1305 (s), 1285, 1265, 1015 (m), 990 (vs), 950 (s), 815 (vs, br), 740 (m), 680 cm^{-1}.

NMR (^1H, ^{13}C) details are recorded in Table I.

Preparation of $Cp_2Zr(CHPMe_3)Cl$ (9). A solution of **8** (0.2 g, 0.58 mmol) in toluene (35 mL) was heated (65–70 °C) in a sealed tube under nitrogen. The initially colorless solution rapidly turned dark yellow and remained homogeneous. After 14 h, the rearrangement to **9**, the sole product, was complete (by ^1H NMR). The mixture was cooled to room temperature, filtered, reduced to a small volume, and refrigerated (−30 °C). Small yellow plates of **9** were filtered off, washed with hexane, and stored under nitrogen. An analysis sample was obtained by recrystallization from toluene.

Anal. Calcd for $C_{14}H_{20}ClPZr$: C, 48.60; H, 5.83; Cl, 10.25. Found: C, 48.46; H, 5.86; Cl, 10.39.

IR (KBr): 3080, 2975 (m), 2905, 1440 (m), 1420 (m), 1370, 1340, 1305 (s), 1285, 1265, 1015 (m), 990 (vs), 950 (s), 815 (vs, br), 740 (m), 680 cm^{-1}.

NMR (^1H, ^{13}C, ^{31}P) details are recorded in Table I.

Reaction of $Cp_2Zr(CHPMe_3)Cl$ (9) with *tert*-Butyl Alcohol. A solution of **9** (60 mg, 0.19 mmol) in toluene (12 mL) was sealed under nitrogen in a small tube (total volume 25 mL), fitted with a stopcock, side arm, and serum cap. *tert*-Butyl alcohol (29.6 mg, 0.4 mmol, 2.1 equiv) was added via a syringe. A white compound precipitated immediately from the yellow solution, which was stirred for 1 h at room temperature. The atmosphere in the reaction vessel was sampled by using an argon-flushed 0.25-mL gastight syringe. No hydrogen was detected by GC (Porapak QS, 20 ft × 0.125 in., 30 °C, nitrogen internal standard). The reaction mixture was filtered, and the white precipitate was washed with hexane. It was identified [^1H NMR (D_2O) δ 1.85 (d, PMe, $^2J_{PH} = 14.8$ Hz); mp >300 °C] as tetramethylphosphonium chloride.[28] The filtrate was pumped down to give a cream solid, which was identified [^1H NMR comparison with an authentic sample prepared by reaction of Cp_2ZrCl_2 with sodium *tert*-butoxide (2 equiv) in diethyl ether: ^1H NMR (benzene-d_6) δ 6.01 (s, 10, Cp), 1.13 (s, 18, Me)] as $Cp_2Zr(O(t\text{-}Bu))_2$ (98% yield by ^1H NMR). A minor reaction product [^1H NMR (benzene-d_6) δ 1.23 (s), 1.04 (s)] was not identified.

Reaction of 7 with Ketones. The concentration of a solution of **7** in benzene-d_6 was determined (^1H NMR, DME internal standard) as 38 mM.

(a) Cyclohexanone. Cyclohexanone (12 μL, 0.11 mmol) was added to 1 mL of this solution (0.038 mmol of **7**) with stirring. The color rapidly changed from dark brown-green to yellow, and an oily solid precipitated. After 30 min, the reaction was complete (by ^1H NMR). Methylenecyclohexane (GC identification, Carbowax 20 M, 20 ft × 0.25 in., 50 °C) was formed in 85% yield together wiith trimethylphosphine oxide (50%). Traces of cyclohexanone and some cyclohexanol were present in the hydrolysate of the reaction mixture (GC analysis, DEGS, 8 ft × 0.25 in., 110 °C).

(b) Acetone. In a similar manner reaction of **9** with excess acetone gave trimethylphosphine oxide (70%) and 2-methylpropene (75% by ^1H NMR), which was identified by GC/MS (Porapak Q, 6 ft × 0.125 in., 140 °C). A white precipitate was not identified.

Reaction of 8 with Cyclohexanone. Cyclohexanone (10 μL, 0.1 mmol) was added to a colorless solution of **8** (0.034 mmol) in toluene-d_8 (1 mL). The mixture darkened to yellow (5 min), then lightened, and precipitated a solid (not identified). After 3 h, methylenecyclohexane (GC identification, Carbowax 20 M, 20 ft × 0.25 in., 50 °C) was present in 76% yield (^1H NMR).

Acknowledgment. The authors acknowledge generous support for this work by the National Science Foundation (Grant CHE 79-00996). K.I.G. also acknowledges support from a University Travelling Scholarship from the Australian National University.

Registry No. **6a**, 69058-71-5; **6b**, 67660-04-2; **7**, 74592-17-9; **8**, 74592-18-0; **9**, 74592-19-1; $Cp_2Zr(dmpe)$, 71844-74-1; $Cp_2Zr(O(t\text{-}Bu))_2$, 74592-20-4; Me_3PCH_2, 14580-91-7; cyclohexanone, 108-94-1; acetone, 67-64-1; methylenecyclohexane, 1192-37-6; trimethylphosphine oxide, 676-96-0; 2-methylpropene, 115-11-7.

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Reactions of the Vanadyl Group: Synthesis of $V{=}S^{2+}$ and VBr_2^{2+} from $V{=}O^{2+}$ Complexes

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The vanadyl ion–Schiff base complexes V=O(salen) and V=O(acen) react with B_2S_3 to afford V=S(salen) and V=S(acen), the first known thiovanadyl compounds. The V=S stretching vibration appears in the 550-cm^{-1} region, and its stretching force constant is substantially less than $k_{V=O}$ in the corresponding vanadyl complexes. The thiovanadyl compounds are relatively stable to air in the solid state, but their solutions are hydrolyzed to the starting vanadyl species. ESR spectra of the thiovanadyl complexes are characteristic of monomeric, axially symmetric V(IV) and show much less **g** tensor anisotropy than their vanadyl analogues; the decrease is primarily located in $g_\perp$. These data are consistent with reduced charge at the vanadium in the $V{=}S^{2+}$ species and more covalent character of the V=S bond than in V=O. V=O(salen) reacts with Ph_3PBr_2 to afford the deoxygenated product VBr_2(salen) and $Ph_3P{=}O$, while other vanadyl complexes afford $V{=}OBr_2(Ph_3P{=}O)_2$.

