hexadienyl ligand,[17a,b,d–g] were present in spectra of [NEt$_4$]3-d_1 and absent from those of [NEt$_4$]3-d_6.[20]

It was initially unclear whether electrophilic addition to 2^{2-} could be extended to carbon-based electrophiles. We have, however, observed that K$_2$2 (freshly prepared from 0.15 g, 0.7 mmol of **1**) reacts with 1 mol-equiv of PhCH$_2$Cl (80 μL) in THF at −78 °C (Scheme I) to give, at room temperature, a species with carbonyl absorptions at 1890 vs, 1792 s, and 1742 s cm^{-1} similar to those of 3$^-$. Addition of [Et$_4$N]Br (0.15 g, 0.7 mmol) at room temperature gave, after 30 min, a suspension from which yellow flakes of the η^5-cyclohexadienyl salt [NEt$_4$][Cr(η^5-C$_6$H$_6$CH$_2$Ph)(CO)$_3$] ([NEt$_4$]4—0.12 g, 0.27 mmol ≡ 40%)[21] were obtained after the solvent was removed under vacuum, the solid was washed with diethyl ether (2 × 50 mL) and redissolved in THF (10 mL), and diethyl ether (50 mL) was added to the filtered solution to crystallize the product.

The spectroscopic characteristics of 4$^-$ establish that the benzyl group is exo, suggesting that the electrophilic carbon reacted directly with the free double bond of 2^{2-}. Thus the ^{1}H NMR spectrum contains a δ 2.45 absorption with the 6-Hz coupling to the vicinal proton characteristic of an endo cyclohexadienyl proton, and the IR spectrum of a KBr pellet of [NEt$_4$]4 did not contain a C–H$_{exo}$ band at 2790 cm^{-1}. Conversely, the IR spectrum of [NEt$_4$][Cr(η^5-C$_6$D$_6$CH$_2$C$_6$H$_5$)(CO)$_3$] (obtained by addition of benzyl chloride to [Cr(η^4-C$_6$D$_6$)(CO)$_3$]$^{2-}$) contained a C–D$_{endo}$ absorption at 2175 cm^{-1} (see data in footnote 18). Although it is reasonable that indirect addition should be unique to the sterically undemanding proton, the observation of both endo and exo addition contrasts with results for isoelectronic Mn complexes: both protonation and electrophilic alkylation of dienes and arenes in [Mn(CO)$_3$]$^-$ complexes are metal mediated and give endo products,[22] while protonation and methylation of [Mn(cyclooctatetraene)(CO)$_3$]$^-$ give exo adducts.[23]

Although 3$^-$ is the parent of a large class of cyclohexadienyl complexes of [Cr(CO)$_3$], neither this nor 4$^-$ have been previously reported, and neither can be prepared by nucleophilic attack on **1**. The generality of the alkylation reaction remains to be established, but our results do establish that electrophilic addition to 2^{2-} provides an alternative route to cyclohexadienyl complexes of [Cr(CO)$_3$] which may significantly extend the established utility of these species as intermediates in organic synthesis.

(20) A three band pattern at 2105 m, 2080 m, 2050 m cm^{-1} was observed in spectra of [NEt$_4$]3-d_6. The 2080-cm^{-1} absorption would correspond to ν_{CH}/ν_{CD} = 1.34, in agreement with expectations. The complexity of the absorptions may reflect activation of combination or overtone bands by Fermi resonance.

(21) ν_{CO} (THF) 1890 vs, 1792 s, 1763 s cm^{-1}; ^{1}H NMR (500 MHz CD$_3$CN) δ 7.15-6.98 (m, 5, phenyl), 5.08 (t of t, $J_{H_a-H_b}$ = 5.5 Hz, $J_{H_a-H_c}$ = 1.2 Hz, 1, H$_a$), 4.48 (d of d, $J_{H_b-H_a}$ = 5.5 Hz, $J_{H_b-H_c}$ = 6.5 Hz, 2, H$_b$), 2.47 (d of d, $J_{H_c-H_b}$ = 6.5 Hz, $J_{H_c-H_{endo}}$ = 5.7 Hz, 2, H$_c$), 2.43 (t of t of t, $J_{H_{endo}-H_c}$ = 6.7 Hz, $J_{H_{endo}-H_c}$ = 5.7 Hz, $J_{H_{endo}-H_b}$ = 1.0 Hz, 1, H$_{endo}$), 1.85 (d, $J_{H_c-H_{endo}}$ = 6.7 Hz, 2, H$_c$); ^{13}C NMR (125 MHz, CD$_3$CN, gated ^{1}H decoupling) δ 224.1 (s, CO), 140.9, 130.2, 128.9, 126.1 (phenyl), 96.7 (d, J = 156 Hz, C$_b$), 76.9 (d, J = 170 Hz, C$_a$), 53.9 (d, J = 163 Hz, C$_c$), 50.4 (t, J = 129 Hz, CH$_2$), 40.3 (d, J = 135 Hz, C$_d$). NMR spectra contain resonances, with appropriate intensity, characteristic of the tetraethylammonium counterion. Anal. Cald for C$_{24}$H$_{33}$CrNO$_3$: C, 66.20; H, 7.58. Found (Dornis und Kolbe, West Germany): C, 65.84; H, 7.73.

