpness of the resonances indicates diamagnetism for these compounds. Particularly interesting is the sharp singlet for the methyl groups on the ligands. Considering the near octahedral structure found for the zirconium benzenedithiol complex,[26] the ligand methyl groups in a toluene-3,4-dithiol complex would display a singlet only if the molecule is undergoing rapid rearrangement, or if the chemical shift differences between various possible isomers are small, or if the isomer with all methyl groups cis is the only one present. In an effort to resolve this question a ^{13}C nmr in DMSO was run on $[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]$. However, the methyl group carbons displayed a sharp singlet and the question is left unanswered.

Polarographic measurements were made in CH_3CN and

Table III. ^{1}H Nmr^a and ^{13}C Nmr^b Spectral Results^c

	Solvent	NCH$_3$	NCH$_2$	CH$_3$	Aromatic	d
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]$	d_6-DMSO	1.04 (24 H, tt)	3.10 (16 H, q)	2.11 (9 H, s)	6.3–7.0 (9 H, m)	
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_4)_3]$	CD CN	1.05 (24 H, tt)	3.06 (16 H, q)		6.90 (12 H, m)	
$[(C_2H_5)_4N]_2[Nb(S_2C_6H_3CH_3)_3]$	d_6-DMSO	1.08 (24 H, tt)	3.10 (16 H, q)	2.11 (9 H, s)	6.3–6.9 (9 H, m)	
$[(C_2H_5)_2NH_2]_2[Ti(S_2C_6H_3CH_3)_3]$	CD$_3$CN^d	1.03	3.82	2.13	6.4–7.0	3.6*
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]^a$	DMSO	6.9	51.4	20.2	122.0, 128.3, 129.2, 146.8, 150.1	

^{a} Ppm downfield from internal TMS. ^{b} Ppm downfield from TMS as a secondary standard, with DMSO as primary standard using the shift of DMSO relative to TMS as 40.4 ppm. Recorded at 306°K with proton decoupling. ^{c} Key: s = singlet, q = quartet, m = complex multiplet, t = triplet, tt = triplet of triplets. ^{d} Intensities are unreliable due to limited solubility of the compound in CD$_3$CN, they are, however, in the approximate ratios expected for the formulation shown. The superious peak, marked by an asterisk, is presumably a solvent impurity.

Table IV. Half-Wave Potentials for Reduction (Volts)

	CH$_3$CN^b	CH$_2$Cl$_2$^{c}
$[(C_2H_5)_4N]_2[Ti(S_2C_6H_4)_3]$	−1.71	a
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]$	−1.71	a
$[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]^d$	a	−0.38^d
$[(C_6H_5)_4As][Ta(S_2C_6H_4)_3]^d$		−0.71^d
Mo(S$_2$C$_6$H$_4$)$_3$^{e}		0.366^e
		−0.232^d
$[(C_6H_5)_4As][Sb(S_2C_6H_4)_3]$		a

^{a} No redox behavior observed. ^{b} Potentials are relative to a Ag|0.1 M AgClO$_4$, 0.1 M (n-C$_3$H$_7$)$_4$NClO$_4$ reference electrode. ^{c} Potentials are relative to a Ag|0.42 M (n-C$_4$H$_9$)$_4$NPF$_6$, 0.05 M (n-C$_4$H$_9$)$_4$NI, saturated AgI reference electrode. ^{d} Corresponds to M(S$_2$C$_6$H$_4$)$_3$$^-$ + e$^-$ → M(S$_2$C$_6$H$_4$)$_3$$^{2-}$. ^{e} Corresponds to Mo(S$_2$-C$_6$H$_4$)$_3$^{0} + e$^-$ → M(S$_2$C$_6$H$_4$)$_3$$^-$.

CH$_2$Cl$_2$ and are given in Table IV. In CH$_3$CN, highly irreversible[27] reductions for which the number of electrons could not be determined were observed for Ti and Zr and in all other cases neither oxidation nor reduction was observed. In CH$_2$Cl$_2$ improved behavior was noted, but even in this case all waves were slightly irreversible. However, the diffusion currents observed for the two reductions of the Mo complex were used as a guide to assign the reductions of Ta and Nb to one-electron reductions, since in the former case one-electron reductions have been shown to occur at voltages consistent with those observed here.[21] In all of our studies, no oxidation waves were observed.

Discussion

The extensive research that dithiolene complexes have generated can be traced to the recognition of two unique properties that the complexes possess: facile one-electron-transfer reactions and, in the case of tris complexes, the stabilization of trigonal prismatic coordination geometry.

