CF_3^h), a multiplet at ϕ −76.5 (2, CF_2^e), a triplet of doublets at ϕ −79.3 (3, CF_3^a, $^4J_{FF}$ = 8.8 Hz, $^3J_{FF}$ = 1.5 Hz), a broad multiplet at ϕ −82.0 (2, CF_2^d), a multiplet at ϕ −140.0 (1, CF^b), and a multiplet at ϕ −168.0 (1, CF^f).

$CF_3^aCF^b(ONF_2^c)CF_2^dOCF^eOCF^f(CF_3^g)CF^hF^iOCF^j(CF_3^k)$. Removal of volatile products at −78 °C gives about 0.5 mL of a colorless liquid. The yield by gas chromatography (4 ft; inlet and detector temperature 150 °C; column temperature 55 °C) is 15.4%. The vapor-phase infrared spectrum (2 torr) is as follows: 1423 m, 1296 sh, 1260 vs, 1176 s, 1142 m, 1051 s, 986 m, 918 w, 852 m, 833 w, 767 w, 750 vw, 746 vw, 686 vw, 626 w cm^{-1}. The room-temperature ^{19}F NMR gave the following signals: a broad singlet at ϕ +128.2 (2, F^c), a multiplet at ϕ −73.4 (2, F^d), a multiplet at ϕ −76.4 (1, F^i), a multiplet at ϕ 79.1 (3, F^a), a multiplet at ϕ −81.9 (1, F^b), a multiplet at ϕ −82.8 (1, F^i), a multiplet at ϕ −83.3 (3, F^g), a doublet of doublets at ϕ −84.1 (3, F^k, $^4J_{FF}$ = 4J_FF $^4J_{FF}$ 21.2 Hz, $^3J_{FF}$ = 8.1 Hz), a multiplet at ϕ −84.3 (1, F^h), a multiplet at ϕ −134.4 (1F, F^e), a multiplet at ϕ −139.9 (1, F^b).

Registry No. $CF_3CF(ONF_2)(CF_2)_4CF_3$, 91391-15-0; $(CF_3)_2CF-ONF_2$, 84194-25-2; $CF_3CF(ONF_2)SF_5$, 91391-16-1; $CF_3CF(ONF_2)C(O)F$, 91391-17-2; $F_2NOCF_2CF_2OCF_2CF_3$, 91391-18-3; $F_2N-OCF_2CF_2OCF_2CF(CF_3)OCF_2CF_2CF_3$, 91391-19-4; $CF_3CF(ONF_2)CF_2OCF_2CF(SO_2F)CF_3$, 91391-20-7; $F_2NOCF_2CF_2Cl$, 24684-27-3; $F_2NOCF_2CF_2Br$, 24684-28-4; C_3F_6, 116-15-4; C_7F_{14}-1-ene, 355-63-5; $F_2C=CFOC_2F_5$, 10493-43-3; $F_2C=CFOCF_2CF(CF_3)O-C_3F_7$, 1644-11-7; $F_2C=CFCl$, 79-38-9; $F_2C=CFBr$, 598-73-2; $CF_2=CFCF_2OCF_2CF(SO_2F)CF_3$, 67635-65-8; $CF_2=CFCF_2OC-FOCF(CF_3)CF_2OCF(CF_3)$, 67641-34-3; $CF_3CF(ONF_2)CF_2OCF-OCF(CF_3)CF_2OCF(CF_3)$, 91391-21-8; (trifluorovinyl)sulfur pentafluoride, 1186-51-2; *cis*-perfluoro-2-butene, 1516-65-0; *trans*-perfluoro-2-butene, 1516-64-9; perfluorocyclobutene, 697-11-0; 1,2-dichloro-1,2-difluoroethylene, 598-88-9; 1,1-dichloro-2,2-difluoroethylene, 79-35-6; trifluoroacryloyl fluoride, 667-49-2.