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Highly Oxidizing Organometallics: The Preparation of Magnetic Charge Transfer Salts Derived from (MeCp)VCl$_3$

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High oxidation state organometallic compounds have recently commanded much attention because of their structural properties, their catalytic applications, and their stabilization of bare main group ligands. It is striking, however, that few high oxidation state organometallics are *oxidizing*. This is due to the fact that the most actively studied species feature third-row metals and strong π-donor oxo ligands.[1] The complex (MeCp)VCl$_3$ is unusual in this regard as it is indeed a rare example of a highly oxidizing organometallic complex. In this paper we describe the exploitation of the oxidizing power of (MeCp)VCl$_3$ for the preparation of some unusual organometallic charge transfer salts.[2]

The compound, (MeCp)VCl$_3$, **1**, has the remarkably positive reduction potential of +425 mV (versus Ag/AgCl).[3,4] Under *strictly* anhydrous conditions this couple is reversible as is the (MeCp)VCl$_3^{0/+}$ couple at 1690 mV.[5] Compound **1** appears to be among the most strongly oxidizing *neutral* organometallic complexes known.

The interaction of **1** with the organic donor tetramethyltetrathiafulvalene[6] (TmTTF) was studied. When this reaction is conducted at 1:1 stoichiometry in CH$_2$Cl$_2$ solution, we observed the precipitation of black microcrystalline [TmTTF]$_x$[(MeCp)-VCl$_3$]. Slow recrystallization of this material from CH$_2$Cl$_2$ gave two pure species. The less soluble material analyzes as [TmTTF][(MeCp)VCl$_3$] (**2**).[7] The cyclic voltammogram of **2** in CH$_2$Cl$_2$ consists of several reversible processes and is not the superposition of the CVs for **1** and TmTTF.[8] These results will be described in detail in the full report.

A single-crystal X-ray diffraction study[9] of **2** reveals that the TmTTF$^+$ subunits assemble as a zigzag chain of TmTTF pairs (Figure 1). The interlamenar distances are extremely short at ca. 3.35 Å (cf. α-graphite, 3.354 Å[10]) and are substantially shorter

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(8) Cyclic voltammetry data (E_p (mV) versus Ag/AgCl, 10^{-1} M TBAHFP, 10^{-3} M complex, n(e$^-$) from i_p versus $\nu^{1/2}$): (MeCp)VCl$_3^{0/-}$, E^{ox} ≃ 455, E^{red} ≃ 395; TmTTF$^{0/+}$, E^{ox} ≃ 320, E^{red} ≃ 260; **2**, E^{ox} ≃ 315 (n = 1), E^{ox} ≃ 435 (n = 1), E^{red} ≃ 255 (n = 2).

(9) [TmTTF][(MeCp)VCl$_3$]: opaque plate 0.1 × 0.2 × 0.4 mm, $P2_1/c$, a = 8.310 (2) Å, b = 10.112 (8) Å, c = 24.035 (5) Å, β = 91.90 (2)°, V = 2018 (2) Å^3, and ρ_{calcd} = 1.635 g/cm^3 for Z = 4. Enraf-Nonius CAD4 automated κ-axis diffractometer, 25 °C, Mo Kα 3.0 < 2θ < 46.0° (±h–k–l), 3206 reflections (2802 unique, R_i = 0.024, 1343 observed, I > 2.581(I)); corrected for anomalous dispersion, absorption (maximum and minimum numerical transmission factors, 0.926 and 0.766, for μ = 12.73 cm^{-1}), Lorentz and polarization effects. Solution SHELXS-86 (all but Cp ring atoms) and difference Fourier syntheses. H atoms were fixed in "idealized" positions, but the remaining atoms were independently refined (SHELX). R = 0.058 and R_w = 0.061.