Introduction

The vanadyl ion, $V{=}O^{2+}$, is ubiquitous in vanadium chemistry. The deep blue or green color of its complexes is well-known to all those who have studied the chemistry of this element, and $V{=}O^{2+}$ has been described as "perhaps the most stable diatomic cation known."[1] Numerous complexes of V(IV) have been prepared and studied, but in almost every instance the $V{=}O^{2+}$ group was present. Italian workers have shown, however, that certain vanadyl complexes $V{=}OL_n$ react with $SOCl_2$ to form SO_2 and VCl_2L_n.[2] We have discovered a synthetic route to the previously unknown thiovanadyl species, $V{=}SL_n$, which involves reaction of $V{=}OL_n$ complexes with B_2S_3, and report the details of the preparation and characterization here. A preliminary account of this work has already appeared.[3] We have also studied the reactions of

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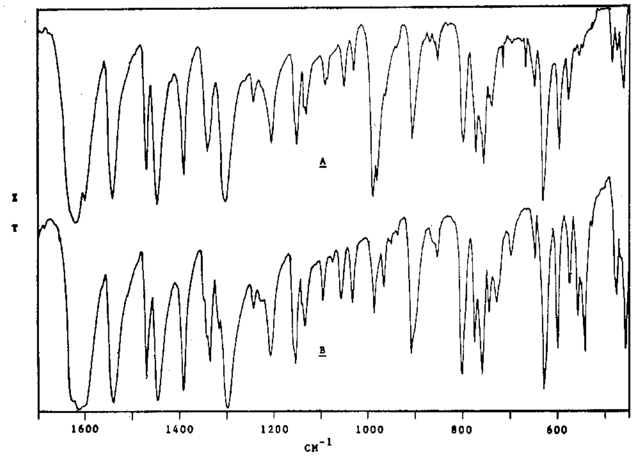

Figure 1. Infrared spectra (1700–450 cm^{-1}) of (A) V═O(salen) and (B) V═S(salen) (Nujol mulls).

vanadyl complexes with Ph_3PBr_2; V═O(salen)[4] afforded the brominated, deoxygenated product VBr_2(salen) while other V═OL_n species gave V═$OBr_2(O{=}PPh_3)_2$.

Results and Discussion

I. Reaction of Vanadyl Complexes with B_2S_3. A. Synthesis and Properties. Our search for a synthetic route to thiovanadyl complexes first centered on two common reagents which might effect the V═O to V═S transformation: H_2S and P_4S_{10}. The former is used to convert MO_4^{n-} to MS_4^{n-} (M = Re, n = 1; M = Mo or W, n = 2; M = V, n = 3),[5] and the latter reacts with certain acyloins to give thiophosphates, useful intermediates in the synthesis of metal 1,2-dithiolate complexes.[6] Use of these reagents in a variety of conditions only led to intractable and highly malodorous mixtures of products. It appeared that these reactants attacked the vanadyl complexes at several sites rather than showing the desired selectivity for the V═O bond.

In contrast, reaction of V═OL_n complexes with excess B_2S_3 under carefully controlled conditions led to one major product, V═SL_n, with no indication of attack on the coordinated ligands. Previous work has shown B_2S_3 to be a useful reagent for the conversion of ketones to thioketones[7,8] under mild conditions. The lack of side reactions with B_2S_3 may be due to the low acidity of its oxygenated form (B_2O_3, if the reaction goes to completion).

With careful exclusion of oxygen and water, a 1.5:1 mole ratio of B_2S_3 and V═O(salen) was mixed in CH_2Cl_2 to afford V═S(salen) in 40–60% yield (depending on reaction time and temperature). There appeared to be a rapid initial reaction, forming a dark brown suspension, which upon filtration and evaporation gave a copper-colored solid composed of starting material, product, and other unidentified species. Continued reaction led to higher product yield and purity (as judged by the decrease, to absence, of ν(V═O)).

The large, deep magenta flakes of V═S(salen) obtained were recrystallized from CH_2Cl_2–hexane and gave the expected analytical data (see the Experimental Section). V═S(salen) was found to be inert to atmospheric oxidation or hydrolysis in its solid state at room temperature, showing no color change on exposure to air for several months, although it exudes an odor of H_2S and infrared analysis shows the presence of V═O groups after such treatment. In sharp contrast, a 10^{-2} M solution of this complex in dry degassed CH_2Cl_2 changed color from magenta to green after 0.5-min swirling in air, forming V═O(salen), quantitatively, with the liberation of H_2S.

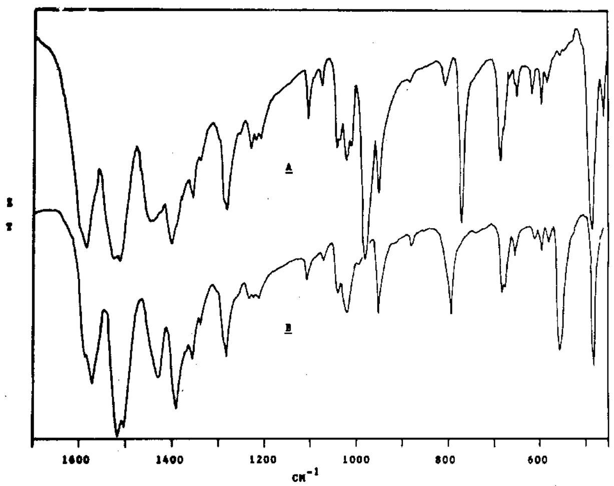

Figure 2. Infrared spectra (1700–450 cm^{-1}) of (A) V═O(acen) and (B) V═S(salen) (Nujol mulls).

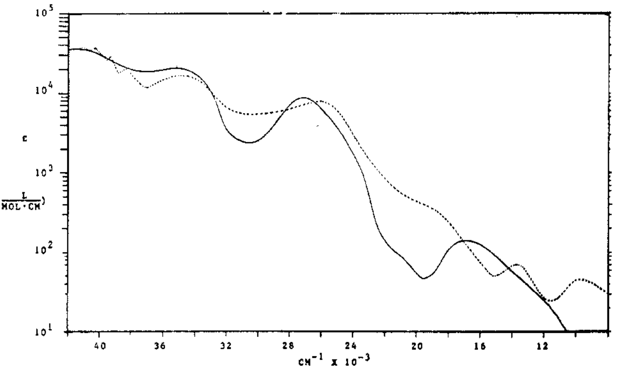

Figure 3. UV–visible spectra of V═O(salen), —, and V═S(salen), --- (CH_2Cl_2 solution, 26 °C).