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Reactions of Bis(2,2,2-trifluoroethyl) Sulfite, Bis(hexafluoroisopropyl) Sulfite, and Diethyl Sulfite with Chlorine Fluoride: Evidence of an Arbuzov Rearrangement

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Polyfluoroalkyl or alkyl sulfites, $(R_fO)_2SO$ [R_f = CF_3CH_2, $(CF_3)_2CH$, CH_3CH_2], gave fluorosulfates, R_fOSO_2F, when reacted with chlorine fluoride. With $(CF_3CH_2O)_2SO$, XeF_2 also gave the fluorosulfate. An Arbuzov rearrangement is suggested as a plausible reaction mechanism. The fluorosulfates were also obtained in lower yields from the reactions of $R_fOH\cdot Et_3N$ with SO_2ClF.

Polyfluoroalkyl sulfites, $(R_fO)_2SO$, were first reported in 1974.[2,3] However, in spite of the ease of their syntheses, the reaction chemistry of these stable compounds is entirely unexplored. The bis(perfluoroalkyl) sulfides, R_fSR_f' (R_f = CF_3; R_f' = CF_3, C_2F_5, C_3F_7) can be oxidatively fluorinated with ClF to bis(perfluoroalkyl)sulfur difluorides, $R_fSF_2R_f'$,[4] or to bis(perfluoroalkyl)sulfur tetrafluorides, $R_fSF_4R_f'$,[5] depending upon the stoichiometry and reaction conditions employed. Although an earlier attempt to oxidize bis(nonafluoro-*tert*-butyl) sulfite to $[(CF_3)_3CO]_2S(O)F_2$ with ClF had been unsuccessful,[2] we investigated the analogous reactions of ClF with several other sulfites, including bis(2,2,2-trifluoroethyl) sulfite, $(CF_3CH_2O)_2SO$, bis(hexafluoroisopropyl) sulfite, $[(CF_3)_2CHO]_2SO$, and diethyl sulfite, $(C_2H_5O)_2SO$. We, also, were unable to isolate $(R_fO)_2S(O)F_2$, but instead we are now able to report a new route to fluorosulfates and the previously unknown fluorosulfate $(CF_3)_2CHOSO_2F$. Formation of fluorosulfates from sulfites and ClF can be rationalized by invoking an Arbuzov rearrangement. Although a common occurrence in reactions of phosphorus compounds,

Arbuzov rearrangements have been reported only infrequently in the case of sulfur compounds.[6]

Results and Discussion

One of the examples of an Arbuzov rearrangement in sulfur compounds[6] is

$$R = CH_3$$
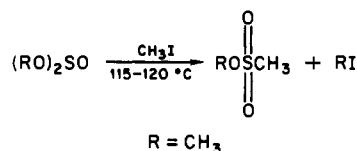
Later workers[7] demonstrated that this rearrangement was catalyzed by tertiary amines and the yields of the sulfonate products depend on the size of the R group, no reaction occurring when R is *n*-butyl. Chlorine behaves as a suitable electrophile with organosulfites to form chlorosulfates.[8]

In our unsuccessful attempts to synthesize $(R_fO)_2S(O)F_2$ from the reactions of ClF with $(R_fO)_2SO$, polyfluoroalkyl fluorosulfates were formed.

(1) PRF Summer Faculty Research Participant. On leave from the Department of Chemistry, Baldwin-Wallace College, Berea, OH.
(2) De Marco, R. A.; Kovacina, T. A.; Fox, W. B. *J. Fluorine Chem.* **1975**, *5*, 221.
(3) Kovacina, T. A.; De Marco, R. A.; Fox, W. B.; Young, D. E. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 763.
(4) Sauer, D. T.; Shreeve, J. M. *J. Fluorine Chem.* **1971/72**, *1*, 1.
(5) Abe, T.; Shreeve, J. M. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 465.