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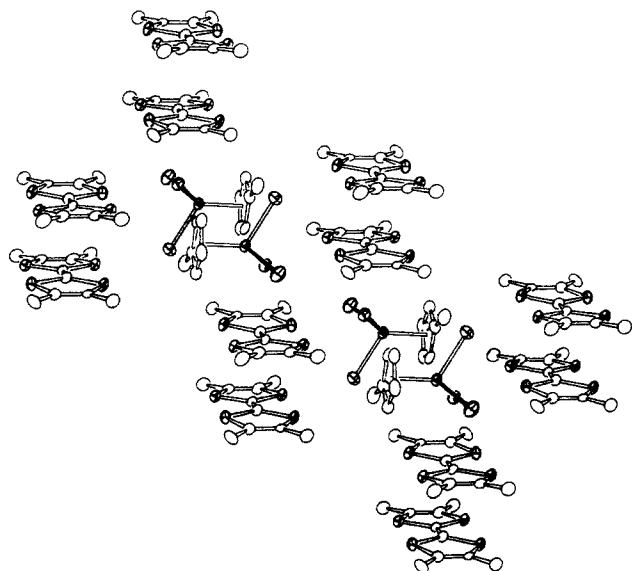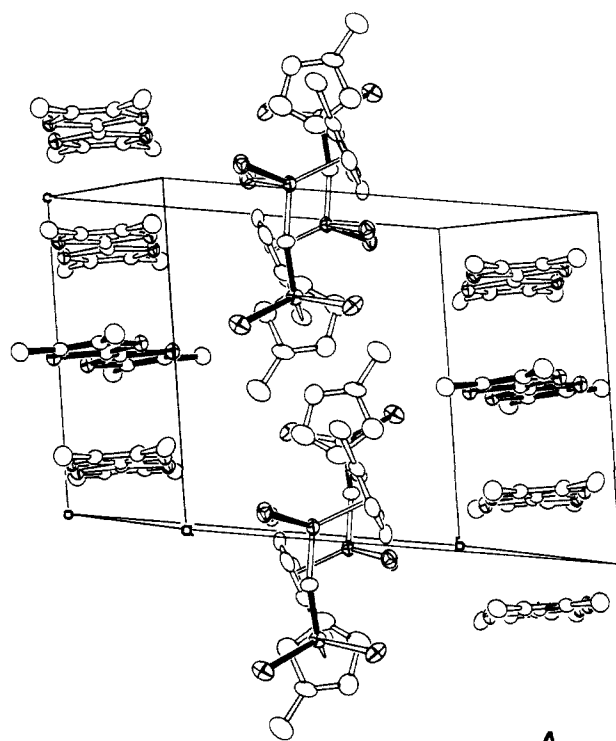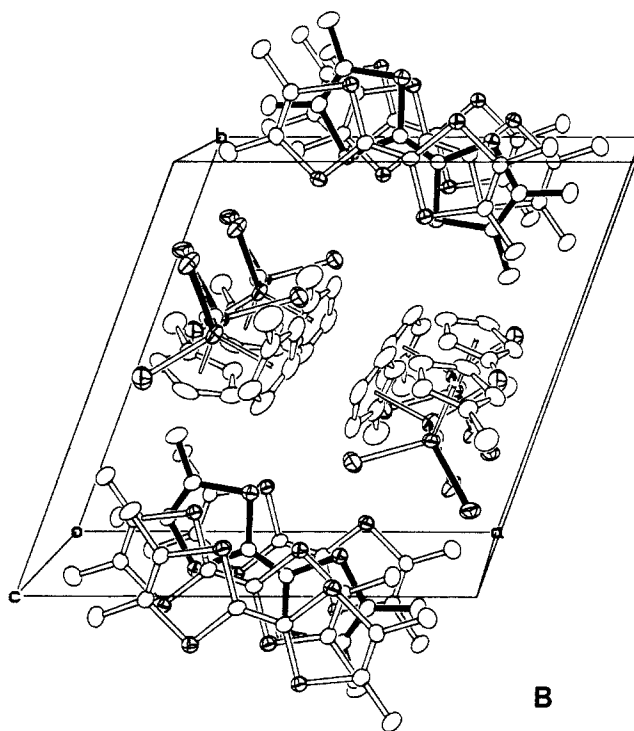
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Figure 1. The structure of [TmTTF][(MeCp)VCl₃]. The view is along the *b–c* diagonal.

than other partially oxidized TmTTF derivatives (e.g., [TmTTF]₂X, ∼3.5 Å).[11] The short anion–cation contacts[12] may be responsible for the contracted interlamenar distances: the shortest V–Cl bond is directed toward three sulfur atoms, with Cl···S distances of 3.479 (5) to 3.683 (5) Å. The (MeCp)VCl₃⁻ species are situated in pockets defined by the TmTTF pairs. The V–Cl distances in the salt are all ∼0.11 Å longer than found for (MeCp)VCl₃. Magnetic susceptibility measurements indicate that **2** has an effective magnetic moment at 300 K of μ_{eff} = 3.04 μ_B which slowly decreases until apparent spin-pairing occurs at ca. 30 K. The magnetic susceptibility of **2** is field independent from 100 G to 48 kG.

