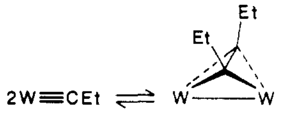
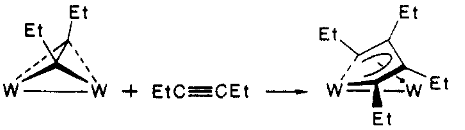
Alkyne metathesis, which is known for $(t\text{-BuO})_3W{\equiv}CR$ compounds,[9] involves the reversibility of (6i) and would be terminated by (6ii).



(7i)



(7ii)

Evidence for equilibria involving tungsten alkylidynes and ditungstatetrahedra supported by alkoxide ligands, (7i), has previously been noted,[10] as has the coupling reaction (7ii).[7]

Reactions between I and C_2H_2, 2 equiv (also in separate experiments $^*C_2H_2$, 2 equiv, where *C represents 92 mol % ^{13}C), show formation of $W_2(\mu\text{-}C_4Et_2H_2)(\eta^2\text{-}C_2H_2)(O\text{-}i\text{-}Pr)_6$ in which the carbon atoms of the ethyne are scrambled over all four sites of the μ-C_4 ring, as might have been anticipated for a reversible reaction, (6i), followed by either (6ii) or (7).

Further studies are in progress.[11]

Registry No. I, 104240-17-7; II, 104215-35-2; III, 104240-18-8; $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$, 104215-36-3; $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5; EtC≡CEt, 928-49-4.

Supplementary Material Available: A summary of data collections, tables of program MU output, crystal and diffractometer data, fractional coordinates, anisotropic temperature factors, and bond distances and angles, a listing of standard data type, and figures of VERSORT drawings, ORTEP drawings, space-filling-model drawings, and a plot of standards (35 pages); a list of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(7) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6806.

(8) Chisholm, M. H.; Conroy, B. K.; Huffman, J. C., unpublished results.

(9) Schrock, R. R.; Sancho, J. *J. Mol. Catal.* **1982**, *15*, 75. Schrock, R. R. *ACS Symp. Ser.* **1983**, *No. 24*, 369.

(10) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794. Chisholm, M. H.; Conroy, B. K.; Huffman, J. C.; Marchant, N. S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 446.

(11) We thank the National Science Foundation and the Wrubel Computing Center for support.

Synthesis, Structure, and Electrical Properties of $[(MeCp)_5V_5S_6][(TCNQ)_2]$

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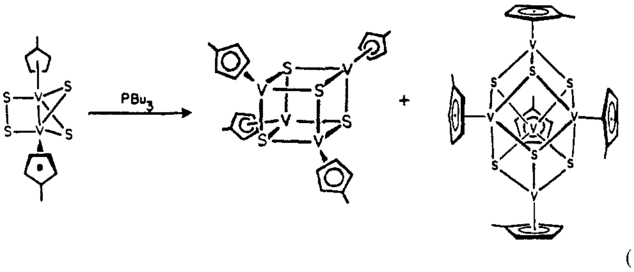
Summary: Desulfurization of $(MeCp)_2V_2S_4$ with PBu_3 gives $(MeCp)_4V_4S_4$ (**1**) and $(MeCp)_5V_5S_6$ (**2**). Compounds **1** and **2** were characterized by ^1H NMR spectroscopy and mass spectrometry. Compound **2** forms the charge-transfer salt [**2**]$[(TCNQ)_2]$ which was characterized by X-ray crystallography as its CH_2Cl_2 solvate. The cluster consists of a trigonal-bipyramidal V_5 core inside of a trigonal prism of six sulfur atoms. Four-probe conductivity measurements show that [**2**]$[(TCNQ)_2]$ is a *n*-type semiconductor ($E_g \approx 0.25$ eV).

We wish to describe the synthesis and characterization of $(MeCp)_5V_5S_6$ (MeCp = η^5-$CH_3C_5H_4$). This work provides some insights into how cyclopentadienyl metal chalcogenide clusters form from simple precursors. Furthermore our structural work establishes the presence of unusual intracluster sulfur–sulfur interactions. These results are supplemented by electrical measurements on $[(MeCp)_5V_5S_6][(TCNQ)_2]$.

