for speculation, although this seems to be a reasonable interpretation.

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Registry No. CH_3Cl, 74-87-3; CH_3Br, 74-83-9; CH_3O^-, 3315-60-4; *t*-BuO^-, 16331-65-0; HCC^-, 29075-95-4; F^-, 16984-48-8; CD_3S^-, 73142-80-0; $CH_3CO_2^-$, 71-50-1; $H_2C{=}C(CH_3)O^-$, 71695-00-6; PhN^-, 76619-58-4; CH_2CN^-, 21438-99-3; *c*-$C_5H_5^-$, 12127-83-2; PhO^-, 3229-70-7; $CF_3COCH_2^-$, 64723-97-3; CH_3SCH_3, 75-18-3; CH_3F, 593-53-3; $HCCCH_3$, 74-99-7; CH_3CN, 75-05-8; CH_3OCH_3, 115-10-6; Cl^-, 16887-00-6.

Orthoquinone Complexes of Vanadium and Their Reactions with Molecular Oxygen

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Abstract: Reactions carried out between $V(CO)_6$ with 3,5-di-*tert*-butyl-1,2-benzoquinone and $VO(acac)_2$ with 3,5-di-*tert*-butylcatechol have been found to give as a common product $V(3,5\text{-DBSQ})_3$. The $V(CO)_6$ reaction has been followed with EPR spectroscopy. Prior to observation of the 10-line radical spectrum of $V(3,5\text{-DBSQ})_3$, an 8-line vanadium spectrum is observed that appears related to a mixed quinone–carbonyl species. The reaction between $V(3,5\text{-DBSQ})_3$ and molecular oxygen has been followed, and the product $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ has been characterized structurally. It crystallizes in the triclinic space group $P\bar{1}$ in a unit cell of dimensions $a = 11.486$ (4) Å, $b = 11.633$ (4) Å, $c = 13.102$ (4) Å, $\alpha = 100.58$ (2)°, $\beta = 108.81$ (3)°, $\gamma = 97.82$ (3)°, and $V = 1592.7$ (9) Å^3. The dimeric molecule is located about a crystallographic center of inversion. Catecholate ligands bridge adjacent vanadium(V) ions through one oxygen; semiquinone ligands are chelated to the metals. Terminal oxo ligands bond at the sixth coordination sites of the metals. The complex exhibits an EPR spectrum which is that of a semiquinone coupled weakly with one vanadium (2.85 G) center. Further reaction with molecular oxygen gives V_2O_5 and the benzoquinone. Features of this reaction sequence are compared with related members of the series synthesized previously with molybdenum.

The chemistry of reactions carried out between vanadium ions of various charge and catechol has been a subject of interest for several years. Catechols were investigated as analytical agents for use in the photometric determination of vanadium.[1] This procedure took advantage of the intense charge-transfer bands associated with high-oxidation-state vanadium complexes formed with catecholate ligands. Recent work has been related to the biological activity of vanadium[2] and to application of the strong reducing power of vanadium(II)–catechol systems to the reduction of N_2 to ammonia, CO to methanol, and acetylenes to olefins.[3,4] Early experiments directed at understanding the chemistry of vanadium–catechol systems were carried out in protic media and appeared to give contradictory results. Within the past few years reports have appeared that focus on the pH dependence of these reactions, studies that have provided detailed characterization of reaction products.[5,6] Reactions carried out with vanadyl ion can be represented in two chemical equations. Equation 1 gives

$$VO^{2+} + 2(1,2\text{-}(HO)_2C_6H_4) \rightarrow VO(Cat)_2^{2-} + 4H^+ \quad (1)$$

$VO(Cat)_2^{2-}$ ion as the reaction product. A neutral VO(Cat) species that appears as an intermediate in the stepwise formation of the dianion has been isolated and characterized.[6,7] Equation 2 describes the formation of $V(Cat)_3^{2-}$. The tris(catecholate)-

$$VO(Cat)_2^{2-} + 1,2\text{-}(HO)_2C_6H_4 \rightarrow V(Cat)_3^{2-} + H_2O \quad (2)$$

vanadium(IV) dianion can be either reduced or oxidized to give the vanadium(III) or vanadium(V) forms of the complex.[6,8]

A report by Wilshire and Sawyer concerning the reversible addition of O_2, NO, and CO to a vanadium(IV) complex prepared with 3,5-di-*tert*-butylcatechol (3,5-DBCat) was of considerable interest to us and other groups for its potential relationship to the gas-molecule reduction reactions discussed above.[9] Subsequent attempts to prepare the subject complex of this work, $V(3,5\text{-DBCat})_2$, by the groups of both Raymond[6] and Sawyer[8] have failed. The reaction described in the initial report by Wilshire and Sawyer used vanadyl acetylacetonate as a reagent with the reaction carried out either in methanol or Me_2SO in the absence of additional acid or base (eq 3). Reactions described by Raymond and Sawyer in their recent reports were carried out under basic conditions and produced $VO(3,5\text{-DBCat})_2^{2-}$ ion as the product by the process described in reaction 1.

$$VO(acac)_2 + 2(1,2\text{-}(HO)_2C_6H_4) \rightarrow V(3,5\text{-DBCat})_2 + 2H(acac) + H_2O \quad (3)$$

An alternate route to catecholate or, more generally, quinone complexes employs a reduced form of the metal and the oxidized form of the quinone ligand. We have used this approach with a wide variety of metals and have shown that in many cases the same products are obtained by this procedure as are obtained when using the oxidized metal–catechol route. A specific example that is pertinent to the work described in this report is found with

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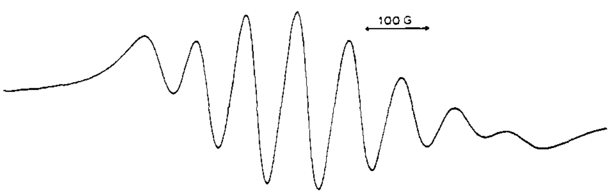
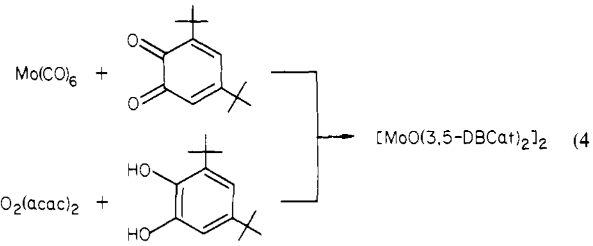


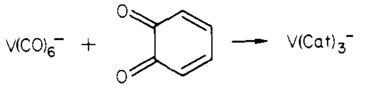
Figure 1. EPR spectrum of $V(O_2C_6H_2(t\text{-}Bu)_2)(CO)_n$ in toluene under an inert atmosphere.