Our polarographic results show that the electron transfer properties of the early transition metal benzenedithiolates are more limited than in previously studied compounds.[2] A reasonable explanation for this can be obtained from considerations of the electronic properties of the ligand system and the position of these elements in the transition metal series. As will be shown below, in most of our compounds the ligand system can most conveniently be described as being close to the dithiolate, C$_6$H$_4$S$_2$$^{2-}$, limit. Consequently, they will impart high formal oxidation states[28] to the transition metal and, not unexpectedly, the oxidation process in these complexes is not energetically favorable.[29] During reduction we are producing early transition metals in low oxidation states, which is contrary to their generally accepted chemical behavior.[31] It is interesting to note, in this regard, that the relatively well behaved Nb and Ta complexes contain those early transition metals for which numerous complexes in the 4+ oxidation state have recently been isolated.[32] Due to the limited information gained from polarographic studies, we have concentrated much of our efforts toward the elucidation of the structural features of our complexes.

One structural tool that has been used successfully in previous studies is infrared spectroscopy. Schrauzer[33] has shown that the highly delocalized square planar and trigonal prismatic complexes with substituted ethylenedithiol ligands display three strong absorptions at about 1400, 1110, and 860 cm^{-1} corresponding to $\nu_{C=C}$ for the first band and primarily $\nu_{C=S}$ for the latter two. In going from the dithioketone to the dithiolate resonance extreme, the first band increases in energy while the latter two decrease in energy. Unfortunately, strong coupling of vibrations within the benzene system for benzene-1,2-dithiol and toluene-3,4-dithiol complicates this simple picture. Instead, ir spectra of compounds with these ligands display large numbers of bands which undergo only small shifts as the metal atom is changed. Thus, ir spectroscopy has not been of much help in determining structures for benzenedithiol complexes.

Much more meaningful conclusions have been obtained by the study of uv and visible spectra. Both Gray[21] and Schrauzer[33] have pointed out that an intense absorption in the visible region of the spectrum is an indication of highly delocalized bonding and consequently trigonal prismatic geometry. Molecular orbital calculations by these two authors have led them to assign this low energy transition to an essentially ligand (π_v) → metal (d$_{x^2-y^2}$, d$_{xy}$) and a ligand (π) → ligand (π*) transition, respectively. Notably, the latter assignment by Schrauzer suggests that this transition will show little dependence upon the metal, and indeed studies by Schrauzer and Mayweg show that, in the case of substituted ethylenedithiol complexes, shifts of this low energy band with a change in the metal are slight. In contrast to this, the assignment of Gray predicts that an increase in metal d-orbital energy will cause a hypsochromic shift of this band. We wish to point out that, in the case of benzene-1,2-dithiol and toluene-3,4-dithiol complexes, the position of this low energy transition undergoes marked changes with a change in the central metal atom and thus we find it most appropriate to interpret our results according to the assignment of Gray.[34] Particularly important is the isoelectronic series Mo(S$_2$C$_6$H$_4$)$_3$, Nb(S$_2$C$_6$H$_4$)$_3$$^-$, and Zr(S$_2C_6H_4$)$_3$$^{2-}$, where increasing d-orbital energies are accompanied by not only a hypsochromic shift of the lowest energy transition, Table I, but also a change in geometry from trigonal prismatic to nearly octahedral.[26] However, as was pointed out earlier, a number of factors such as increasing overall charge, increasing ionic radius, as well as the change in d-orbital energies could contribute to the observed structural changes. For this reason, the possibility offered by our study to compare the series of compounds Nb(S$_2$C$_6$H$_4$)$_3$$^-$, Ta(S$_2C_6H_4$)$_3$$^-$, and Sb(S$_2C_6H_4$)$_3$$^-$ is of importance. Examination of the electronic spectra of these three compounds suggests increasing distortion toward octahedral geometry in the order: Nb < Ta < Sb. However, any structural changes which occur in this series may be attributed to changes in energy of d orbitals capable of overlapping with the appropriate ligand orbitals and not to other factors; *i.e.,* the overall charge in the series remains constant and the size of the central metal is being kept essentially the same. Thus, it is extremely interesting to note that the Nb complex is trigonal prismatic[26] while the Ta complex is severely dis-