The addition of tributylphosphine to a solution of $(MeCp)_2V_2S_4$[1] results in the rapid formation of the phosphine sulfide and two black compounds which were separated by sublimation at 150 °C (0.03 mmHg) (eq 1). The more volatile species is $(MeCp)_4V_4S_4$ (**1**). This 56e cubane was obtained in ca. 40% yield and was fully characterized.[2,3] The less volatile product of the desulfurization reaction is the weakly paramagnetic $(MeCp)_5V_5S_6$ (**2**).[4] The ^1H NMR spectrum of **2** is consistent with a trigonal-bipyramidal cluster as two sets of MeCp resonances are observed in a 2:3 ratio. The structure of a derivative of **2** lends credence to this assignment (*vide infra*) as does Bottomley's recent structural characterization of the closely related compounds $Cp_5Ti_5S_6$ and $Cp_5V_5O_6$.[5] In contrast to the present work, Bottomley's clusters were prepared from monometallic precursors and sources of atomic sulfur (H_2S) and oxygen (N_2O).



(1)

The formation of **1** and **2** occurs via an aggregation process induced by desulfurization of the V_2S_4 precursor. This aggregation is analogous to the well-known clusterification of metal carbonyls induced by decarbonylation.[6]

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(1) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6321.

(2) Many details can be found in C. M. Bolinger's Ph.D. Thesis (University of Illinois at Urbana-Champaign, 1984). The structures of $(MeCp)_4V_4S_4$ and its cation have been determined by Professor A. L. Rheingold at the University of Delaware and will be discussed in a full report of the V_4S_4 chemistry (Boyd, P. D. W.; Darkwa, J.; Rauchfuss, T. B.; Rheingold, A. L., in preparation). The reaction of *t*-BuSH and $(MeCp)_2V$ also gives $(MeCp)_4V_4S_4$: Eremenko, I. L.; Pasynskii, A. A.; Katugin, A. S.; Ellert, O. G.; Shkloyer, V. E.; Struchkov, Yu. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1669.

(3) Anal. Calcd for $C_{24}H_{28}S_4V_4$: C, 44.65; H, 4.35; V, 31.42. Found: C, 44.60; H, 4.44, V, 31.42. ^1H NMR ($CDCl_3$ solution): δ 59.2 ($\Delta\nu_{1/2}$ = 72 Hz), 58.4 (72 Hz), 7.6 (14 Hz). EIMS (*m/e*): 648, M^+; 569 $(M - MeCp)^+$; 490 $(M - 2MeCp)^+$; 411 $(M - 3MeCp)^+$; 332 $(M - 4MeCp)^+$.

(4) Anal. Calcd for $C_{30}H_{35}S_6V_5$: C, 42.76; H, 4.19. Found: C, 42.85; H, 4.36. ^1H NMR ($CDCl_3$): δ 5.18 (130 Hz), 4.72 (94 Hz), 2.09 (13 Hz), 1.86 (5 Hz). The yield of **2** was typically 10%. The $\mu_{eff} = 0.98\ \mu_B$ (uncorrected).

(5) $Cp_5V_5O_6$: Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 5651. $Cp_5Ti_5S_6$: Bottomley, F.; Egharevba, G. O.; White, P. S. *J. Am. Chem. Soc.* **1985**, *107*, 4353.

(6) For an example see Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* 1976, *98*, 7433.

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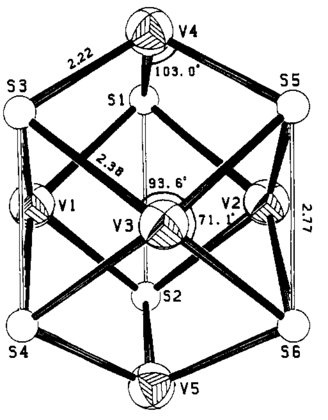

Figure 1. Schematic view of the metal sulfur core in [2][(TCNQ)$_2$]. Two types of short V–V distances are observed: V(apical)–V(equatorial) = 2.97–3.01 Å and V(equatorial)–V(equatorial) = 3.21–3.25 Å.