molybdenum. Dimeric $[MoO(3,5\text{-}DBCat)_2]_2$ can be prepared by either procedure, (eq 4).[10] When the $V(CO)_6^-$ anion and the



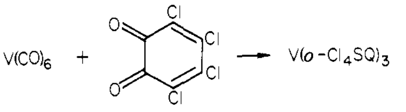
(4)

o-benzoquinone form of the organic ligand are used, tris(catecholate)vanadium(V) complexes can be formed in high yield (eq 5). Similar reactions carried out with neutral $V(CO)_6$ gave rather



(5)

different results. With tetrachloro-1,2-benzoquinone, the tris complex $V(O_2C_6Cl_4)_3$ is formed (eq 6).[12] It has a monomeric,

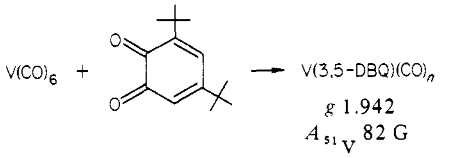


(6)

octahedral structural and seems to be quite similar to the tris(tetrachlorosemiquinone) complexes of Cr and Fe.[13] A similar reaction carried out with 9,10-phenanthrenequinone gave only V_2O_5. In this report we present our attempt at reproducing reaction 3. We have sought to better understand the chemistry involved by also investigating the $V(CO)_6$–3,5-di-*tert*-butyl-1,2-benzoquinone reaction. The results of this study have provided insights into the nature of metal carbonyl–quinone reactions and also into the sequence of reactions that take place between metal quinone complexes and molecular oxygen.

Experimental Results

Reaction of $V(CO)_6$ with 3,5-Di-*tert*-butyl-1,2-benzoquinone. Under normal conditions, paramagnetic $V(CO)_6$ does not show an EPR spectrum at room temperature. However, quinone addition products with odd-electron configurations would be EPR active, and this becomes a useful spectroscopic technique for monitoring the $V(CO)_6$–quinone reactions. Immediately upon addition of 3,5-di-*tert*-butyl-1,2-benzoquinone to a toluene solution of $V(CO)_6$ under inert conditions, the mixture turns an intense blue and an EPR signal appears (eq 7). The spectrum, shown in Figure 1, is not unusual for vanadium compounds. It consists of eight lines due to coupling of the unpaired electron with the ^{51}V nucleus. It has a g value of 1.942 and vanadium hyperfine coupling constant of 82.2 G (75×10^{-4} cm^{-1}). Octahedral complexes that lack oxo ligands have comparable spectral parameters.[14] Over the period of an hour the spectrum begins to change to a new pattern consisting of 10 lines. This is shown in Figure 2. The new spectrum is centered about a g value of 2.004 and is stable in solution indefinitely in the absence of oxygen (eq 8). The g value of this spectrum suggests that the paramagnetic center is an organic radical. On the basis of results obtained with the tetrachloroquinone ligand and from a parent ion peak observed in the mass spectrum at 712, we formulate this product as $V(3,5\text{-}DBSQ)_3$. Calculations carried out on the neutral $V(SQ)_3$ complexes indicate that the unpaired electron is contained in a molecular orbital of a_2 symmetry that is delocalized over all three quinone ligands.[15] In the absence of ligand substituents that might couple with the electron spin, $V(o\text{-}Cl_4SQ)_3$ showed only weak coupling to the vanadium of 4.1 G. The structure of $V(3,5\text{-}DBSQ)_3$ is likely of C_3 symmetry similar to the chromium analogue.[16] Additional coupling to ring protons including *t*-Bu substituents of the equivalent ligands is to be expected. Spectrum simulation is complicated by the number of spins, but calculations give the best results for a *localized* model with coupling of 2.1 G to the vanadium and 4.2 G to a single ring proton. Further support for a localized ligand-based electronic structure is found in the absence of temperature dependence; the 10-line spectrum has been observed at −100 °C. An EPR study by Kabachnik on the neutral P(V) compound $P(3,5\text{-}DBCat)_2(3,5\text{-}DBSQ)$ showed localized behavior at temperatures below −60 °C but a spectrum at room temperature that indicated equivalence of all three quinone ligands.[17]



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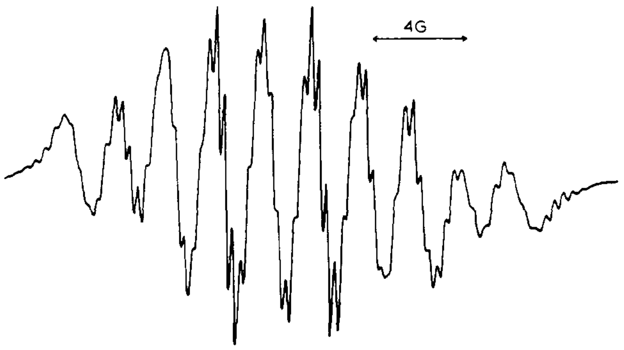
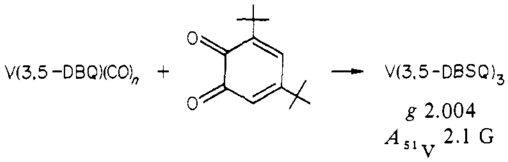


Figure 2. EPR spectrum of $V(O_2C_6H_2(t\text{-}Bu)_2)_3$ in toluene under an inert atmosphere.



(8)

The precursor compound exhibiting the eight-line spectrum is likely a species containing carbonyl ligands. Reactions between $Mn_2(CO)_{10}$ and *o*-benzoquinones initially produce a stable semiquinone–carbonyl complex, $Mn(CO)_5(SQ)$, prior to the formation of $Mn(SQ)_2$.[18] The number of carbonyl ligands bonded to the vanadium center is unknown as is the formal charge on the metal ion.

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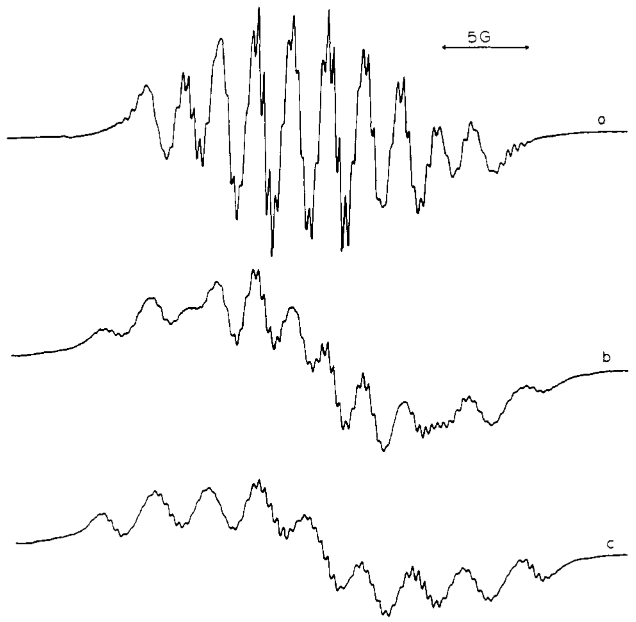

Figure 3. EPR spectra showing the development of the spectrum of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ with decay of the $V(O_2C_6H_4(t\text{-Bu})_2)_3$ spectrum in the presence of O_2.