Table I. Electronic Spectra of Vanadyl, Thiovanadyl, and VX_2L_n Complexes[a]

compd	λ_{max} (ϵ)
V═O(salen)	593 (143), 472 sh (93), 367 (8.8×10^3), 286 (1.8×10^4)
V═S(salen)	1033 (45), 730 (71), 513 sh (393), 382 (7.7×10^3), 286 (1.6×10^4), 261 (2×10^4), 254 (2.9×10^4), 248 (3.6×10^4), 243 (3.7×10^4)
V═O(acen)	617 (68), 555 (70), 430 sh (93), 347 sh (5.4×10^3), 319 (2.0×10^4), 237 (6.9×10^3)
V═S(acen)	978 (50), 675 (28), 496 sh (4.9×10^2), 352 sh (9.5×10^3), 320 (1.3×10^4), 253 (1.6×10^4)
VBr_2(salen)	638 (2.5×10^3), 365 sh (5.5×10^3), 288 sh (1.7×10^4), 286 sh (1.7×10^4), 251 (2.9×10^4)
VCl_2(salen)	611 (2.5×10^3), 390 sh (3.7×10^3), 371 sh (4.1×10^3), 348 sh (4.8×10^3), 312 sh (1.2×10^4), 288 sh (1.5×10^4), 250 (2.7×10^4)
V═$OBr_2(O{=}PPh_3)_2$	714 (33), 467 sh (6.7), 409 (12.9)
V═$OCl_2(O{=}PPh_3)_2$	725 (34), 401 (8.8)

[a] λ_{max} in nm; ϵ in L mol^{-1} cm^{-1}; CH_2Cl_2 solutions, 26 °C.

V═O(acen) was also found to react cleanly with B_2S_3 to afford a new compound formulated as V═S(acen). The reaction proceeded similarly to that of V═O(salen), requiring ca. 24 h for completion, and the isolated product had a color similar to that of V═S(salen). Elemental analysis and other

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(4) H_2(salen) is the 2:1 Schiff base of salicylaldehyde and ethylenediamine, while H_2acen is the analogue from acetylacetone.

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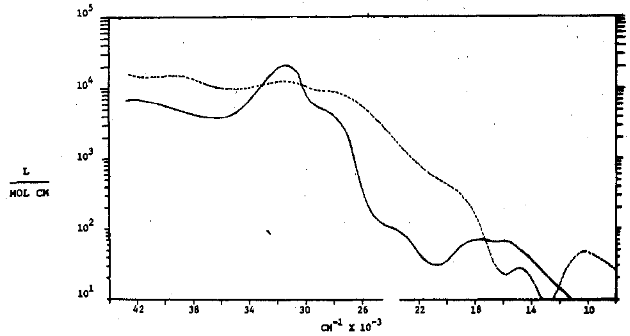

Figure 4. UV–visible spectra of V=O(acen), —, and V=S(acen), --- (CH_2Cl_2 solution, 26 °C).

Table II. Infrared Bands of $[Z{=}MY_3]^{2-}$ Ions

	ν(M=Z), cm^{-1}		
$[Z{=}MY_3]^{2-}$	obsd	calcd[a]	ref
$[O{=}MoSe_3]^{2-}$	858		11
$[S{=}MoSe_3]^{2-}$	471	644	5
$[O{=}WSe_3]^{2-}$	878		11
$[S{=}WSe_3]^{2-}$	468	641	12

[a] Calculated on the basis of mass change; force constants for M=O and M=S bonds assumed to be identical. See text.

data (vide infra) agree with this composition. V=S(acen) could be recrystallized from CH_2Cl_2, forming deep magenta rhombohedra. The crystals are unreactive to water or atmospheric oxygen at room temperature over several months' time, and in contrast to V=S(salen) its solutions in organic solvents are decomposed to V=O(acen) only after several hours' exposure to the atmosphere.

The infrared spectrum (Figure 1) of V=S(salen) lacked the V=O stretching vibrations of the starting material at 989 and 982 cm^{-1}, but absorptions characteristic of the chelated ligand remained. New absorptions were observed at 730 (m) and 543 (m–s) cm^{-1}. The intense V=O stretch of V=O(acen) is similarly absent in the infrared spectrum of V=S(acen) (Figure 2), and the only major new band appears at 556 cm^{-1}. These low-energy bands at ca. 550 cm^{-1} have been assigned as ν(V=S) (vide infra).

Significant differences in the UV–visible spectra of the vanadyl and thiovanadyl complexes were observed and are consistent with the change in color of the solids ($V{=}O^{2+}$, blue-green; $V{=}S^{2+}$, magenta). Absorptions assigned[9] to d → d transitions in the vanadyl complexes are observed at lower energies in the thio analogues. These spectral data are presented in Figures 3 and 4 and in Table I. Electron spin resonance (ESR) spectra of the vanadyl and thiovanadyl complexes were measured and compared. These results, discussed later in this paper, were in agreement with our formulation of the thiovanadyl compounds as monomeric, structural analogues of their $V{=}O^{2+}$ partners. Further structural confirmation has been obtained from a single-crystal X-ray diffraction study on V=S(acen).[10]

B. Assignment of ν(V=S). The difference in mass between oxygen and sulfur is expected to lead to a V=S stretching frequency lower in energy than ν(V=O). On the assumption that the mass change is the only significant alteration, a 20–30% frequency decrease is predicted, and ν(V=S) would thus appear in the 700-cm^{-1} region.

During the reaction of B_2S_3 with V=O(salen), the infrared bands at 989 and 982 cm^{-1} [assigned as ν(V=O)] decrease in intensity, and new absorptions appear at 730 and 543 cm^{-1}. Similarly, the strong ν(V=O) of V=O(acen) at 980 cm^{-1} disappears as the reaction with B_2S_3 continues, and an intense new band at 556 cm^{-1} grows in. Bands due to the salen^{2-} and acen^{2-} ligands show little change. These observations suggest that $\nu(V{=}S^{2+})$ in the salen and acen complexes occurs in the 540–560-cm^{-1} range, but two major questions still remain to be answered: (a) If ν(V=S) truly is in the 550-cm^{-1} region, why is it so much lower in frequency than predicted by the change in mass from oxygen to sulfur, and (b) what is the 740-cm^{-1} band observed in V=S(salen) but not in V=S(acen)?

Table III. ESR Spectral Parameters of Vanadyl and Thiovanadyl Complexes[a]

	VO(salen)	VS(salen)	VO(acen)	VS(acen)
a_0	−98.76 (9)	−89.7 (4)	−99.1 (2)	−89.6 (2)
$a_\parallel$	−174.6 (3)	−155.9 (3)	−171.9 (4)	−157.5 (6)
$a_\perp$	−63.1 (6)	−60.2 (4)	−63.1 (6)	−55.9 (6)
g_0	1.974	1.964	1.977	1.965
$g_\parallel$	1.957	1.957	1.963	1.961
$g_\perp$	1.982	1.964	1.982	1.969

[a] All *a* values are in gauss; estimated standard deviations in the last figures are given in parentheses.