Attempts to grow crystals of [TmTTF]₂(MeCp)VCl₃ resulted in crystals of [TmTTF]₃[{(MeCp)VCl₂}₂(μ-O)]₂ (**3**).[13] This fascinating species, which apparently arises by partial oxygenation of the 2:1 salt, is comprised of a partially oxidized stack of TmTTF together with a mixed-valence bimetallic anion (Figure 2). The lattice is comprised of layers of TmTTF stacks separated by (MeCp)₂V₂Cl₄O⁻ units. The TmTTF chains exhibit a periodicity such that every third TmTTF molecule is tilted by 3° relative to the stacking vector. The oxo-bridged divanadium anion is unsymmetrical with V–O distances of 1.772 (4) and 1.833 (4) Å.[14] In this case the interlamenar distances between the TmTTF units are normal at 3.56 (1) Å. Preliminary magnetic susceptibility measurements indicate **3** has a highly coupled magnetic system.[15] At a field of 10 KG, **3** exhibits a temperature independent magnetic moment of 3.65 μ_B (per [(MeCp)₂V₂Cl₄O][TmTTF]₃/₂) down to 20 K, whereupon a ferromagnetic transition occurs, resulting in μ_{eff} = 3.9 μ_B at 5 K. The magnetic moment of **3** is field dependent below 20 K. A single-crystal two-probe conductivity[16] measurement along the *c* axis (TmTTF-stacking vector)

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(13) [TmTTF]₃[{(MeCp)VCl₂}₂(μ-O)]₂: opaque green crystal 0.2 × 0.5 × 0.6 mm, P1̄ (av of normalized structure factors and successful refinement), *a* = 12.984 (5) Å, *b* = 13.154 (4) Å, *c* = 10.770 (4) Å, *α* = 98.45 (3)°, *β* = 93.56 (3)°, *γ* = 70.22 (3)°, *V* = 1712 (1) Å³ and ρ_{calcd} = 1.568 g/cm³ for Z = 1. Syntex P2₁ automated four-circle diffractometer, 25 °C, Mo Kα 3.0 < 2θ < 50.0° (±h±k+l), 6661 reflections (6058 unique, R_i = 0.032, 4034 observed, I > 2.58σ(I)); corrected for anomalous dispersion, absorption (maximum and minimum numerical transmission factors, 0.759 and 0.479, for μ = 12.18 cm⁻¹), Lorentz and polarization effects. MULTAN-81 located V, Cl, and S atoms. H atoms were fixed in "idealized" positions, and remaining atoms were independently refined. R = 0.050 and R_w = 0.059.

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A

B

Figure 2. Two views of the structure of [TmTTF]₃[(MeCp)₂V₂Cl₄O]₂, the unit cell is indicated (A) down the *a* axis end-on to the TmTTF units and (B) down the *c* axis, the stacking direction.

indicates this compound is a semiconductor (E_g = 0.54 eV; 5.1 × 10⁻⁶ Ω⁻¹ cm⁻¹ at 300 K) with a slightly decreased band gap at lower temperatures.

To summarize, we have shown the oxidizing power of certain high oxidation state organometallics can be exploited for the

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preparation of a new class of charge-transfer salts.[17]

Registry No. 1, 111005-01-7; **2,** 113378-54-4; **3,** 113403-22-8; TmT-TF, 50708-37-7.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for 2 and 3 (8 pages); tables of observed and calculated structure factors for 2 and 3 (23 pages). Ordering information is given on any current masthead page.