Table V. Metal–Sulfur Stretching Frequencies (cm^{-1})^{b,c}

$[(C_2H_5)_2NH_2]_2[Ti(S_2C_6H_3CH_3)_3]$	393 w sh, 382 m, 356 s, 336 w sh
$[(C_2H_5)_4N]_2[Ti(S_2C_6H_3CH_3)_3]$	392 w sh, 382 m, 354 s, 336 w sh
$[(C_2H_5)_4N]_2[Ti(S_2C_6H_4)_3]$	392 m sh, 388 s, 343 s
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]$	379 w, 321 s
$[(C_2H_5)_4N]_2[Zr(S_2C_6H_4)_3]$	378 w sh, 370 w, 319 vs, 304 sh
$[(C_2H_5)_4N]_2[Hf(S_2C_6H_3CH_3)_3]$	377 vw, 311 s
$[(C_2H_5)_4N][Ta(S_2C_6H_3CH_3)_3]$	392 w, 339 s
$[(C_6H_5)_4As][Ta(S_2C_6H_4)_3]$	391 m, 370–320 s^a
$[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$	399 m sh, 360 s, 340 sh^a
$[(C_4H_9)_4N][Nb(S_2C_6H_3CH_3)_3]$	398 w, 364 m, 336 sh
$[(C_6H_5)_4As][Sb(S_2C_6H_4)_3]$	340 s^a

^{a} This region obscured by $[(C_6H_5)_4As]^+$. ^{b} Key: w = weak; m = medium; s = strong; v = very; sh = shoulder. ^{c} Spectra as KBr pellets.

torted;[36] further the powder diffraction pattern for the Sb complex is different from both Nb and Ta, thereby indicating a different structure for this complex than exhibited by Nb and Ta. The pitfalls of utilizing electronic spectra as structural probe are illustrated by $Ti(S_2C_6H_3CH_3)_3{}^{2-}$. Whereas the observation of a low energy high intensity band, similar to the one found in the corresponding Nb complex, would indicate a geometry close to a trigonal prism, the actual structure is octahedral.[37] It appears then that the diagnostic value of the electronic spectra is only valid for complexes containing closely related transition metal ions (*i.e.*, second and third row metals) and that extension to the first period is a hazardous business at best. Furthermore, whether our arguments about matching ligand and metal d-orbital energies can be extended to other transition metal dithiolenes will have to await the test of time. It is conceivable that the early transition metals, with few d electrons, are more sensitive to changes in orbital energies of the metal and ligands and will respond with more drastic changes in electronic structure and geometry than the corresponding Mo, W, and Re dithiols. Obviously, further systematic synthetic, structural, and theoretical studies are needed to sort out all of the factors involved.

A further word about our polarographic results is warranted at this time. For a LUMO of substantial metal character, as suggested by Gray,[21] the first reduction potential of our complexes should shift to more negative potentials with increasing metal d-orbital energies. Both our data and that of Gray, *et al.*,[21] verifies the expected trend; *i.e.*, potentials become more negative in the order Mo < Nb < Ta. An exception to this statement seems to occur with $Ti(S_2C_6H_4)_3{}^{2-}$. However, the highly irreversible nature of this reduction wave prevents one from making any definite statements. Indeed, this wave may represent a two-electron reduction, and thus would be consistent with the statement above.

Table V shows a tentative assignment of metal–sulfur stretching frequencies. Within the group of complexes studied here, there appears to be a shift of all bands to lower energy with increased deviation from trigonal prismatic geometry, and in particular a strong band in the region of 340–310 cm^{-1} is found for complexes known to be significantly distorted. That is, there is a change from a few weak bands in the trigonal prismatic compounds to a situation where one band dominates the spectrum in the complexes approaching octahedral symmetry. The number of bands expected for D_{3h} and O_h extremes is 2 and 1, respectively, from symmetry considerations. However, the actual symmetries involved in most of these compounds are much lower and would give rise to a large number of bands. Thus, the number of bands, albeit consistent with the structural features, is not a good structural guide in these complexes. Also, the intensity correlations suggested above may not apply to other ligand systems, but few data are available for comparison.

Finally even though we believe that the variable coordination geometry observed in the reported complexes identifies matching of ligand orbital and metal d-orbital energies and the consequent delocalized bonding as a very important stabilizing force for the prismatic geometry, we can only reiterate comments made by previous workers in this field. We have much work to do before understanding the electronic and structural subtleties of transition metal dithiolenes.