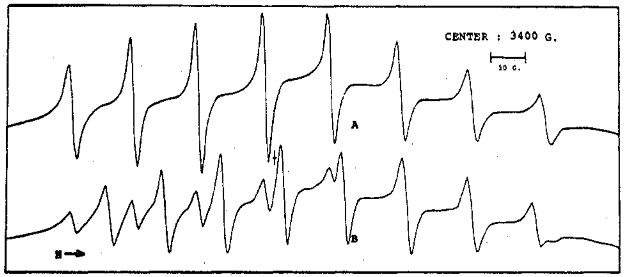

Figure 5. ESR spectra of (A) V=O(salen) and (B) partially hydrolyzed V=S(salen) (CH_2Cl_2 solution, 25 °C).

The fallacy in the reduced-mass calculation is in the assumption of an invariant stretching force constant $k_{V=X}$ as X is varied from O to S. Examination of the infrared data available for other transition-metal species which have multiple bonds to chalcogens (Table II) shows a consistent pattern: ν(M=S) is consistently lower in energy than that calculated from ν(M=O) on the basis of mass change. This indicates that, for early transition metals in high oxidation states, the M=O bonds have substantially higher stretching force constants than their M=S analogues. For example, Müller has calculated the W=O and W=S force constants in $O{=}WSe_3^{2-}$ and $S{=}WSe_3^{2-}$ to be 6.66 and 3.47 mdyn Å^{-1}, respectively.[5,11,12] When such a force constant decrease is included in the calculation along with the mass change, ν(V=S) is predicted to occur at ca. 550 cm^{-1}.

Alternately, it can be surmised that, since the force constant of the V=O bond in V=O(salen) and the W=O bond in $O{=}WSe_3^{2-}$ have similar force constants ($k_{W=O}$ = 6.66, $k_{V=O}$ = 7.00 mdyn Å^{-1}), the thio analogues should have similar properties. Since $k_{W=S}$ in $S{=}WSe_3^{2-}$ is 3.47 mdyn Å^{-1}, ν(V=S) is calculated to appear between 490 and 590 cm^{-1}. The observed asymmetric stretching frequency of VS_4^{3-}, 470 cm^{-1}, is just below this range, but as the isolated V=S bonds of the thiovanadyl complexes discussed here are expected to occur at higher energy than in the delocalized tetrathioanion, the lower limit on an isolated V=S bond should be above 470 cm^{-1}.

It thus appears that ν(V=S) in the new complexes should be assigned to the bands which appear in the 540–560-cm^{-1} region, rather than around 700 cm^{-1}. The 730-cm^{-1} band

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observed in the spectrum of V═S(salen) thus does not arise from the new vanadium–sulfur bond but may correspond to a weak band, observed at 740 $\mathrm{cm^{-1}}$ in the starting material, which shifts slightly in frequency and grows in intensity upon replacement of oxygen by sulfur.

C. ESR Spectra. The isotropic ESR spectral parameters, g_0 and a_0, as well as the principal components of the $\langle \mathbf{g} \rangle$ tensor and the hyperfine interaction tensor $\langle \mathbf{a} \rangle$, for V═S(salen), V═S(acen), and their oxo analogues, are presented in Table III. The isotropic parameters were determined from X-band spectra of 60:40 CH_2Cl_2-toluene solutions of these complexes at 0 °C. The tensor components were calculated from X-band spectra measured on frozen solutions (−160 °C) of the same composition.

The thiovanadyl complexes exhibit eight-line isotropic solution spectra, indicative of a d^1 V(IV) (100%, $I = {}^7/_2$) nucleus. Both of these spectra also contain lines due to small amounts of vanadyl impurities in the thiovanadyl complexes (see Figure 5). The parallel and perpendicular components of the axially symmetric $\langle \mathbf{g} \rangle$ tensor are given by eq 1 and 2,[13] where g_e =

$$g_{\parallel} = g_e - \frac{8\lambda(\beta_1{}^*\beta_2{}^*)^2}{\Delta E(^2B_2 \rightarrow {}^2B_1)} \tag{1}$$

$$g_{\perp} = g_e - \frac{2\lambda(\beta_2{}^*\epsilon_\pi{}^*)^2}{\Delta E(^2B_2 \rightarrow {}^2E)} \tag{2}$$

2.0023, the free-electron g value, λ is the spin–orbit coupling constant, and $\beta_1{}^*$, $\beta_2{}^*$, and $\epsilon_\pi{}^*$ are the coefficients of the vanadium $d_{x^2-y^2}$, d_{xy}, and (d_{xz}, d_{yz}) orbitals.

Inspection of the data reveals that the $\langle \mathbf{g} \rangle$ tensor anisotropy is significantly smaller for the V═S complexes than for the V═O species. The overwhelming difference is accounted for by a decrease in $g_\perp$. According to the equations above, $g_\perp$ should be affected much more than $g_\parallel$ by a change in the ligand field anisotropy, since it is dependent on $\Delta E(^2B_2 \rightarrow {}^2E)$, an in-plane to out-of-plane transition. The band assigned to this transition in the optical spectra of the V═O complexes is red shifted about twice as much as the other bands when the oxygen is exchanged with sulfur (Table I). This is consistent with the observed change in $g_\perp$.

The coefficient of the metal $3d_{xy}$ orbital in the $^2B_2$ molecular orbital (ground-state HOMO), $\beta_2{}^*$, may be calculated by subtracting eq 3 and 4 and solving for $\beta_2{}^*$,[13] where $\Delta g_\parallel = g_e$

$$A_\parallel = -P[(\beta_2{}^*)^2(\kappa + {}^4\!/_7) + \Delta g_\parallel + {}^3\!/_7\Delta g_\perp] \tag{3}$$

$$A_\perp = -P[(\beta_2{}^*)^2(\kappa - {}^2\!/_7) + {}^{11}\!/_{14}\Delta g_\perp] \tag{4}$$

$$A_\parallel - A_\perp = -P[{}^6\!/_7(\beta_2{}^*)^2 + \Delta g_\parallel - {}^5\!/_{14}\Delta g_\perp] \tag{5}$$

$- g_\parallel$, $\Delta g_\perp = g_e - g_\perp$, κ is related to the unpaired spin density at the nucleus, and $P = g\beta g_N\beta_N\langle r^{-3}\rangle$, where r is the radial extension of the 3d orbital. The value of P used in these calculations is proportional to $\langle r^{-3}\rangle$ for the metal 3d orbitals, making it a function of the electronic charge on the metal.