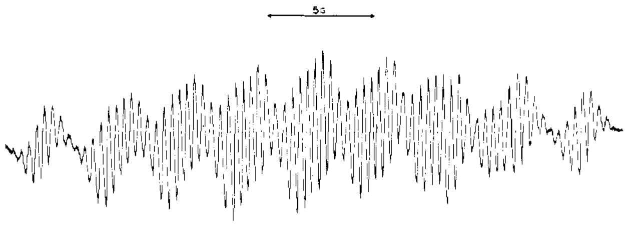

Figure 4. EPR spectrum of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ in toluene.

Reaction of $V(DBSQ)_3$ with O_2. The next series of experiments were directed at investigating the reaction between the vanadium–quinone complexes prepared in the previous section and molecular oxygen. In one particular experiment the EPR sample tube used to follow the $V(CO)_6$ reaction was exposed to oxygen. As gas diffused through the solution a rapid change in the EPR signal occurred, the 10-line spectrum of $V(3,5\text{-DBSQ})_3$ disappeared and was replaced by a 9-line spectrum. This process is shown in Figure 3, and a clearly resolved view of the nine-line spectrum is shown in Figure 4. The g values of the two spectra are essentially the same, 2.004, the value of an organic free radical, and the color of the solution remained unchanged. The spectrum shown in Figure 4 is that of a single, paramagnetic 3,5-di-*tert*-butyl-1,2-semiquinone ligand coupled weakly to a single, diamagnetic vanadium center. Simulation of the spectrum has provided accurate values for the coupling constants. Coupling to the metal and to the proton at the 4-position of the quinone ring is equal in magnitude with a value of 2.85 G, and coupling to the protons of the *t*-Bu group at the 5-position of the ring is 0.35 G. For comparison, the free semiquinone shows coupling of 3.8 G to the proton at the 4-position with coupling of 0.3 G to the *t*-Bu group at the 5-position.[19]

If the reaction between $V(CO)_6$ and the benzoquinone is carried out under conditions that less than rigorously exclude oxygen, large crystals of the species showing the nine-line spectrum can be obtained. X-ray methods have been used to determine the molecular structure of this compound. The results of this investigation provided in the following section have shown that it is $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$.

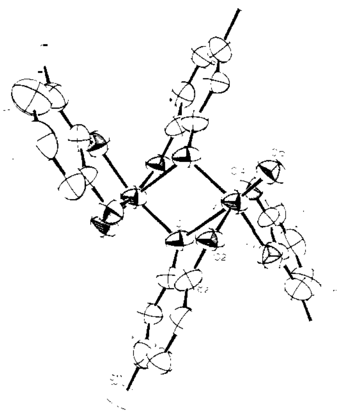

Figure 5. View of the $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ complex molecule with the *tert*-butyl methyl carbon atoms omitted.

Upon further exposure to oxygen, the nine-line spectrum of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ slowly disappeared. NMR analysis showed the appearance of 3,5-di-*tert*-butyl-1,2-benzoquinone, and solid V_2O_5 separated from the solution. Equations describing the reactions with oxygen are given (eq 9 and 10), and

$$V(3,5\text{-DBSQ})_3 + O_2 \rightarrow [VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2 + 2(3,5\text{-DBQ}) \quad (9)$$

$$VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2 + 1.5O_2 \rightarrow V_2O_5 + 4(3,5\text{-DBQ}) \quad (10)$$

the sum total of eq 7–10 is the benzoquinone-catalyzed conversion of $V(CO)_6$ to V_2O_5. The synthetic utility of this process is indeed limited, but it is of interest that intermediate compounds can be isolated along the way. Tetrachloro-1,2-benzoquinone is not a particularly effective catalyst, forming the stable $V(o\text{-}Cl_4SQ)_3$ complex in the first step of the reaction; 9,10-phenanthrenequinone is more effective, rapidly forming V_2O_5 even in the presence of only small quantities of oxygen. Perhaps the most important contribution derived form this particular sequence of reactions is that they have provided a basis for understanding the chemistry of other vanadium–quinone reactions and have explained the puzzling diversity of the reactions observed with $Mo(CO)_6$.[20]

Description of the $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ Molecule. Crystals of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ were obtained directly from reactions carried out in a number of different solvent media. All were found to be solvates, and all were observed to lose solvate molecules at room temperature, resulting in crystal deterioration. Two structure determinations were undertaken; one on the complex obtained as an anisole solvate and a second investigation on crystals obtained from methanol. Anisole was found to give the most durable crystal structure of the solvents used. The methanol solvate crystals remained crystalline for less than the period of 1 h. A structure determination using a crystal coated with an amorphous resin was performed to verify that the molecular structure of the complex molecule was the same in the two investigations. Both forms of the complex showed the same infrared and UV–vis spectral bands and were found to have identical structures. The results of the more accurate determination carried out on the anisole solvate are presented in this section.

The crystal structure of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2\cdot C_6H_5OCH_3$ consists of well-separated complex and anisole molecules both located about crystallographic inversion centers. This results in disorder of the methoxy group of the anisole.

The neutral complex molecule is a centrosymmetric dimer. Views of the molecule are shown in Figures 5 and 6; bond distances, angles, and dihedral plane calculations are given in Tables III and IV. Each metal has a distorted octahedral coordination geometry with a terminally bonded oxo ligand, O(5), occupying one site. Adjacent vanadium atoms are bridged by the oxygen atoms of two quinone ligands. Bridging quinones are chelated to one metal and bridge to the second through an outer-oxygen electron pair. The V–O(1) bonds of the chelate rings are located