Registry No. $[(C_2H_5)_4N]_2[Ti(S_2C_6H_3CH_3)_3]$, 52843-45-5; $[(C_2H_5)_2NH_2]_2[Ti(S_2C_6H_3CH_3)_3]$, 52843-47-7; $[(C_2H_5)_4N]_2[Zr(S_2C_6H_3CH_3)_3]$, 52843-42-2; $[(C_2H_5)_4N]_2[Zr(S_2C_6H_4)_3]$, 52843-43-3; $[(C_2H_5)_4N]_2[Hf(S_2C_6H_3CH_3)_3]$, 52843-38-6; $[(C_4H_9)_4N][Nb(S_2C_6H_3CH_3)_3]$, 52843-40-0; $[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$, 50589-75-8; $[(C_6H_5)_4As][Ta(S_2C_6H_4)_3]$, 52882-44-7; $[(C_6H_5)_4As][Sb(S_2C_6H_4)_3]$, 52843-36-4; $[(C_2H_5)_4N][Ti(S_2C_6H_4)_3]$, 52882-42-5; $[(C_2H_5)_4N][Ta(S_2C_6H_3CH_3)_3]$, 52843-32-0; ^{13}C, 14762-74-4; $Ti[N(C_2H_5)_2]_4$, 4419-47-0; $Hf[N(C_2H_5)_2]_4$, 19824-55-6.

Supplementary Material Available. A listing of ir maxima for the compounds described in this article will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40307L.

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(17) o–Aminothiophenol, toluene-3,4-dithiol, and benzene-1,2-dithiol may cause severe dermatitis if contacted and should only be used with protective gloves.
(18) This analysis was performed by M-H-W Lab., except for Ti which was determined by ignition to the oxide in this laboratory; unless stated otherwise, all other analyses were by the analytical services of the University of Alberta.
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(28) Even though it is not very constructive to talk about oxidation states in

these highly delocalized covalent compounds, we do so here only for the sake of simplicity. In terms of an MO model we are arguing that the make up of the filled bonding orbitals is mainly ligand in character. Therefore, in the resulting complexes the effective charge on the metal is high.

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(34) A recent photoelectron study by Finster, *et al.,*[35] of $Mo[S_2C_2(CN)_2]_3{}^{2-}$, $Mo[S_2C_6H_2(CH_3)_2]_3$, and $Mo(S_2C_2H_2)_3$ seemingly favors Schrauzer's MO scheme by concluding that the electrons added in forming the reduced $Mo(mnt)_3{}^{2-}$ complex go into primarily ligand orbitals and specifically onto the sulfurs, thus breaking down the interligand S–S

bonding found in neutral trigonal prismatic complexes and leading to octahedral geometry for the 2– and 3– complexes. We wish to point out that Gray's[21] scheme can equally well accommodate the experimental results. The maleonitrile dithiolate ligand, as a result of its stable orbitals, will render the 4e' MO more ligand in character and as a result addition of two electrons into the 3a' MO, which is mainly metal in character, can still result in a higher effective charge on Mo in keeping with the PE result. The change in geometry is also readily explained; addition of electrons to the 3a' orbital, which is antibonding with respect to the metal ligand (π_h) overlap, and the increase in ligand character of the 4e' orbital both tend to reduce the delocalized bonding between the metal and dithiol and consequently disfavor the trigonal prismatic geometry. Indeed, it will be shown further in the discussion that we believe this delocalized bonding to be primarily responsible for the stabilization of the trigonal prism.

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Organoactinides and Organolanthanides. XII. Bimetallic Tris(cyclopentadienyl)uranium Derivatives with Uranium–Carbon σ Bonds

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New σ-bonded organouranium complexes of the type Cp₃U–R (Cp = η^5-C₅H₅; R = acetylide, ferrocenyl) and (Cp₃U)₂–R (R = ferrocenyl, *p*-phenyl) have been prepared from Cp₃U–Cl and the respective RLi, RNa, or RLi₂ reagents in THF. The ferrocenyl complexes are the first σ-bonded organoactinide compounds where the R group is an organometallic moiety and the (Cp₃U)₂–R complexes are the only organometallics known to contain two organoactinide moieties bound to the same R group. Infrared and proton nmr spectra support the presence of the R groups as being σ bonded. A mechanism based on large contact effects is used to explain the large isotropic shifts in the nmr spectra. All of the complexes have marked thermal stability and a mass spectrum of the Cp₃U–ferrocene derivative is reported. Magnetic susceptibility studies at various temperatures indicate enhanced spin–spin interactions present in the (Cp₃U)₂–R complexes which are absent in their Cp₃U–R analogs. Other differences between the Cp³U–R complexes and their "dimeric" analogs are noted.