The value of P normally used for vanadyl complexes is 383.7 MHz.[14] This corresponds to an effective charge of +2. When vanadyl complexes are compared, values of $(\beta_2{}^*)^2$ are first calculated (eq 5). With use of these values, along with the observed energies for the electronic transitions $^2B_2 \rightarrow {}^2B_1$ and a spin–orbit coupling constant (λ) of 248 $\mathrm{cm^{-1}}$, $(\epsilon_\pi{}^*)^2$ and $(\beta_1{}^*)^2$ are next calculated from eq 1 and 2. Changes in the values of these coefficients are then interpreted in terms of differences in bonding occurring between the vanadium and the "in-plane" ligands. The bonding within the vanadyl group is assumed to remain relatively unaffected by altering the other ligands.

Table IV. Calculated P Values and Orbital Coefficients

	VO(salen)	VO(acen)	VS(salen)	VS(acen)
P, MHz	348.0	334.1	293.7	313.6
$\epsilon_\pi{}^*$	0.655	0.663	0.749	0.685
$(\beta_1{}^*)^2$	0.386	0.356	0.313	0.308

Table V. Variation of P Values with Charge on Vanadium

P, MHz	charge on V	P, MHz	charge on V
515.6	+4	383.7	+2
449.7	+3	323.8	+1

In the case at hand, the bonding with the "in-plane" ligands is essentially invariant (notice the constancy of $g_\parallel$ values between corresponding vanadyl and thiovanadyl complexes), but the axial ligand field is changing (oxygen is replaced by sulfur). Instead of holding P constant and calculating $(\beta_2{}^*)^2$ for different complexes, we have assumed a constant value for $(\beta_2{}^*)^2$ and have calculated the values of P. The value of P is dependent upon the effective charge on the vanadium (vide supra), and this charge should differ for the vanadyl and thiovanadyl systems, as sulfur is more polarizable and less electronegative than oxygen. The values of P calculated from eq 5, for $(\beta_2{}^*)^2 = 1$, along with values of $(\epsilon_\pi{}^*)^2$ and $(\beta_1{}^*)^2$ calculated from eq 1 and 2, are assembled in Table IV. Values of P corresponding to different electronic charges on vanadium are listed in Table V.[14]

The values of P for the thiovanadyl(IV) complexes are consistently smaller than for their oxo analogues. This indicates that the charge on the vanadium is smaller for the thiovanadyl species (Table V). This is consistent with the theoretical work of Hatfield et al.[15] where they calculate the charge on the vanadium in $VOCl_4{}^{2-}$ and $VSCl_4{}^{2-}$ to be +0.851 and +0.690, respectively. The calculated decrease in P is also consistent with the observed decrease in the isotropic coupling, a_0, when oxygen is replaced by sulfur. Since P is proportional to $\langle r^{-3}\rangle$, a decrease in P implies an increase in the mean radial extension of the vanadium $3d_{xy}$ orbital which contains the unpaired electron. This decreases the overlap of the vanadium $3d_{xy}$ and 2s orbitals. Since it is this overlap which makes a large negative contribution to the isotropic coupling (via a spin polarization mechanism), a decrease in this overlap also decreases a_0.[16] Finally, the V═S bond is expected to have a greater covalent nature than the V═O bond. The lower charge on the vanadium in the thiovanadyl complexes is consistent with this idea.

The ESR parameters obtained for these thiovanadyl complexes are interesting when compared with the values measured for the vanadium species deposited on catalysts during petroleum hydrodesulfurization; the latter are believed to be at least partially responsible for catalyst deactivation. Silbernagel[17] has shown a correlation between the ESR anisotropies of vanadium complexes and their covalent or ionic nature. In plots of $g_\perp - g_\parallel$ vs. $a_\parallel/a_\perp$, he has identified, in a limited number of samples, three regions corresponding to covalent and ionic species and vanadyl supported on silica or alumina. The spent desulfurization catalysts showed ESR anisotropies outside all of these areas, with large values for both parameters.

We have compared the anisotropies of the vanadyl and thiovanadyl complexes discussed in this paper, as well as recent data on V(IV) in acidic and basic media.[13] While V═O$(OH_2)_5{}^{2+}$ fits well in Silbernagel's "ionic complex" area, V═O$(OH)_3{}^-$ [or V═O$(OH)_3(OH_2)_2{}^-$] is somewhat more extreme in $a_\parallel/a_\perp$ than the identified area of "covalent complexes". More interestingly, while the anisotropies we

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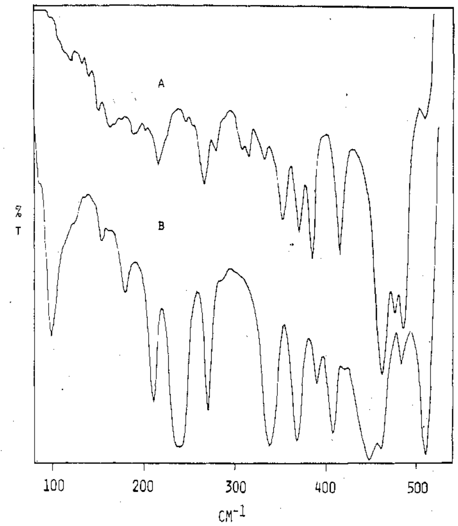

Figure 6. Infrared spectra (540–80 cm^{-1}) of (A) V=O(salen) and (B) VBr_2(salen) (Nujol mulls).

measured for V=O(salen) and V=O(acen) put them in positions close to the covalent–ionic borderline (but low in both $a_{\|}/a_{\perp}$ and $g_{\perp} - g_{\|}$), the thiovanadyl complexes appear well removed from any of the defined regimes, with significantly lower anisotropies. The quite different behavior seen in the $V{=}O^{2+} \rightarrow V{=}S^{2+}$ and fresh → sulfided catalyst transformations suggests that thiovanadyl complexes are poor models for the catalyst poisons. Although the catalyst deactivating agents undoubtedly contain sulfur and vanadium, it is unlikely that they contain isolated $V{=}S^{2+}$ groups.