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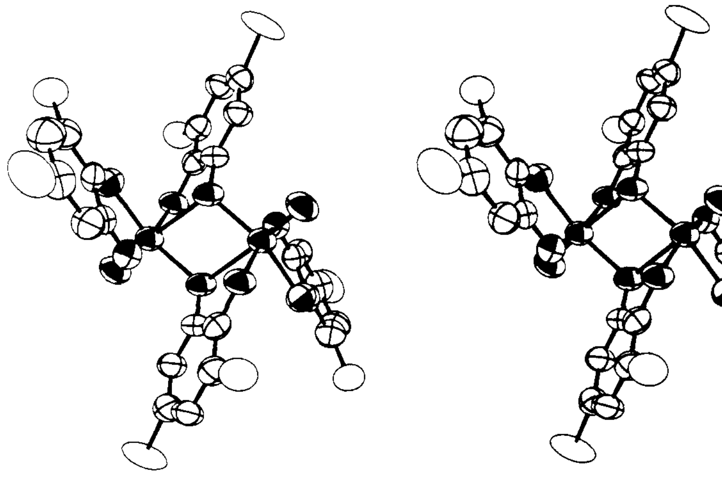


Figure 6. Stereoview of the $[VO(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]_2$ molecule.

trans to the oxo ligand while the bridge bonds, V′–O(1), are trans to the oxygen donor atoms of chelated quinone ligands. The oxo ligand is quite strongly bonded to the metal with a V–O(5) length of 1.581 (4) Å, and the trans influence of this ligand is reflected in the V–O(1) length of 2.267 (4) Å, compared with the V′–O(1) length of 1.956 (5) Å. The relative strength of the bonds to the adjacent metals stabilizes the dimeric structure. The remaining quinone ligands are chelated to the metals through oxygen atoms O(3) and O(4) with bond lengths of 1.975 (5) and 1.987 (5) Å, respectively. For comparison, the $VO(Cat)_2^{2-}$ ion, containing two more electrons than the present compound, is monomeric; it has a slightly longer V═O length of 1.616 (4) Å and V—O lengths for the catechol ligands of 1.956 (6) Å.[6]

It is of interest to consider the relationship between the structural features of the molecule and the charge distribution. Features that have been found to have a direct relationship with the charge on the quinone ligands are the C–O bond length and the length of the bond between quinone carbon atoms.[11] Catecholate ligands have C–O lengths of 1.34–1.35 Å and C–C values of 1.40 Å. In the present molecule the C(1)–O(1) and C(2)–O(2) lengths are 1.349 (7) and 1.359 (7) Å, the C(1)–C(2) length is 1.40 (1) Å, and the bridging quinone ligand is clearly catecholate. The chelated ligand has shorter C–O lengths of 1.292 (8) and 1.322 (8) Å and a longer C(15)–C(16) value of 1.44 (1) Å. These lengths are indicative of semiquinone coordination, although the O(3)–C(16) length is slightly larger than values encountered for semiquinone ligands in other structures.

Structural features of the complex molecule indicate that it is a diradical in solid state, with paramagnetic semiquinone ligands chelated to diamagnetic vanadium(V) centers. The gross features of the molecule are similar to the closely related molybdenum complex $[MoO(3,5\text{-}DBCat)_2]_2$, with allowance made for the difference in charge and its effect on the structure of the chelated ligands.[10] In coordinating solvents the molybdenum dimer was found to dissociate, giving two solvated monomers, and a question arose concerning the relationship between the structure of $[VO(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]_2$ in the solid state and in solution. Electronic spectra were recorded on the complex in the solid state and in toluene solution under conditions that give the nine-line EPR spectra. The solid-state spectrum is shown in Figure 7. In solution, the band at 640 nm becomes less intense relative to other bands and broader; the 300-nm band disappears entirely. From this result it is not clear whether the complex remains in dimeric form or dissociates. The EPR spectrum provides the most convincing evidence for retention of the dimeric structure in solution. If the dimer were to dissociate, the two quinone ligands would be symmetrically equivalent and a more complicated proton-coupling pattern might be expected. Further, the dimeric structure is more tightly bonded in the vanadium case than with molybdenum. The V′–O(1) bridge bond has the shortest V–O length of the structure, excluding the oxo ligand, while the related bonds of the molybdenum dimer are relatively long. Even with the weaker bridge bond the molybdenum dimer remains associated in toluene solution, the medium used for EPR studies on the vanadium dimer.

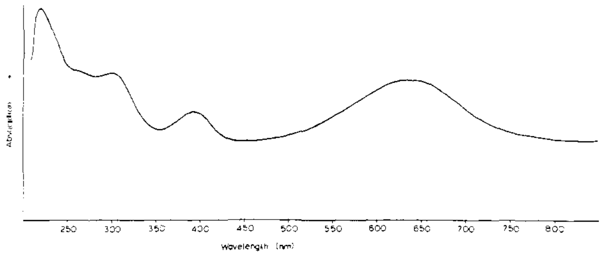


Figure 7. Optical spectrum of $[VO(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]_2$ recorded on a solid sample.

Reaction of $VO(acac)_2$ with 3,5-Di-*tert*-butylcatechol. In two previous investigations the reaction between vanadyl acetylacetonate and 3,5-di-*tert*-butylcatechol has been investigated. In both cases basic conditions were used, either the disodium salt of the catechol[8] or excess triethylamine,[6] and the reaction followed the path described in eq 1, giving $VO(3,5\text{-}DBCat)_2^{2-}$ anion as the product. We have investigated the reaction carried out in the absence of base and have tried to follow the course of the reaction using the spectral information obtained with the $V(CO)_6$ reaction. Two products are obtained when the reaction is carried out in dry methanol: crystals of $[VO(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]_2$ form as the methanol solvate and a slightly more violet amorphous solid can be isolated by solvent evaporation. This material gives a strongly coupled vanadyl EPR spectrum with a *g* value of 1.97 and vanadium hyperfine coupling value of 108.5 G (100×10^{-4} cm^{-1}). It appears to be the material reported by Sawyer to be "$V(3,5\text{-}DBCat)_2$" in his initial report.[9] Characterization of this product has been difficult, but it appears to be the $VO(3,5\text{-}DBCat)_2^{2-}$ anion.

The $VO(acac)_2$ reaction has been carried out under nitrogen by using either methanol or toluene as the solvent medium and following the reaction spectrally with EPR. Under these conditions the product observed is $V(3,5\text{-}DBSQ)_3$, identified by its characteristic 10-line EPR spectrum (Figure 2). Steps leading to this product remain unclear, but it likely results from oxidation of the dianion $V(3,5\text{-}DBCat)_3^{2-}$. Formation of $VO(3,5\text{-}DBCat)_2^{2-}$ can be supressed by use of dry toluene rather than methanol and by employing rigorously anhydrous conditions, suggesting that it results from a process similar to the reverse of reaction 2 in the introduction.

As in the $V(CO)_6$ reaction, exposure to air results in conversion of $V(3,5\text{-}DBSQ)_3$ to $[VO(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]_2$.