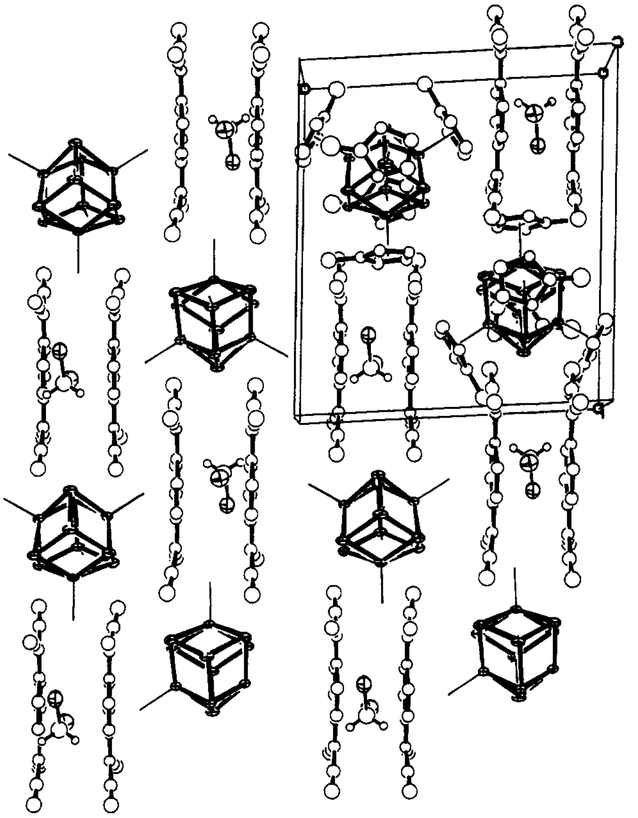

Figure 2. ORTEP packing diagram of [2][(TCNQ)$_2$] viewed along the *c* axis and showing the unit cell; selected MeCp groups were omitted for clarity.

Desulfurization of a 1:1 mixture of (MeCp)$_2$V$_2$S$_4$ and Cp$_2$V$_2$S$_4$ gave all five Cp$_{4-x}$(MeCp)$_x$V$_4$S$_4$ products as assayed by electron-impact mass spectrometry. On the basis of this result, it appears that the (RCp)$_2$V$_2$S$_x$ unit does *not* remain intact during the desulfurization–aggregation process as is also indicated by the formation of **2**. It is also mechanistically significant that **2** is not further reactive toward phosphines. Furthermore, it appears that the V$_4$ cluster **1** is not a precursor to **2**.[7] We recently reported a similar aggregation process whereby (C$_5$Me$_4$Et)$_2$Ru$_2$S$_4$ is converted into (C$_5$Me$_4$Et)$_4$Ru$_4$S$_6$ upon treatment with phosphines.[8]

The cyclic voltammogram of **2** shows three waves at 1393 (irrev), 546 (i_a/i_c = 1.0), and −367 mV (i_a/i_c = 1.2) vs. Ag/AgCl.[9] The rich redox properties of **2** led us to attempt the preparation of charge-transfer salts. An increasing number of organometallic compounds have been shown to form electrically and magnetically interesting charge-transfer salts[10] although this approach has not been extended to metal sulfide clusters.[11] Treatment of toluene solutions of **2** with 1 or 2 equiv of tetracyanoquinonedimethane (TCNQ) leads to the precipitation of glistening dark green crystals analyzing as [**2**][(TCNQ)$_2$].[12]