(6) Arbuzov, B. A. *Zh. Russ. Fiz.-Khim. Ova., Chast Khim.* **1909**, *41*, 429; *Method. Chim.* **1978**, *7B*, 704.
(7) Bissinger, W. E.; Kung, F. E.; Hamilton, C. W. *J. Am. Chem. Soc.* **1948**, *70*, 3940.
(8) Buncel, E. *Chem. Rev.* **1970**, *70*, 323 and references therein.
(9) Mohrig, J. R.; Keegstra, K. *J. Am. Chem. Soc.* **1967**, *89*, 5492.
(10) Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 2886.

$$(R_fO)_2SO + 2ClF \rightarrow R_fOSO_2F + R_fF + Cl_2$$

R_f (% yield) = CF_3CH_2,[9] (98–100), $(CF_3)_2CH$ (80), CH_3CH_2[10] (45)

Caution! Chlorine fluoride is an extremely potent and reactive oxidizing agent. Cocondensing ClF and diethyl sulfite, $(C_2-H_5O)_2SO$, resulted in violent explosions upon final distillation, even in millimole scale. Extreme caution should be exercised in using ClF with alkyl compounds, and scale-up of this particular reaction should be avoided.

The formation of these fluorosulfates can be rationalized via an Arbuzov rearrangement where fluorination of the sulfites did occur and the resulting product
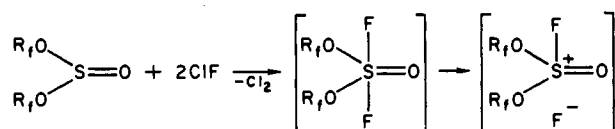

rearranged to give a sulfonium ion. The fluoride ion that is formed attacked the α-carbon of the R_fO group. This resulted in the formation of R_fF and the fluorosulfate:
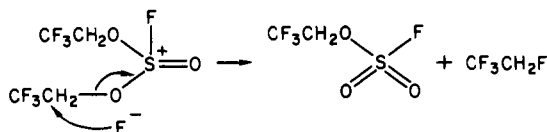
The alkyl fluorides, which were formed in amounts equal to those of the fluorosulfates, were identified by NMR. The postulated five-coordinated difluoro intermediate or the sulfonium ion was not isolated.

Each of the above fluorosulfates can also be obtained by the reaction of sulfuryl chloride fluoride with the triethylamine adduct of the alcohol:

$(C_2H_5)_3NH^+Cl^-$

$R_f = CF_3CH_2, (CF_3)_2CHO, CH_3CH_2$
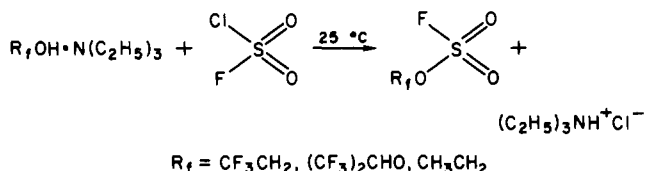
The yields of the products (45–50%) are much lower by this method compared to the reaction of the sulfite with ClF. Yields are affected by the order of addition; i.e., reactions in which the amine was added to SO_2ClF or in which the alcohol and amine were not premixed gave much lower yields (20–30%).

2,2,2-Trifluoroethyl fluorosulfate, $CF_3CH_2OSO_2F$, was also prepared by the reaction of $(CF_3CH_2O)_2SO$ and XeF_2. This reaction may also occur via the formation of a fluorosulfonium ion that further dissociates into the stable fluorosulfate species.

While $CF_3CH_2OSO_2F$ is a very stable colorless liquid with a vapor pressure of ~58 torr at 25 °C, both $C_2H_5OSO_2F$ and $(CF_3)_2CHOSO_2F$ slowly decompose in Pyrex glass on long standing at 25 °C. The decomposition products include SO_3, SiF_4, and an unidentified residue. Each compound has a characteristic band for $\nu_{S=O}$(asym) at 1460–1470 cm^{-1} and for ν_{S-F} at ~850 cm^{-1}. The mass spectrum for each of these fluorosulfates shows a molecular ion at an intensity of <5% of the base peak at 69 (CF_3^+). Other major peaks which are typical are assigned to $R_fOSO_2^+$, R_fOSO^+, SO_2^+, and SO^+.