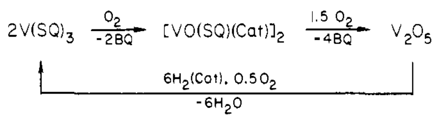
Conclusions

Whether the reaction is carried out with $V(CO)_6$ and the oxidized form of the quinone or with $VO(acac)_2$ and the catechol,

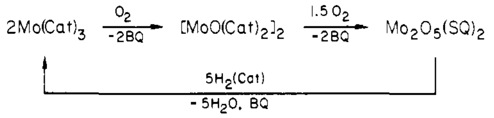
Table I. Crystallographic Data for $[VO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2 \cdot C_6H_5OCH_3$

M_r, 1123.28	$\mu = 3.69$ cm^{-1}
triclinic	D(calcd) = 1.172 g/cm^3
space group $P\bar{1}$	D(exptl) = 1.09 (8) g/cm^3
$a = 11.486$ (4) Å	Mo Kα radiation, $\lambda = 0.71069$ Å
$b = 11.633$ (4) Å	scan rate, 2°/min
$c = 13.102$ (4) Å	2θ limits, $3 \leqslant 2\theta \leqslant 45$
$\alpha = 100.58$ (2)°	scan range, ±0.7
$\beta = 108.81$ (3)°	data collected, 3423
$\gamma = 97.82$ (3)°	data $F_o^2 > 3\sigma(F_o^2)$, 1985
$V = 1592.7$ (9) Å^3	$P = 0.04$
$Z = 1$	

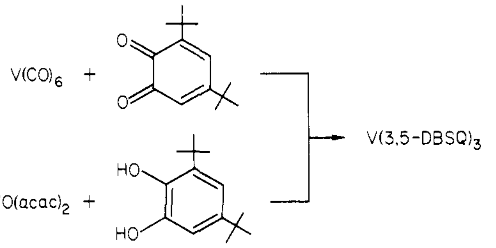
Scheme I



Scheme II



the product is the species giving the EPR spectrum shown in Figure 3, V(3,5-DBSQ)$_3$. Charge distribution in this molecule remains unclear. A tautomeric form that may be more appropriate in view of its EPR spectrum is V(3,5-DBCat)$_2$(3,5-DBSQ), with a d^0 V(V) center. Fenske's calculations seem more consistent with V(III), and V(o-Cl$_4$SQ)$_3$ is isostructural with its Cr(III) and Fe(III) analogues, which are clearly semiquinone compounds. This complex reacts with molecular oxygen in a stepwise manner, first forming [VO(3,5-DBSQ)(3,5-DBCat)]$_2$ and then V$_2$O$_5$ by the process summarized in Scheme I. Conversion of V$_2$O$_5$ to V(3,5-DBSQ)$_3$ has not been described in detail, but the intense blue color and EPR signal of V(3,5-DBSQ)$_3$ can be clearly seen in reactions carried out in an EPR tube containing the oxide and the catechol under anaerobic conditions. The net reaction amounts to conversion of O$_2$ to water using catechol as the electron and proton source.



(11)