II. Reactions of Vanadyl Complexes with Ph_3PBr_2. The oxophilic nature of Ph_3PBr_2 has been well established in organic chemistry. This reagent is useful in the conversion of alcohols and phenols into alkyl and aryl bromides,[18] carboxylic acids and anhydrides into acid bromides,[19] and N,N′-disubstituted ureas to carbodiimides.[20] We have studied the reactions of this reagent with vanadyl complexes to see if it can convert $V{=}OL_n$ species to VBr_2L_n and $Ph_3P{=}O$, a reaction similar to that of $SOCl_2$ with $V{=}OL_n$ which affords VCl_2L_n and SO_2.[2] The desired product was formed in one case, V=O(salen) + Ph_3PBr_2 → VBr_2(salen) + $Ph_3P{=}O$, but in other cases examined this reagent was found to react with the coordinated ligands and displace them, forming $V{=}O(Ph_3P{=}O)_2Br_2$.

Addition of solid, powdered V=O(salen) to a solution of Ph_3PBr_2 in CH_3CN and stirring for 24 h afforded VBr_2(salen) in high yield. This black solid is soluble in DMF and Me_2SO at room temperature and in hot CH_3CN and CH_3NO_2 and insoluble in benzene and hexane. It is susceptible to hydrolysis, forming the vanadyl starting material, but can be safely stored in a desiccator.

The infrared spectrum of VBr_2(salen) showed no sign of the V=O stretching vibrations of the starting material (at 989 and 982 cm^{-1}), but a new band, assigned as ν(V–Br), appeared at 241 cm^{-1} (Figure 6). The analogous compound VCl_2(salen) exhibits an infrared absorption at 301 cm^{-1}. A lower energy band in VCl_2(salen) at 135 cm^{-1} correlates well with a VBr_2(salen) band at 98 cm^{-1}. Assignment of these bands to vanadium–halogen stretches must be qualified, for in analogous complexes[21] these bands appear 40–60 cm^{-1} higher in energy. Nevertheless these bands exhibit the expected mass-dependent frequency shifts,[22,23] and they are the major new absorptions which arise in the spectra.

In principle, infrared measurements should be able to discern between cis and trans isomers of MX_2L_4 complexes. The former isomer should have three infrared-active M–X bands, the latter only two. In practice, the three bands of the cis isomers are not always observed.[21,22,24] We suggest a trans structure for VBr_2(salen), based upon the two V–Br stretches identified and the desirable[25] planar coordination of the $salen^{2-}$ ligand. Exceptions to the latter are well established, however.[26–28]

The electronic spectra of V=O(salen), VBr_2(salen), and VCl_2(salen) are presented in Table I. Solid VBr_2(salen) showed a room-temperature magnetic moment of 1.71 μ_B, in agreement with the formulation as a discrete monomer. The ESR spectrum of VBr_2(salen) was a clean eight-line pattern which showed axial symmetry, in agreement with the proposed structure.

In contrast to this result, we find that other vanadyl complexes react with Ph_3PBr_2 in a different way. Vanadyl phthalocyanine and Ph_3PBr_2 showed no sign of reaction at room temperature over several days, but decomposition into unidentifiable products occurred in refluxing benzonitrile (205 °C). The other 4N-donor complex studied, $V{=}O(phen)_2(ClO_4)_2$, showed a similar lack of reaction when treated with Ph_3PBr_2 in refluxing CH_3CN. V=O(acpn), where pn = 1,3-propanediamine, showed a color change from blue to dark blue-green upon treatment with Ph_3PBr_2, but this color faded to light yellow on cooling the reaction mixture to 0 °C for 2 h, and no characterizable products could be isolated.

When the ligands bound to the vanadyl group were entirely oxygen donors, Ph_3PBr_2 attacked these sites in preference to the vanadyl group, and $V{=}OBr_2(O{=}PPh_3)_2$ was isolated in high yields. Numerous color changes occurred during these reactions, suggesting a multistep process, but attempts at isolating intermediates were unsuccessful, the only isolable species being $V{=}OBr_2(O{=}PPh_3)_2$. This result was obtained with $V{=}O(acac)_2$, sterically hindered $V{=}O(dpm)_2$ (dpm = dipivaloylacetonate, $OCC(CMe_3)CHC(CMe_3)CO^{2-}$), $V{=}O(dbm)_2$ (dbm = dibenzoylmethane), and $V{=}O(hfac)_2$ (hfac = hexafluoroacetylacetonate). These results indicate that the course of the reaction is not influenced by steric or electronic effects as much as it is by the nature of the atoms coordinated to the vanadium atom of the vanadyl group.

The product $V{=}OBr_2(O{=}PPh_3)_2$ was soluble in $CHCl_3$ and CH_2Cl_2 and was decomposed by HNO_3 to afford $O{=}PPh_3$ (identified by its infrared spectrum and melting point). It exhibited characteristic infrared bands at 1012 cm^{-1}, assigned as ν(V=O), and at 1139 cm^{-1}, ν(P=O). Analytical data on the products from all three reactions were in close agreement and were consistent with our formulation (see the Experimental Section). A band in the infrared spectrum at 353 cm^{-1} can be assigned as ν(V–Br); ν(V–Cl) in $V{=}OCl_2(O{=}PPh_3)_2$ prepared by reaction of VCl_3 and $O{=}PPh_3$ appears at 387 cm^{-1}.[29]

Solid $V{=}OBr_2(O{=}PPh_3)_2$ exhibited a magnetic moment of 1.82 ± 0.02 μ_B, in good agreement with the expected value for a monomeric V(IV) complex. A solution of this species

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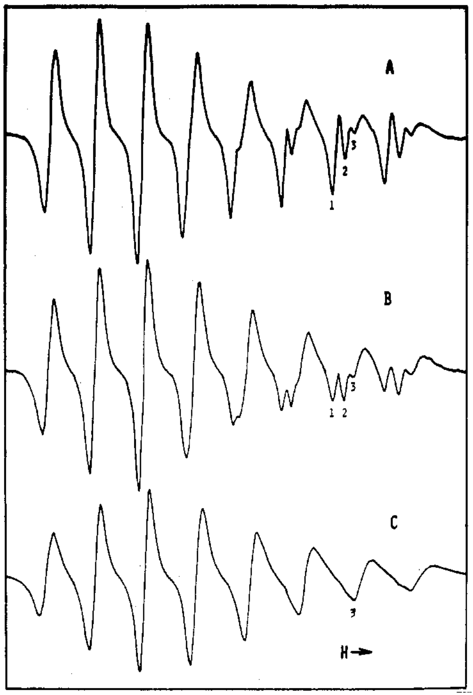