Needles of [**2**][(TCNQ)$_2$]·CH$_2$Cl$_2$ were grown from CH$_2$Cl$_2$–hexane solutions. A single-crystal X-ray diffraction study[13] confirmed the V$_5$ core in [**2**][(TCNQ)$_2$] is trigonal bipyramidal wherein each face is capped by triply bridging sulfur atoms (Figure 1). The anions occur as cofacial pairs normal to the *a* axis, with a minimum interplanar distance of 3.37 (1) Å and dihedral angle of 0.7° (Figure 2). The closest anion–cation contacts exist between nitrogen atoms of the TCNQ moieties and Cp hydrogen atoms (2.6 Å for six contacts based on "idealized" hydrogen positions). The vanadium centers on the pseudo C$_3$ axis have short V–S contacts of 2.22 (1) Å which are indicative of multiple V–S bonding.[1,14] The three equatorial vanadium centers feature normal V–S distances of 2.38 (1) Å. More striking however are the S···S distances, three of which are much shorter than the V···V contacts. The sulfur atoms are arrayed in pairs parallel with the C$_3$ axis of the cluster core, and the S···S distances within these pairs average 2.77 (4) Å. This value is comparable to the transannular distances seen in S$_8^{2+}$ (2.83 Å)[15] These distances are intermediate between normal S–S bonds (2.00–2.15 Å) and the sum of the van der Waals radii (3.60 Å).[16] Such interactions indicate that the valence molecular orbitals feature substantial S–S bonding character. Thus, the V$_5$S$_6$ core in [**2**][(TCNQ)$_2$] is held together by a combination of V–S, V–V, *and* S–S bonds. Other examples

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[7] Many control experiments were conducted. Thermolysis of **1** at 120 °C does not give **2**. Compound **1** and (MeCp)$_2$V$_2$S$_4$ appear to react to give a charge-transfer salt, but **2** is not formed. Pure Cp$_2$(MeCp)$_2$V$_4$S$_4$ has been prepared in separate experiments.[2] The EI mass spectrum of a 1:1 mixture of **1** and Cp$_4$V$_4$S$_4$ shows *no* evidence of Cp–MeCp scrambling.

[8] Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114.

[9] Measured on 10^{-3} M CH$_2$Cl$_2$ solutions (10^{-1} M Bu$_4$NPF$_6$) with a Pt disk working electrode using a BAS-100 electrochemical analyzer. Under our conditions, the $E_{1/2}$ for Cp$_2$Fe was found at +500 mV.

[10] For a review of metal complex salts of TCNQ see: Endres, H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983. Some more recent developments: Lequan, R.-M.; Lequan, M.; Jaoven, G.; Ovahab, L.; Batail, P.; Padiou, J.; Sutherland, R. G. *J. Chem. Soc., Chem. Commun.* **1985**, 116. Inoue, M.; Inoue, M. B. *Inorg. Chem.* **1986**, *25*, 37.

[11] We are aware of only one cluster–TCNQ salt: Goldberg, S. Z.; Spivak, B.; Stanley, G.; Eisenberg, R.; Braitsch, D. M.; Miller, J. S.; Abkowitz, M. *J. Am. Chem. Soc.* **1977**, *99*, 110.

[12] Anal. Calcd for C$_{54}$H$_{43}$N$_8$S$_6$V$_5$: C, 51.84; H, 3.46; N, 8.96. Found: C, 51.73; H, 3.62; N, 8.52. The yield of [**2**][(TCNQ)$_2$] was 65%.

[13] [(MeCp)$_5$V$_5$S$_6$][(TCNQ)$_2$] crystallized in the centrosymmetric triclinic space group $P\bar{1}$ with a = 14.306 (2) Å, b = 15.999 (10) Å, c = 11.938 (3) Å, α = 95.62 (4)°, β = 93.69 (2)°, γ = 86.02 (3)°, and Z = 2. Diffraction data (graphite-monochromated Mo radiation, $\lambda(K\alpha)$ = 0.71073Å, $2 < 2\theta < 46°$, $\pm h,-k,\pm l$) were collected at room temperature on an Enraf-Nonius CAD4 diffractometer and were numerically corrected for absorption (transmission range 0.954–0.833). The number of independent reflections was 7504, 4004 of which were observed ($I > 2.58\sigma(I)$). The structure was solved by direct methods (MULTAN) and difference Fourier synthesis. One dichloromethane solvate molecule was located. The vanadium, chlorine, and sulfur atoms were refined with anisotropic thermal coefficients; the remaining non-hydrogen atoms were isotropically refined. Hydrogen atoms were fixed in "idealized" positions. The highest peaks in the final difference Fourier map (less than 1 e/A^3) indicated a minor disorder in the Cp ring carbon atom positions. Final agreement factors were R = 0.063 and R_w = 0.067.