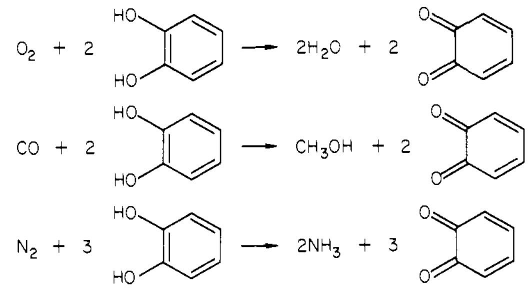
Table II. Final Positional and Thermal Parameters for $[VO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2 \cdot C_6H_5OCH_3$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V	0.07881 (10)	0.01159 (10)	0.13846 (14)	3.81 (6)	4.58 (7)	5.05 (9)	1.68 (5)	0.81 (5)	1.45 (6)
O(1)	−0.0669 (3)	0.0682 (4)	0.0413 (5)	3.8 (2)	4.6 (2)	5.3 (3)	1.8 (2)	1.0 (2)	1.0 (2)
O(2)	0.1501 (4)	0.1549 (3)	0.1598 (4)	4.1 (2)	4.9 (2)	5.5 (3)	2.1 (2)	0.7 (2)	1.2 (2)
C(1)	−0.0355 (6)	0.1803 (6)	0.0905 (7)	4.6 (4)	3.4 (4)	4.7 (5)	1.5 (3)	1.3 (3)	0.9 (3)
C(2)	0.0821 (6)	0.2286 (6)	0.1576 (7)	4.0 (4)	4.5 (4)	3.9 (5)	0.7 (3)	0.7 (3)	0.9 (3)
C(3)	0.1221 (6)	0.3428 (6)	0.2144 (7)	4.7 (4)	4.2 (4)	4.5 (4)	0.6 (3)	0.6 (3)	1.1 (3)
C(4)	0.0393 (7)	0.4055 (5)	0.2048 (7)	6.5 (4)	3.7 (3)	5.5 (5)	2.1 (3)	0.0 (4)	0.8 (3)
C(5)	−0.0779 (6)	0.3566 (6)	0.1383 (7)	5.3 (4)	5.5 (4)	5.0 (5)	2.2 (3)	0.5 (3)	1.6 (3)
C(6)	−0.1158 (6)	0.2453 (6)	0.0814 (7)	5.2 (4)	3.9 (3)	5.0 (5)	1.4 (4)	0.8 (3)	1.1 (3)
C(7)	0.2533 (6)	0.3971 (6)	0.2865 (8)	5.3 (4)	4.6 (4)	6.8 (5)	0.8 (3)	0.2 (3)	1.1 (3)
C(8)	0.3359 (7)	0.3710 (7)	0.1931 (9)	5.2 (5)	8.5 (4)	9.2 (5)	1.1 (4)	1.5 (4)	3.1 (4)
C(9)	0.2760 (7)	0.5227 (6)	0.3439 (9)	5.8 (4)	5.8 (4)	11.3 (5)	0.2 (3)	−1.2 (4)	0.6 (4)
C(10)	0.2842 (7)	0.3505 (7)	0.3896 (9)	8.3 (4)	7.7 (4)	6.9 (4)	1.3 (3)	−1.5 (3)	2.7 (3)
C(11)	−0.1673 (7)	0.4348 (7)	0.1388 (10)	6.5 (4)	5.3 (4)	12.4 (4)	3.8 (3)	−0.8 (4)	2.2 (3)
C(12)[b]	−0.2861 (16)	0.3724 (17)	0.0643 (25)	5.2 (7)	10.2 (7)	12.7 (10)	5.6 (5)	−0.9 (4)	−2.6 (6)
C(13)[b]	−0.1811 (16)	0.4861 (16)	0.2860 (15)	7.7 (8)	7.6 (8)	4.6 (12)	5.6 (6)	2.5 (8)	−0.5 (9)
C(14)[b]	−0.1039 (18)	0.5334 (15)	0.1080 (19)	12.1 (10)	5.3 (7)	10.4 (16)	7.5 (9)	6.0 (10)	4.5 (10)
C(12)[b]	−0.2749 (25)	0.3908 (23)	0.186 (4)	12.4 (15)	13.7 (12)	31.2 (19)	11.1 (11)	15.8 (13)	13.1 (15)
C(13)[b]	−0.1138 (24)	0.5550 (21)	0.188 (3)	9.5 (14)	6.9 (13)	24.1 (21)	6.1 (11)	1.4 (14)	−4.2 (15)
C(14)[b]	−0.2140 (23)	0.4058 (20)	−0.0140 (20)	14.7 (14)	16.1 (12)	7.6 (20)	12.9 (12)	0.4 (13)	4.6 (16)
O(3)	0.0118 (4)	0.0791 (4)	0.2880 (5)	5.3 (3)	6.0 (3)	5.0 (3)	1.7 (2)	0.9 (2)	1.5 (2)
O(4)	−0.0563 (4)	−0.1116 (4)	0.1231 (5)	5.5 (2)	5.3 (2)	5.0 (3)	1.6 (2)	1.4 (2)	2.0 (2)
C(15)	−0.1302 (6)	−0.0901 (6)	0.1975 (8)	4.8 (4)	4.5 (4)	4.4 (5)	1.1 (3)	1.1 (4)	2.2 (4)
C(16)	−0.0912 (7)	0.0193 (7)	0.2929 (8)	5.5 (4)	5.8 (5)	4.1 (6)	2.0 (4)	1.6 (4)	2.7 (4)
C(17)	−0.1552 (7)	0.0555 (6)	0.3844 (9)	4.9 (4)	5.8 (4)	6.5 (5)	1.4 (3)	1.5 (3)	2.1 (4)
C(18)	−0.2580 (7)	−0.0200 (8)	0.3752 (9)	6.8 (4)	8.0 (5)	7.3 (6)	2.9 (4)	1.9 (3)	2.5 (4)
C(19)	−0.3009 (7)	−0.1324 (7)	0.2773 (9)	5.2 (4)	7.0 (4)	6.9 (5)	1.0 (3)	0.8 (3)	3.1 (3)
C(20)	−0.2346 (7)	−0.1652 (6)	0.1869 (8)	4.9 (4)	5.5 (4)	6.2 (5)	1.2 (3)	1.9 (3)	2.5 (3)
C(21)	−0.1136 (7)	0.1675 (6)	0.4889 (8)	7.0 (4)	5.7 (4)	5.8 (5)	2.3 (3)	1.2 (3)	1.0 (3)
C(22)	−0.2008 (9)	0.1845 (8)	0.5822 (9)	13.3 (5)	9.3 (4)	7.5 (5)	4.9 (3)	5.5 (4)	1.7 (3)
C(23)	−0.1051 (7)	0.2570 (7)	0.4328 (9)	9.0 (4)	6.9 (4)	7.3 (5)	2.6 (4)	2.0 (3)	2.4 (4)
C(24)	0.0079 (8)	0.1757 (8)	0.5630 (9)	10.4 (4)	9.2 (4)	6.8 (4)	3.8 (3)	−1.0 (3)	0.5 (3)
C(25)	−0.4181 (7)	−0.2039 (7)	0.2836 (10)	5.8 (4)	7.1 (4)	12.3 (5)	0.3 (3)	1.7 (3)	5.0 (4)
C(26)	−0.5210 (7)	−0.1487 (9)	0.2644 (12)	4.7 (4)	15.7 (5)	15.6 (5)	3.1 (4)	3.2 (3)	6.8 (4)
C(27)	−0.4095 (10)	−0.2170 (11)	0.4091 (11)	12.3 (5)	19.3 (4)	11.8 (5)	−1.6 (4)	2.3 (4)	11.8 (4)
C(28)	−0.4466 (8)	−0.3171 (8)	0.1797 (13)	7.5 (5)	8.1 (4)	17.7 (7)	−0.1 (4)	1.7 (4)	3.8 (5)
O(5)	0.1904 (4)	−0.0230 (4)	0.1959 (5)	5.4 (2)	6.2 (2)	6.9 (3)	2.6 (2)	0.3 (2)	2.3 (2)
				Anisole Solvate					
C(29)	−0.4072 (20)	−0.023 (3)	−0.024 (5)	10.5 (11)	39.0 (17)	77.5 (23)	18.5 (13)	26.3 (15)	50.0 (21)
C(30)	−0.4531 (17)	0.0700 (13)	0.1080 (16)	18.2 (8)	16.4 (9)	19.9 (9)	3.4 (7)	6.2 (8)	14.2 (8)
C(31)	−0.3899 (28)	−0.020 (5)	−0.005 (6)	18.8 (13)	53.1 (22)	65.9 (31)	17.4 (12)	16.2 (15)	53.7 (18)
O(6)[b]	−0.4207 (14)	0.1161 (17)	0.1070 (17)	10.1 (7)	22.4 (12)	14.5 (13)	9.1 (11)	5.9 (12)	9.2 (10)
C(32)[b]	−0.4681 (28)	0.164 (3)	0.268 (3)	16.2 (11)	25.9 (18)	11.7 (21)	8.2 (13)	3.8 (18)	2.2 (14)

[a] The anisotropic thermal parameters (A^2) are of the form $\exp[-0.24(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. [b] Occupancy factor of 0.50.

Of particular interest is the relationship between the vanadium chemistry included in this report and the chemistry of molybdenum. This similarity is apparent in eq 4 and 13 but extends further to the series of compounds shown in Scheme II related by addition or removal of oxo and quinone ligands. Examples of each member have been synthesized and $Mo_2O_5(phenSQ)_2$[21] has been converted to $Mo(phenCat)_3$ by treatment with an oxygen atom acceptor.[22] Conversion of $Mo(Cat)_3$ to $Mo_2O_5(SQ)_2$ by reaction with O_2 was suspected but never observed, and the stability of the three types of compounds, prepared with different quinone ligands, toward further oxidation indicated an unexpected dependence on the quinone. Oxygen-atom transfer reactions are related to the biological function of a large class of enzymes containing molybdenum atoms in the active site[23] and occur in commercial oxidation processes catalyzed by molybdenum.[24] The reactions observed with vanadium and molecular oxygen tie the three forms of the molybdenum series together in a stepwise oxidation process that has important implications in the utility of these compounds as catalysts in organic oxidation reactions.[25] The catalytic properties of both the molybdenum and vanadium complexes clearly merit further investigation.