Second-order effects in the NMR spectra are observed in fluoroalkyl sulfite esters and alkyl sulfite esters due to the nonequivalence of groups attached to the alkoxy α-carbon.[3,10-13]

In the new fluorosulfates, $CF_3CH_2OSO_2F$, $CH_3CH_2OSO_2F$, and $(CF_3)_2CHOSO_2F$, all NMR spectra are first order. In the ^{19}F NMR spectrum for $(CF_3)_2CHOSO_2F$ there was no spin–spin coupling between the two CF_3 groups, which is in contrast with the sulfite, $[(CF_3)_2CHO]_2SO$, where $J_{CF_3-CF_3'}$ was 9.5 Hz.[2]

Experimental Section

Materials. The sulfites, $(CF_3CH_2O)_2SO$ and $[(CF_3)_2CHO]_2SO$, were prepared according to the literature method.[2,3] The other reactants, CF_3CH_2OH (PCR), $(CF_3)_2CHOH$ (PCR), $(CF_3)_3COH$ (PCR), ClF (Ozark-Mahoning), and XeF_2 (PCR) were used as received without further purification. Triethylamine (Baker) was distilled from KOH and kept over 3-Å molecular sieves for 18 h prior to use.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge. Most of the starting materials and products were measured quantitatively with *PVT* techniques. Products were purified by fractional condensation (trap-to-trap distillation) or by use of an Aerograph A-90-P gas chromatograph. For gas chromatographic separations, the columns were constructed of 0.25-in. copper or aluminum tubing packed with 30% Kel-F No. 3 oil (3M Co.) on Chromosorb P. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer with a 10-cm cell using KBr windows. ^{19}F and ^{1}H NMR spectra were obtained on a JEOL FX90Q FT NMR spectrometer by using CCl_3F and tetramethylsilane as an external reference, respectively. $CDCl_3$ was used as a solvent. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-6E spectrometer operating at an ionization potential of 15 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Reaction of Bis(2,2,2-trifluoroethyl) Sulfite, $(CF_3CH_2O)_2SO$, and Chlorine Fluoride, ClF. A 75-mL Hoke bomb was charged with 2.56 mmol of $(CF_3CH_2O)_2SO$ and 10 mmol of ClF at −196 °C and then warmed slowly to −78 °C over a period of 2 h. Warming from −78 °C to room temperature occurred in a period of 12 h. 2,2,2-Trifluoroethyl fluorosulfate, $CF_3CH_2OSO_2F$, was obtained in a 98–100% yield. This compound is a colorless liquid and has a vapor pressure of 58 torr at 25 °C. The ^{19}F NMR spectrum of $CF_3CH_2OSO_2F$ consists of a doublet of triplets assigned to CF_3 at ϕ −74.1 and a triplet of quartets for SF at ϕ +38.7. The ^{1}H NMR spectrum contains a doublet of quartets for CH_2 at δ 4.7. The various coupling constants are found to be $^5J_{CF_3-SF}$ = 2.6 Hz, $^3J_{CH_2-CF_3}$ = 7.5 Hz, and $^4J_{SF-CH_2}$ = 0.5 Hz. The infrared spectrum is as follows: 2980 (w), 1470 (vs), 1292 (vs), 1235 (s), 1185 (vs), 1055 (s), 970 (ms), 860 (s, br), 815 (ms), 670 (m, br), 570 (s), 545 (w), 485 (m) cm^{-1}. The mass spectrum contained a molecular ion and an appropriate fragmentation pattern. The molecular weight of $CF_3CH_2OSO_2F$ was found to be 179 (calculated 182).

Anal. Calcd for $CF_3CH_2OSO_2F$: S, 17.58; F, 41.76. Found: S, 17.38; F, 41.2%.

Reaction of Bis(2,2,2-trifluoroethyl) Sulfite, $(CF_3CH_2O)_2SO$, and Xenon Difluoride, XeF_2. Bis(2,2,2-trifluoroethyl) sulfite (1 mmol) was condensed into a 50-mL Pyrex reactor equipped with a Teflon stopcock containing 1.2 mmol of XeF_2. The reaction mixture was warmed from −196 °C to room temperature within 3 h. The infrared spectrum of the fraction that is involatile at −30 °C confirmed the formation of $CF_3CH_2OSO_2F$ in 60% yield.