[14] Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 7800.

[15] Gillespie, R. J. *Chem. Soc. Rev.* **1979**, *8*, 315.

[16] An excellent discussion of the structural chemistry of relevant, simple sulfur compounds can be found in: Greenwood, N. N.; Earnshaw, A. *The Chemistry of the Elements*; Pergamon: Oxford, 1984.

of intermediate range interactions between main group centers have recently been identified in other main group–transition metal clusters.[17] A fuller assessment of the situation here awaits the structural characterization of neutral **2**.

Electrical measurements show that [**2**][(TCNQ)$_2$] is an *n*-type semiconductor. Four probe conductivity measurements were obtained along the needle axis which is parallel to the long axis of the TCNQ molecules.[18] Plots of $-\ln (R)$ vs. kT from 300 to 220 K (5° intervals) give a band gap of 0.24 and 0.26 eV for two different crystals. These values are comparable to the band gap for PbTe (0.27 eV).[20] Thermoelectric power measurements at several different temperatures (T_{av} = 262.3 K), again along the needle axis, indicate that electrons are the majority carriers. Given the synthetic manipulability of metal sulfide clusters,[21] there is reason to expect that the electrical properties of this type of compound can be developed much further. The incentives for such an undertaking are accentuated by the extraordinary properties observed for those metal sulfide clusters prepared by traditional high-temperature methods.[22]

Acknowledgment. This research was supported by the National Science Foundation through Grants NSF CHE 84-10779 and NSF-DMR 83-16981. We also acknowledge partial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank David Morse and Gregg Zank for experimental assistance. We also thank Dr. J. S. Miller (Du Pont) for preprints of some relevant work.

Supplementary Material Available: Tables of positional and thermal parameters for [(MeCp)$_5$V$_5$S$_6$][(TCNQ)$_2$] (5 pages); a listing of structure factors for [(MeCp)$_5$V$_5$S$_6$][(TCNQ)$_2$] (17 pages). Ordering information is given on any current masthead page.

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(17) Bogan, L. E., Jr.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 3843. Whitmire, K. H.; Raghuveer, K. S.; Churchill, M. R.; Fettinger, J. C.; See, R. F. *J. Am. Chem. Soc.* **1986**, *108*, 2778.

(18) Electrical measurements were obtained in the standard four-probe configuration utilizing a Keithley Model 220 current source in conjunction with a Keithley Model 192 digital multimeter. For thermopower measurements, samples were suspended between independently controlled copper and sapphire blocks as described elsewhere. All data acquisition and temperature control functions were automated with an IBM AT computer.[18]

(19) Lyding, J. W.; Hubacek, J. S.; Gammie, G.; Thorne, R. E. *Phys. Rev. B: Condens. Matter* **1986**, *33*, 4341.

(20) Streetman, B. G. *Solid State Electronic Devices*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1980.

(21) Bolinger, C. M.; Weatherill, T. D.; Rauchfuss, T. B.; Rheingold, A. L.; Day, C. S.; Wilson, S. R. *Inorg. Chem.* **1986**, *25*, 634. Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. Adams, R. D.; Babin, J. E.; Mahtab, R.; Wang, S. *Inorg. Chem.* **1986**, *25*, 4. Curtis, M. D.; Williams, P. D. *Inorg. Chem.* **1983**, *22*, 2661.

(22) Maple, M. B. *Phys. Today* **1986**, 72. Chevrel, R.; Hirrien, M.; Sergent, M. *Polyhedron* **1986**, *5*, 87.