The net reaction of Schemes I and II is the metal-catalyzed reduction of O_2 to water by oxidation of catechol. Similar reactions can be written for the reduction of CO and N_2 in the system developed by Shilov.[3] Mechanistic proposals for the Shilov system have focused on the vanadium(II) ions as the sources of charge, with complete reduction of N_2 requiring oxidation of six V(II) ions to V(III). Evidence has been presented that suggests that the divalent metal ions are contained in trimeric units, with adjacent metals bridged by oxygen atoms of catecholate ligands.[26] While no evidence has appeared which indicates that benzoquinone is a product of the Shilov system, the results of the present study suggest that catechol oxidation could also contribute to the reduction process. This provides an alternate source of charge other than oxidation of a large number of metal ions.



Experimental Section

Vanadium hexacarbonyl [$V(CO)_6$] was prepared by literature procedures[27] and was sublimed before use. Vanadyl acetylacetonate [$VO(acac)_2$] was prepared by standard methods[28] and was recrystallized from dichloromethane. Anisole and toluene were dried by distillation over Na/Pb alloy. Methanol was distilled over $MgSO_4$. Other chemicals were obtained from commercial sources and used as received.

$V(CO)_6$ + 3,5-Di-*tert*-butyl-1,2-benzoquinone. Reactions were carried out under inert conditions by using standard Schlenk apparatus. Freshly sublimed $V(CO)_6$ (0.05 g, 0.23 mmol) and 3,5-di-*tert*-butyl-1,2-benzoquinone (0.13 g, 0.70 mmol) were combined in a reaction flask, and 30 mL of toluene was condensed into the vessel. The mixture immediately turned dark blue. This reaction was followed by using EPR spectroscopy with the results described in the Experimental Results section. On the basis of the EPR spectra, formation of $V(3,5\text{-DBSQ})_3$ was essentially quantitative as was formation of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ in the presene of small amounts of oxygen. Upon reduction of the solvent volume, crystals of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ formed as the toluene solvate. Loss of solvent prevented precise chemical analyses, but the compound was found to be isostructural with $[MoO(3,5\text{-DBCat})_2]\cdot C_6H_5CH_3$ by using crystallographic methods.

Table III. Intramolecular Bond Distances (Å) and Angles (deg) for $[VO(O_2C_6H_2(t\text{-Bu})_2)_2]_2$

	Distances from the V Atom		
V–O(1)	2.267 (4)	V–O(4)	1.987 (5)
V–O(2)	1.827 (4)	V–O(5)	1.581 (4)
V–O(3)	1.975 (5)	V–O(1)'	1.956 (5)
		V–V'	3.333 (3)
	Angles about the V Atom		
O(1)–V–O(1)'	76.0 (2)	O(2)–V–O(5)'	99.4 (2)
O(1)–V–O(2)	76.3 (2)	O(2)–V–O(1)	103.1 (2)
O(1)–V–O(3)	82.0 (2)	O(3)–V–O(4)	78.2 (2)
O(1)–V–O(4)	82.8 (2)	O(3)–V–O(5)	103.4 (2)
O(1)–V--O(5)	173.0 (2)	O(3)–V–O(1)'	153.6 (2)
O(2)–V–O(3)	85.3 (2)	O(4)–V–O(5)	102.6 (2)
O(2)–V–O(4)	155.0 (2)	O(4)–V–O(1)'	84.7 (2)
		O(5)–V–O(1)'	99.9 (2)
	Bond Distances within the Bridging 3,5-Di-*tert*-butylcatecholate Ligand		
O(1)–C(1)	1.349 (7)	C(3)–C(4)	1.39 (1)
O(2)–C(2)	1.359 (7)	C(4)–C(5)	1.39 (1)
C(1)–C(6)	1.40 (1)	C(5)–C(6)	1.35 (1)
C(1)–C(2)	1.39 (1)	C(3)–C(7)	1.55 (1)
C(2)–C(3)	1.38 (1)	C(5)–C(11)	1.59 (1)
	Angles within the Bridging 3,5-Di-*tert*-butylcatecholate Ligand		
V–O(1)–V'	104.0 (2)	C(2)–C(1)–C(6)	121.0 (7)
V–O(1)–C(1)	105.7 (4)	O(2)–C(2)–C(1)	114.6 (6)
V–O(2)–C(2)	120.0 (4)	O(2)–C(2)–C(3)	124.9 (6)
O(1)–C(1)–C(2)	116.1 (6)	C(1)–C(2)–C(3)	120.5 (6)
O(1)–C(1)–C(6)	122.8 (6)		
	Bond Distances within the Chelated 3,5-Di-*tert*-butylsemiquinone Ligand		
O(3)–C(16)	1.322 (8)	C(18)–C(19)	1.48 (1)
O(4)–C(15)	1.292 (8)	C(19)–C(20)	1.37 (1)
C(15)–C(16)	1.44 (1)	C(20)–C(15)	1.38 (1)
C(16)–C(17)	1.37 (1)	C(17)–C(21)	1.50 (1)
C(17)–C(18)	1.37 (1)	C(19)–C(25)	1.53 (1)
	Angles within the Chelated 3,5-Di-*tert*-butylsemiquinone Ligand		
V–O(3)–C(16)	115.1 (5)	C(15)–C(16)–C(17)	121.7 (8)
V–O(4)–C(15)	117.6 (4)	O(4)–C(15)–C(16)	113.1 (7)
O(3)–C(16)–C(15)	114.8 (7)	O(4)–C(15)–C(20)	123.1 (7)
O(3)–C(16)–C(17)	123.4 (8)	C(16)–C(15)–C(20)	123.7 (8)

$VO(acac)_2$ + 3,5-Di-*tert*-butylcatechol. Methanol (30 mL) was distilled into a mixture of $VO(acac)_2$ (0.27 g, 1.0 mmol) and 3,5-di-*tert*-butylcatechol under an inert atmosphere. The mixture immediately turned dark blue. EPR spectra for both a minor product and $V(3,5\text{-DBSQ})_3$ were observed at this point. Exposure to a small quantity of oxygen resulted in formation of large prismatic crystals of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ over the period of several hours.

$[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ + O_2. Exposure of a toluene solution of $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$ to either pure O_2 or air for a period of 2 days resulted in a marked color change, from intense blue to green, and precipitation of V_2O_5. The solution is EPR inactive, and the only organic species present in solution was found by NMR to be 3,5-di-*tert*-butyl-1,2-benzoquinone.

Physical Measurement. Optical spectra were recorded on a Cary 219 spectrophotometer. Electron paramagnetic resonance spectra were recorded on a Varian E-109 X-band spectrometer using DPPH as the g marker ($g = 2.0037$). Nuclear magnetic resonance spectra were recorded on a Varian E390 spectrometer.