Figure 7. ESR spectra of $V{=}OBr_2(O{=}PPh_3)_2$ solutions in CH_3CN: (A) 5×10^{-3} M complex; (B) 5×10^{-3} M complex plus 1×10^{-2} M $O{=}PPh_3$; (C) 5×10^{-3} M complex plus 0.1 M $O{=}PPh_3$; 1 = $V{=}OBr_2(NCCH_3)_2$; 2 = $V{=}OBr_2(NCCH_3)(O{=}PPh_3)$; 3 = $V{=}OBr_2(O{=}PPh_3)_2$.

in CH_3CN showed a complex ESR spectrum which could be interpreted as three superimposed spectra and which suggested reaction with solvent, as indicated by eq 6 and 7. Confirmation of this interpretation was obtained by recording ESR spectra of $V{=}OBr_2(O{=}PPh_3)_2$ in CH_3CN with increasing amounts of $O{=}PPh_3$ added. Representative spectra are depicted in Figure 7 and show the shift in equilibrium consistent with eq 6 and 7. Spectra measured in CH_2Cl_2, a noncoordinating solvent, showed a single eight-line pattern attributed to $V{=}OBr_2(O{=}PPh_3)_2$.

$$V{=}OBr_2(O{=}PPh_3)_2 + CH_3CN \rightarrow V{=}OBr_2(O{=}PPh_3)(N{\equiv}CCH_3) + O{=}PPh_3 \quad (6)$$

$$V{=}OBr_2(O{=}PPh_3)(N{=}CCH_3) + CH_3CN \rightarrow V{=}OBr_2(N{\equiv}CCH_3)_2 + O{=}PPh_3 \quad (7)$$

Summary

Under the proper conditions the $V{=}O^{2+}$ bond in $V{=}OL_n$ complexes can undergo substitution or replacement reactions, forming $V{=}S^{2+}$ complexes with B_2S_3 or VBr_2^{2+} species with Ph_3PBr_2. The latter reaction more often leads to $V{=}OBr_2(O{=}PPh_3)_2$, depending on the ligands attached to the $V{=}O^{2+}$ group in the starting material.

Experimental Section

Physical Measurements. Mid-infrared spectra (4000–400 cm^{-1}) were recorded on either a Perkin-Elmer Model 337 or a Beckman Model IR-12 spectrophotometer or a Digilab FTS 15-B Fourier transform infrared machine. Samples were measured as Nujol mulls or KBr disks. Far-infrared spectra (550–50 cm^{-1}) were recorded on a Digilab 14 or 15-B instrument or on a Nicolet FT IR at Harvard University. Samples were prepared as very concentrated Nujol mulls pressed between polyethylene plates.

Ultraviolet, visible, and near-infrared spectra were recorded by using a Cary 14 or 15 spectrophotometer at ambient temperature in $CHCl_3$ or CH_2Cl_2 solvent with use of 1.000- or 10.000-cm matched cells. Samples of water- or air-sensitive compounds were prepared in a drybox and tightly capped prior to removal for measurement.

Magnetic susceptibility measurements were made at ambient temperature by the Faraday method using a previously described apparatus.[30] X-Band ESR spectra were recorded on a Varian Model V-4502 spectrometer. The cavity temperature was regulated with a Varian V-4540 temperature controller, and the spectra were calibrated by using both DPPH (g = 2.0036) and a proton oscillator for magnetic field calibration.

Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Air- and/or water-sensitive compounds were handled in a Vacuum Atmospheres Co. drybox. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Solvent and Reagent Purification. Benzene was dried by refluxing over $LiAlH_4$ or CaH_2 and deoxygenated by either saturation with N_2 or repeated vacuum freeze–pump–thaw cycles. Methylene chloride was dried with CaH_2 and degassed by freeze–pump–thaw. Acetonitrile was purified by using Coetzee's alternate method II[31] and deoxygenated by N_2 saturation or freeze–pump–thaw. All other solvents were reagent grade and were used without further purification.

Ethylenediamine and 1,2-diaminopropane were shaken over KOH, distilled under N_2, and stored over 4-Å molecular sieves. Salicylaldehyde was freshly distilled under nitrogen before use. All other reagents were used without further purification.

Preparation of Starting Materials. Literature methods were used for the synthesis of $VO(acac)_2$,[32] $VO(dbm)_2$,[33] VO(salen),[34] VO(acpn)[35] and VO(acen);[35] the products were recrystallized from $CHCl_3$, CH_3CN, CH_3OH, $C_6H_5CH_3$, and CH_2Cl_2, respectively. $VO(dpm)_2$ and $VO(hfac)_2$ were prepared as previously described[33] and purified by vacuum sublimation. Triphenylphosphine dibromide was prepared in situ and used without further purification.[36]

Preparation of V=S(salen). With use of flame-dried glassware and carefully dried and deoxygenated solvents, 1.50 g (4.5 mmol) of VO(salen) in 200 mL of CH_3CN—an emerald green solution—was reacted with 0.795 g (7 mmol) of B_2S_3 (Alfa, added as a solid) and taken to reflux temperature for 48 h. The resulting brown suspension was filtered through Munktell 120H paper (which removed the very small particles), a further 0.1 g of B_2S_3 was added to the filtrate, and the resulting suspension was stirred a further 48 h. The suspension was filtered, and the filtrate was slowly treated with hexane and cooled. The deep magenta crystals which formed were filtered, washed with hexane, and dried in vacuo. The yield was 1.05 g (67%). Anal. Calcd for $VSC_{16}H_{14}N_2O_2$: V, 14.58; S, 9.18; C, 55.02; H, 4.04; N, 8.02. Found: V, 14.13; S, 9.20; C, 53.70; H, 3.99; N, 7.02.

Preparation of V=S(acen). To a deep blue solution of 2.57 g (8.87 mmol) of VO(acen) in 125 mL of dry CH_2Cl_2 was added 1.04 g (8.87 mmol) of solid B_2S_3. The reaction mixture was stirred for 24 h and filtered through very fine pore size paper, and hexane was slowly added to the bright orange filtrate until a precipitate began to form. This solid was filtered and discarded after it was allowed to settle for several hours. Additional hexane was added to the filtrate, and it was held at 0 °C overnight. The deep magenta crystals were filtered, washed with hexane, dried in vacuo, and stored in a sealed vial inside the drybox. The yield was 1.24 g (46%). Anal. Calcd for $VSC_{12}H_{18}N_2O_2$: V, 16.68; S, 10.50; C, 47.21; H, 5.94; N, 9.18. Found: V, 15.41; S, 10.52; C, 47.56; H, 6.16; N, 9.15.