Reaction of Sulfuryl Chloride Fluoride, SO_2ClF, and 2,2,2-Trifluoroethanol, CF_3CH_2OH. 2,2,2-Trifluoroethanol (1 mmol) and triethylamine (1 mmol) were condensed into a 50-mL Pyrex reactor equipped with a Teflon stopcock, and the resultant mixture was warmed to room temperature for ~20 min. The mixture was frozen to −196 °C, and the SO_2ClF (1 mmol) was condensed into the reactor. The vessel was then slowly warmed to room temperature and left for ~24 h. The infrared spectrum of the fraction at −30 °C confirmed the formation of $CF_3CH_2OSO_2F$ in 47% yield.

Reaction of Diethyl Sulfite, $(CH_3CH_2O)_2SO$, and Chlorine Fluoride, ClF. Chlorine fluoride (10 mmol) was condensed into a 75-mL Hoke bomb that contained 3.5 mmol of diethyl sulfite at −196 °C. The reaction mixture was warmed from −196 to −78 °C in 3 h and from −78 to −20 °C in 12 h. Trap-to-trap distillation (−30 °C) gave ethyl

(11) Kaplan, F.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 4666.
(12) De Marco, R. A.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 1896.

(13) Darragh, J. I.; Noble, A. M.; Sharp, D. W. A.; Walker, D. W.; Winfield, J. M. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 517.

fluorosulfate, $CH_3CH_2OSO_2F$, in about 45% yield. (*Caution!* Trap-to-trap distillation should be carried out carefully. Explosions occurred when the liquid-nitrogen Dewar was removed from the trap.) The ^{19}F NMR spectrum of $CH_3CH_2OSO_2F$ is comprised of a multiplet at ϕ +36.7 assigned to S–F. The ^1H NMR spectrum shows resonances at δ 1.5 (doublet of triplets, $^3J_{HH}$ = 7.3 Hz, $^5J_{HF}$ < 0.5 Hz) assigned to $-CH_3$ and at δ 4.6 (doublet of quartets, $^4J_{HF}$ = 0.5 Hz) assigned to $-CH_2$. The infrared spectrum is as follows: 2940 (w), 1460 (s), 1280 (sh), 1230 (s), 940 (m), 830 (m), 600 (m) cm^{-1}. The mass spectrum contained a molecular ion peak and the appropriate fragmentation pattern.[14]

Reaction of Bis(hexafluoroisopropyl) Sulfite, $((CF_3)_2CHO)_2SO$, with Chlorine Fluoride, ClF. A 75-mL Hoke bomb was charged with 2.5 mmol of $((CF_3)_2CHO)_2SO$ and 10 mmol of ClF and then slowly warmed to –78 °C in a period of 3 h. Warming from –78 °C to room temperature occurred in a period of 12 h. The contents were distilled, and hexafluoroisopropyl fluorosulfate, $(CF_3)_2CHOSO_2F$, was stopped in a trap at –78 °C in about 80% yield. The vapor pressure of this new compound is approximately 60 torr at 25 °C. The ^{19}F NMR spectrum consists of a heptet at ϕ +44.9 ($^4J_{SF-CF_3}$ = 3.7 Hz) and a doublet of doublets at ϕ –72.0 ($^3J_{CF_3-H}$ = 5.5 Hz). The ^1H NMR spectrum shows a heptet at δ 5.2. There was no SF–CH coupling. The infrared spectrum is as follows: 1470 (vs), 1370 (s), 1300 (s),

1250 and 1215 (s, br), 1120 (sh), 1080 (s), 1030 (w), 900 (vs), 880 (s), 840 (vs), 745 (m), 700 (vs), 625 (vs), 600 (s), 545 (s) cm^{-1}. The molecular weight of the compound by *PVT* methods was found to be 254 (calcualted 250). The mass spectrum contained a molecular ion and an appropriate fragmentation pattern.