Within the past few years, the organometallic chemistry of the actinide elements (especially uranium) has received renewed attention.[3] Emphasis has been on covalent bonding and the role of the 5f electrons in bonding. Streitwieser, *et al.,*[4] have presented evidence for a covalent π bond involving the 5f electrons in "uranocene," $(C_8H_8)_2U$. However, it has only been relatively recently that compounds containing σ-bonded ligands have been prepared and studied. These new types of σ-bonded organoactinide complexes are of the type (η^5-C₅H₅)₃U–R[5] and [(η^5-C₅H₅)₃U]₂-R,[6] where R is an alkynyl, aryl, alkyl, or organometallic ligand. It is becoming clear that these σ-bonded organoactinide compounds will become a wide and varied area of research, especially with regard to covalency[7,8] and 5f electron involvement in the bonding. With respect to our continuing research in this new area, we wish to report the preparation and properties of several new σ-bonded derivatives.

Experimental Section

All reactions and operations were performed using Schlenk techniques or in an inert-atmosphere drybox using dried oxygen-free argon or helium. Tetrahydrofuran (THF) was dried and freed of oxygen by distilling under argon from blue sodium–benzophenone. Other solvents were degassed prior to use and distilled under argon from finely divided lithium aluminum hydride. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Melting points were determined in sealed argon-filled capillaries and are uncorrected.

Tris(η^5-cyclopentadienyl)(acetylenyl)uranium. Into a centrifuge Schlenk tube were placed 2.35 g (5.0 mmol) of (η^5-C₅H₅)₃U–Cl[9] and 0.26 g (5.4 mmol) of ethynylsodium.[10] Approximately 80 ml of THF was transferred into the tube and the resulting suspension was allowed to stir overnight at room temperature. During this time, the solution changed from dark red-brown to dark green-brown. After centri-

fugation, the solution was transferred into a large Schlenk tube and the THF was removed by distillation *in vacuo* leaving a dark green-brown solid; yield ~95%. One gram of this material was continuously extracted with 50 ml of pentane for 10 hr, leaving a dark red-brown residue on the frit. The resulting pentane suspension was centrifuged and the bright yellow-green product was washed once with 25 ml of pentane and dried *in vacuo* at room temperature to yield 0.78 g of (η^5-C₅H₅)₃UC≡CH. *Anal.* Calcd for C₁₇H₁₆U: C, 44.55; H, 3.52; U, 51.98. Found: C, 43.99; H, 3.65; U, 51.93.

Tris(η^5-cyclopentadienyl)(ferrocenyl)uranium. Into a centrifuge Schlenk tube were placed 0.87 g (4.5 mmol) of ferrocenyllithium[11] and 2.10 g (4.5 mmol) of (η^5-C₅H₅)₃U–Cl. Approximately 60 ml of THF was cooled to –78° and transferred onto the solids. After stirring at –78° for 1 hr, all of the insoluble material had dissolved and the solution, intensely red, was allowed to warm gradually to room temperature and to stir overnight. The THF was removed *in vacuo* and the brown solid dried as before. The solid was then placed in a Schlenk–Soxhlet extractor equipped with a frit and continuously extracted with hexane for 18 hr. At this time, the extraction being complete, the solution was centrifuged and the hexane transferred away leaving a brown solid which was washed with hexane and dried leaving 2.1 g (75%) of (η^5-C₅H₅)₃U–(C₅H₄)Fe(C₅H₅). *Anal.* Calcd for C₂₅H₂₄FeU: C, 48.56; H, 3.90; Fe, 9.03; U, 38.49. Found: C, 47.56; H, 5.21; Fe, 8.62; U, 38.13.

1,1'-Bis[tris(η^5-cyclopentadienyl)uranium]ferrocene. Into a centrifuge Schlenk tube were weighed 1.95 g (4.16 mmol) of (η^5-C₅H₅)₃U–Cl and 0.66 g (2.10 mmol) of (η^5-C₅H₄Li)₂Fe·C₆H₁₆N₂.[12] Approximately 60 ml of THF, cooled to –78°, was transferred onto the solids and the resulting suspension was allowed to stir with gradual warming. At –50°, all of the solid had dissolved and the solution was then warmed to between –20 and –30°. Stirring was maintained for 4 hr during which time a voluminous green precipitate appeared in solution. At this point the tube was warmed to room temperature and centrifuged, and the THF was transferred off. The green solid was washed three times with 20-ml portions of THF and then dried *in vacuo.* It was further purified by continuous extraction with THF