Structure Determination of $[VO(O_2C_6H_2(t\text{-Bu})_2)_2]_2\cdot C_6H_5OCH_3$. Deep blue crystals of $[VO(O_2C_6H_2(t\text{-Bu})_2)_2]_2$ were obtained from an anisole solution under N_2. The crystal selected for data collection was coated with a thin film of amorphous resin to prevent loss of solvent and was mounted on a Syntex $P\bar{1}$ automated diffractometer equipped with a

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J. Am. Chem. Soc. 1983, 105, 2686-2694

Table IV. Dihedral Angles and Least-Squares Planes for $[VO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$

Dihedral Angles

plane 1	plane 2	angle, deg
O(1)-V-O(2)	bridging ligand	24.0
O(3)-V-O(4)	chelating ligand	7.6

Least-Squares Planes

atom	deviation, Å	atom	deviation, Å
Bridging Ligand, $4.52x + 3.90y - 11.02z = +0.48$			
V	−0.646	C(3)	0.005 (7)
O(1)	−0.013 (5)	C(4)	0.018 (8)
O(2)	0.000 (5)	C(5)	−0.007 (8)
C(1)	0.024 (7)	C(6)	0.015 (8)
C(2)	0.004 (7)		
Chelating Ligand, $5.89x - 9.18y + 8.08z = -1.67$			
V	−0.196	C(17)	0.010 (8)
O(3)	−0.002 (5)	C(18)	0.023 (9)
O(4)	0.016 (5)	C(19)	0.011 (8)
C(15)	−0.017 (7)	C(20)	−0.028 (8)
C(16)	−0.021 (7)		

graphite crystal monochromator. The centered settings of 15 reflections were used to calculate the cell constants given in Table I. Data were collected at ambient room temperature out to a 2θ value of 45° by using Mo Kα radiation. Standards monitored during data collection showed no significant variation in intensity.

The structure was solved by using standard heavy-atom procedures. Both the complex molecule and the anisole solvate molecule are located about centers of inversion. This results in disorder of the methoxy group of the solvent. Additionally, one *t*-Bu group of the complex was found to have twofold disorder resulting in six half-atom positions for the methyl carbon atoms. These were treated accordingly. The structure was refined by using programs and procedures described previously.[29] Fixed corrections were applied for the hydrogen atoms of the molecules. The final cycle of refinement converged with $R_F = 0.064$ and $R_{wF} = 0.068$. The standard deviation of an observation of unit weight was 1.84. Final positional and thermal parameters and their estimated standard deviations are listed in Table II. Values of F_o and F_c (×10) are available as supplementary material.

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Registry No. $V(3,5\text{-}DBSQ)_3$, 64020-88-8; $[VO(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]_2$, 84850-87-3; $[VO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2;C_6H_5OCH_3$, 84894-07-5; $V(CO)_6$, 14024-00-1; $VO(acac)_2$, 3153-26-2.

Supplementary Material Available: Tables of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Metal-Metal Multiple Bonds. 10. Electrophilic Additions of Halogens and Hydrogen Halides to the Mo-Mo Triple Bond in $Cp_2Mo_2(CO)_4$[1]

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Abstract: The synthesis of $Cp_2Mo_2(CO)_4(\mu\text{-}Cl)(Cl)$ (**6**), $Cp_2Mo_2(CO)_4(\mu\text{-}H)(\mu\text{-}I)$ (**8**), and $Cp_2Mo_2(CO)_4(\mu\text{-}I)_2$ (**2**) is described. Complex **6** is best prepared from $Cp_2Mo_2(CO)_4$ (**1**) and $PhICl_2$ or HCl in toluene. Complex **8** is formed from **1** and HI. Excess HI converts **8** to the diiodide **2**. Reaction of **2** with aluminum hydrides gives **8**, which in turn reacts to give H_2 and **1**. The XPS of **6** shows two types of chlorine in a 1:1 ratio with $2P_{3/2}$ ionization energies of 198.8 and 197.6 eV consistent with bridging and terminal positions, respectively. The different geometrical isomers that are exhibited by the dihalides are discussed. The structures of **2** and **8** were determined by X-ray crystallography. For **2**, the violet isomer forms crystals in the triclinic system, $a, b, c = 6.882$ (1), 10.196 (2), 6.856 (1) Å; $\alpha, \beta, \gamma = 86.08$ (1), 113.83 (1), 102.52 (1)°, $V = 429.5$ (1) Å^3, $Z = 1$, space group $P\bar{1}$, ρ(calcd) = 2.62 g/cm^3. The structure was refined with 1702 reflections with $I > 3\sigma(I)$. The final R values are $R_1 = 0.027$, $R_2 = 0.039$. Some selected interatomic distances are Mo–I = 2.853 (1) Å, Mo···Mo = 4.441 Å, and I···I = 3.581 (1) Å. Selected bond angles are IMoI = 77.76 (2)° and MoIMo = 102.24 (2)°. The HI adduct, **8**, crystallizes in the monoclinic system: $a, b, c = 9.321$ (3), 15.131 (6), 11.394 (4) Å; $\beta = 97.94$ (3)°; $V = 1592$ (1) Å^3, $Z = 4$, space group = $P2_1/n$, ρ(calcd) = 2.25; ρ(obsd) = 2.34 g/cm^3. The structure was refined with 2647 reflections with $I > 3\sigma(I)$ to final R values of $R_1 = 0.063$ and $R_2 = 0.073$. The bridging hydrogen was not located. Selected interatomic distances (Å) and bond angles follow: Mo–Mo = 3.310 (2), Mo–I = 2.760 (**1**); MoIMo = 73.70 (4), IMoMo = 53.15 (av). The nature of the bridging $Mo(\mu\text{-}H)(\mu\text{-}X)Mo$ system is discussed in an EHMO framework, and the significant tilt of the Cp groups is ascribed to a trans influence propagated in the σ(Mo–CO) and π(Mo–Cp) bonding orbitals.

The discovery of the reactivity patterns of metal–metal multiple bonds is an area of considerable current interest.[2,3] The two compounds that have received the most attention in this regard are $Cp_2Mo_2(CO)_4$[2a] and Mo_2X_6 (X = OR, NR_2).[2b] Both of these complexes add nucleophiles and both undergo two-center oxidative addition reactions. The reaction of M≡M triple bonds with halogens and hydrogen halides is of special interest. This interest derives from two sources. First, halogenations and hydrohalogenations of carbon–carbon multiple bonds are important reactions since new functional groups are introduced while the carbon–carbon skeleton is maintained. The resulting halides are in turn useful precursors to a variety of compounds. Can metal–metal multiple bonds serve as inorganic functional groups in the same fashion? Second, the reactivity of dimetal centers, especially multiply bonded centers, has not been systematized,

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