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^{13}C NMR and Polarized IR Spectra of Vicinally Labeled [[13]C2]Cyclobutadiene in an Argon Matrix: Interconversion of Valence Tautomers

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We report the polarized IR spectrum of cyclobutadiene (1) aligned by photoselection and the static ^{13}C NMR spectrum of vicinally ^{13}C-dilabeled 1 in argon matrix. The rate of interconversion between [1,2-[13]C2]-1 (1A) and [1,4-[13]C2]-1 (1B) exceeds 10^3 s^{−1} at ~25 K.
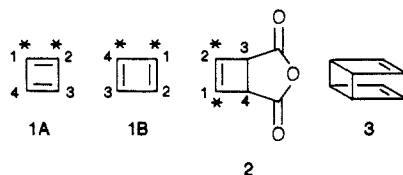
Cyclobutadiene[2] was initially assigned D_{4h} symmetry on the basis of its matrix-isolation IR spectrum,[3,4] in disagreement with most early[5-8] and all recent[9-12] calculations which predict a D_{2h} singlet ground state. Additional IR experiments led to the conclusion that the ground state is in fact rectangular.[13]

Heavy-atom tunneling has been proposed[14] to rationalize the activation parameters for valence tautomerization deduced from

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Table I. Typical Orientation Factors of IR Transitions of Photoaligned Rare-Gas Matrix-Isolated Cyclobutadiene (1)

sym	pol[a]	argon (10 K) $\bar{\nu}$ (cm^{−1})	argon (10 K) K_u[b]	neon (2.8 K) $\bar{\nu}$ (cm^{−1})	neon (2.8 K) K_u[b]
b3u	x	576	0.379	576	0.365
b2u	y	721	0.297		
b2u	y	1245	0.298	1244	0.311
b1u	z	1526	0.290	1527	0.310
b2u[c]	y	3107	0.294		
b1u[c]	z	3124	0.292		

[a] x is the out-of-plane axis, and y is the short and z the long inplane axis. [b] $K_u = \langle\cos^2 \tilde{u}\rangle$, where $u = x, y,$ or $z,$ $\tilde{u}$ is the angle between the molecular axis u and the laboratory axis $Z,$ and the pointed brackets indicate ensemble averaging. The accuracy of the experimental determination from $K_u = d_u/(d_u + 2)$ was about ±0.01; $d_u = E_Z/E_Y,$ where E_Z (E_Y) is the absorbance of light polarized along Z (Y).[21] [c] Assigned on the basis of calculated intensities.
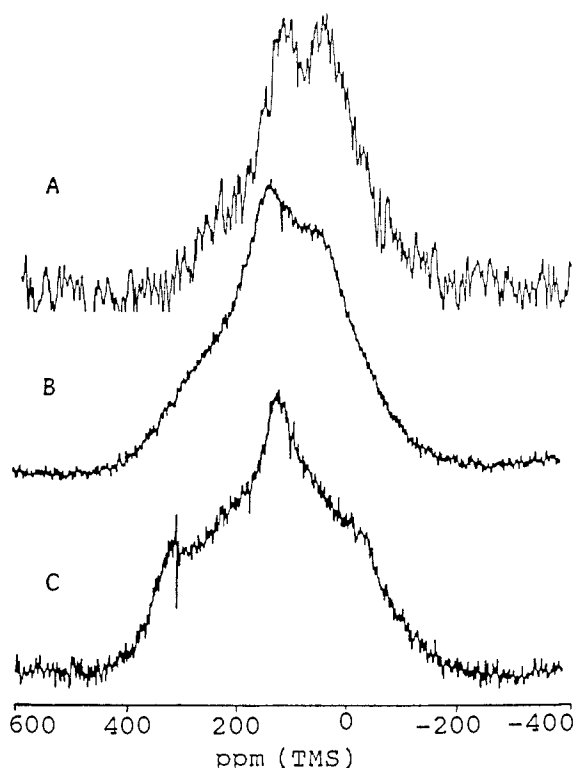
Figure 1. Experimental ^{13}C NMR spectra of (A) cyclobutadiene (1) ^{13}C-labeled in vicinal positions, (B) mixture of isotopomeric labeled cyclobutadiene dimers (3), and (C) [1,2-[13]C2]cyclobutene-3,4-dicarboxylic anhydride (2).

solution-trapping experiments[15,16] on vicinally dideuteriated 1. Calculations[17,18] have yielded tunneling rates of 10^5-10^{11} s^{−1} at −10 °C.

We have used the anhydride 2[19] as a photochemical source[20] of rare-gas matrix-isolated 1. UV irradiation with linearly polarized light produced persistent linear dichroism in the IR bands of argon matrix-isolated 1 and of its overirradiation product, C_2H_2. Persistent partial alignment was also observed for CO_2 produced from 2 with linearly polarized light. In neon matrices, alignment was observed only for 1. Under a variety of conditions, including temperatures as low as 2.8 K in Ne and 3.2 K in Ar, and a

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