Oxidative Decarbonation of an Acetylide Ligand

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Summary: The organometal acetylide bridged dicobalt complexes [Cp(CO)$_2$MC≡CPh][Co$_2$(CO)$_6$] with M = Fe or Ru undergo a nondestructive reaction with oxygen which results in the net loss of one acetylide carbon atom together with a CO ligand and the formation of the alkylidyne-bridged clusters (μ_3-PhC)Co$_2$MCp(CO)$_7$.

It is standard knowledge that most organometallic compounds have to be handled in the absence of air and that their applications involve reductive chemistry, i.e., the use of unsaturated compounds, CO, or H$_2$. Nondestructive oxidative reactions are rare, and only recently has it become obvious that ligand substitutions by oxidants lead to novel classes of compounds.[1] We believe that an extensive chemistry of oxidative ligand transformations has yet to be uncovered. In support of this assumption we report here an oxygen-induced ligand fragmentation.

In the course of cluster construction studies we investigated the trinuclear acetylide complexes **1a**[2] and **1b** which can be considered as metalloalkyne representatives of the well-known Co$_2$(CO)$_6$(μ-alkyne) class. After observing that these compounds are not completely destroyed when their solutions are exposed to air, we optimized their oxidative conversions and found they proceeded according to Scheme I, producing the alkylidyne-bridged MCo$_2$ clusters **2a** and **2b**. In a typical run over 8 h a slow stream of oxygen was bubbled for five 1-min periods into a solution of ca. 1 mmol of **1b** in 20 mL of *n*-hexane and 10 mL of dichloromethane. Filtration, concentration, and crystallization yielded about 50% of **2b**. **2a** was obtained analogously in about 20% yield. Both clusters are fully characterized including elemental analyses. Their identity could be deduced via spectral analogy[3] with that of the corresponding μ_3-MeC-bridged FeCo$_2$ cluster[4] and was confirmed for **2b** by a crystal structure determination.[5] The lack of quantitative conversion in these reactions is due not so much to uncontrolled destruction of the starting compounds 1 but to the fact that the product clusters 2 are quite air-sensitive themselves. Nevertheless this route is the best one so far for producing **2b**-type FeCo$_2$ clusters.[4]

The good yield of **2b** indicates that the 1 → 2 conversions cannot involve sacrificing 50% of the starting material, thereby generating CPh fragments or their precursors which then attack remaining 1, or any similar destructive reaction step. On the other hand, the nonquantitative reactions prevent simple mechanistic conclusions. Qualitative gas analysis showed the gaseous reaction products to contain CO and CO$_2$ from which no conclusions can be drawn since this is not unusual for oxidations of metal carbonyls. Control experiments (heating of **1b** under Ar and treatment of **1b** with H$_2$O/Ar and with H$_2$O/O$_2$)[6] indicate that 1 → 2 is not a thermal interconversion and that water, which can cleave acetylide

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(1) Cf. Herrmann, W. A.; Serrano, R.; Bock,H. *Angew. Chem.* **1984**, *96*, 364; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 383. Mayr, A.; McDermott, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 548. Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1983**, 246.

(2) Yasufuku, K.; Aoki, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1616. Bruce, M. I.; Duffy, D. N.; Humphrey, M. G. *Aust. J. Chem.* **1986**, *39*, 159.

(3) IR data (C$_6$H$_{12}$, cm^{-1}): **2a**, 2082 s, 2040 vs, 2032 vs, 1992 w, 1984 w, 1919 w; **2b**, 2080 s, 2036 vs, 2030 vs, 1988 w, br, 1952 w, br. NMR data (CDCl$_3$, internal Me$_4$Si): **2a**, 7.5 (m, 5 H), 4.43 (s, 5 H); **2b**, 7.4 (m, 5 H), 4.82 (s, 5 H).

(4) Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2409. Jensen, S.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1081.

(5) Crystal data: monoclinic $P2_1/c$, a = 960.3 (1) pm, b = 1253.3 (2) pm, c = 1674.7 (3) pm; β = 98.77 (1)°; Z = 4; 3282 unique refletions; anisotropic refinement, 252 variables; R(unit weights) = 0.036. Details of the structure determination will be given with the full publication.

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