Reaction of VBr_2(salen) with Na_2S. To a solution of 0.1 g (0.21 mmol) of VBr_2(salen) in 100 mL of 3:1 v:v CH_3CN–CH_2Cl_2 was added 0.016 g (0.21 mmol) of solid Na_2S. The dark greenish blue mixture became gold after 4–5 min. The resulting mixture was stirred for 1 h and filtered, the resulting orange solution was evaporated to 10 mL, and an equal volume of hexane was added. The precipitated solid was shown by infrared spectroscopy to be VS(salen) contaminated with a V=O impurity which could not be removed by recrystallization from various solvents.

Reaction of Vanadyl Complexes with Ph_3PBr_2. Acetonitrile solutions of Ph_3PBr_2 were prepared according to the literature method,[36] and the vanadyl complexes were added in stoichiometric amounts either

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as solids or as solutions in dry CH_3CN. Representative reactions are detailed below.

Preparation of VBr_2(salen). To a well-stirred, colorless solution of Ph_3PBr_2 (prepared by reaction of 2.63 g (0.01 mol) of Ph_3P with 0.51 mL (0.01 mol) of Br_2) in 150 mL of dry CH_3CN was added 3.33 g (0.01 mol) of powdered green VO(salen) over a 30-min period under N_2. The resulting black mixture was stirred for 24 h, and the solid product was filtered under N_2, washed with cold dry CH_3CN, dried overnight in vacuo, and stored in the drybox. The yield was 3.97 g (87%). Anal. Calcd for $VBr_2N_2C_{16}H_{14}$: V, 10.68; Br, 33.50; N, 5.87; C, 40.28; H, 2.96. Found: V, 8.48; Br, 33.25; N, 6.22; C, 40.57; H, 3.34.

Reaction of $VO(acac)_2$ with Ph_3PBr_2. Over a 20-min period a solution of 2.65 g (0.01 mol) of $VO(acac)_2$ in 500 mL of CH_3CN was added to a solution of 0.02 mol of Ph_3PBr_2 in 75 mL of CH_3CN, prepared as described above. As the addition proceeded, the solution changed color from water-white to yellow, gold, amber, and dark olive-brown. The resulting solution was vacuum evaporated to a volume of 20 mL and extracted with 150 mL of dry benzene. The light blue solid which precipitated was filtered and recrystallized from 50:50 benzene–chloroform. The yield was 6.5 g (83%). Anal. Calcd for $VBr_2C_{36}H_{30}P_2O_3$: V, 6.50; Br, 20.40; C, 55.20; H, 3.86; P, 7.91. Found: V, 6.11; Br, 19.74; C, 54.38; H, 3.65; P, 7.53.

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Registry No. V=O(salen), 36913-44-7; V=S(salen), 74354-69-1; V=O(acen), 19195-97-2; V=S(acen), 74354-70-4; VBr_2(salen), 74498-60-5; VCl_2(salen), 70629-75-3; $V{=}OBr_2(O{=}PPh_3)_2$, 74498-61-6; $V{=}OCl_2(O{=}PPh_3)_2$, 16997-35-6; B_2S_3, 12007-33-9; Ph_3PBr_2, 1034-39-5; $VO(acac)_2$, 3153-26-2.

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Synthesis of Ring-Substituted Derivatives of Cyclopentadienyl Tricarbonyl Complexes of Molybdenum and Tungsten

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The ions $(C_5H_4R)^-$ (R = COMe or CO_2Me), generated by electroreduction of $Fe(\eta^5\text{-}C_5H_4R)_2$ in DMF or THF, react with $M(CO)_3L_3$ (M = Mo or W, L = THF or DMF), giving $[M(\eta^5\text{-}C_5H_4R)(CO)_3]^-$. Treatment of these carbonylate ions with MeI affords $M(\eta^5\text{-}C_5H_4R)(CO)_3CH_3$, and their electrooxidation gives either $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2$ or $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2Hg$ depending on the working electrode employed. Oxidation of $[M(\eta^5\text{-}C_5H_4R)(CO)_3]_2$ with iodine produces $M(\eta^5\text{-}C_5H_4R)(CO)_3I$. The new complexes have been characterized by spectroscopic and electroanalytical methods, and it is suggested that the bulky nature of the R substituent inhibits free rotation about the ring–metal bond.

Introduction

There are, at present, no reports of electrophilic or nucleophilic attack on the cyclopentadienyl rings in $[M(\eta^5\text{-}C_5H_5)(CO)_3]_2$. That this is so is due almost certainly to the oxidative and reductive instability of these dimers. Thus under oxidizing conditions, $[M(\eta^5\text{-}C_5H_5)(CO)_3]_2$ and also $M(\eta^5\text{-}C_5H_5)(CO)_3Q$ (Q = alkyl, aryl, or halide) decompose and so, for example, Friedel–Crafts alkylation or acylation reactions are impossible. In reducing media the dimers readily form the stable carbonylate ions $[M(\eta^5\text{-}C_5H_5)(CO_3]^-$ which easily undergo addition reactions, but at the metal and not the ring.[1,2]

The synthesis of chromium, molybdenum, or tungsten tricarbonyl complexes containing substituted cyclopentadienyl rings can be achieved by four methods: the reaction of $M(CO)_6$ with appropriately substituted cyclopentadienide anions,[3–7] substituted cyclopentadienes,[8,9] or fulvenes[10,11] or treatment of $M(\eta^5\text{-}C_5H_4R)_2H_2$ with CO and BF_3 under pressure in the presence of an aliphatic alcohol.[12] Somewhat exceptionally, $[Mo(\eta^5\text{-}C_5H_4Et)(CO)_3]_2$ can be prepared in very low yield[13] by thermolysis of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Et$. All of the complexes prepared in these ways contain alkyl-ring substituents and, to our knowledge, no compounds containing electron-withdrawing substituents (e.g., COR or CO_2R) have been described.

In our study of the electrochemical reduction of ferrocene derivatives, we showed[14] that $Fe(\eta^5\text{-}C_5H_4R)_2$ is readily decomposed, following a two-electron transfer, to cyclopentadienide ions and metallic iron. Of particular interest in this reaction is the easy formation of substituted cyclopentadienide anions from readily accessible ferrocenyl derivatives. Thus, the ions $(C_5H_4COMe)^-$ or $(C_5H_4CO_2Me)^-$, which are very difficult or even impossible to prepare by conventional methods, are easily obtained, and we have described their use in the syntheses of new metallocene derivatives of cobalt and rhodium.[14]

It was of importance to us to see whether this convenient synthetic route could be extended to the preparation of tricarbonyl compounds of Mo- and W-containing cyclopentadienyl rings substituted by electron-withdrawing groups. Our study was restricted to compounds of Mo and W because

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