Reaction of Hexafluoro-2-propanol, $(CF_3)_2CHOH$, with Sulfuryl Chloride Fluoride, SO_2ClF. Hexafluoro-2-propanol (1 mmol) and triethylamine (1 mmol) were condensed into a 50-mL Pyrex reactor equipped with a Teflon stopcock at –196 °C, and the resultant mixture was warmed to room temperature for ~20 min. The mixture was frozen at –196 °C, and the SO_2ClF (1 mmol) was condensed into the reactor. The vessel was then warmed slowly to room temperature and left for ~20 h. The infrared spectrum of the fraction at –78 °C confirmed the formation of $(CF_3)_2CHOSO_2F$ in 50% yield.

Registry No. $CF_3CH_2OSO_2F$, 66950-71-8; $EtOSO_2F$, 371-69-7; $(CF_3)_2CHOSO_2F$, 38252-04-9; $(CF_3CH_2O)_2SO$, 53749-89-6; $[(CF_3)_2CHO]_2SO$, 53517-89-8; $(EtO)_2SO$, 623-81-4; ClF, 7790-89-8; XeF_2, 13709-36-9; CF_3CH_2OH, 75-89-8; $(CF_3)_2CHOH$, 920-66-1; SO_2ClF, 13637-84-8.

(14) Sauer, D. T.; Shreeve, J. M. *Inorg. Chem.* **1971**, *10*, 358.
(15) Ahmed, M. G.; Alder, R. W.; James, G. H.; Sinnott, M. L.; Whiting, M. C. *Chem. Commun.* **1968**, 1533.

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Reinvestigation of the Electronic and Magnetic Properties of Ruthenium Butyrate Chloride

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The title compound, hereafter referred to as $Ru_2(but)_4Cl$, was studied by powder magnetic susceptibility measurements over the temperature range 5–300 K, by EPR spectroscopy in various glasses at 4 K, and by far-IR spectroscopy in the solid state at room temperature. The compound has a quartet ground state in agreement with previous reports. A large zero-field splitting (D = 77 cm^{-1}) is found. There is no interdimer magnetic interaction despite the polymeric nature of the solid. EPR spectroscopy gave parameters in agreement with the magnetic data that were independent of the solvent and variation in the axial anion. Unpaired electron spin density was delocalized over both Ru atoms in a series of base adducts. Far-IR spectroscopy showed a band assigned to $\nu(RuCl)$ not previously reported. Previous theoretical work is discussed and found to be in agreement with the experimental results.

Introduction

A large number of metal carboxylate dimers are known.[1] One of the most unusual of these is the complex formed with ruthenium, $Ru_2(O_2CR)_4Cl$. In contrast to the metal carboxylate dimers known for Cr, Mo, Re, Tc, Rh, and Cu, this Ru dimer contains an odd number of d electrons. Thus it is formally a $Ru_2^{II,III}$ complex. Structural studies[2] on $Ru_2(but)_4Cl$ (but = butyrate) and other $Ru_2(O_2CR)_4^+$ derivatives[3] indicate that the two Ru atoms are crystallographically equivalent. Furthermore, an earlier report[4] of the magnetic properties and EPR spectra of $Ru_2(but)_4Cl$ gave no support to a localized II,III system. Rather, $Ru_2(but)_4Cl$ was proposed to have a Ru–Ru bond of order 2.5 with three unpaired electrons delocalized over both metal atoms.[2,4] A simplified version of this MO scheme is shown in Figure 1. Scattered-wave Xα calculations have been performed on the $Ru_2(O_2CH)_4^+$ species, and they support this MO scheme.[5] These results have been used with success to explain resonance

Raman[6] and single-crystal polarized electronic spectra[7] of $Ru_2(O_2CR)_4^+$ derivatives.

In order to further understanding of this interesting complex, we decided to examine the magnetic properties of $Ru_2(but)_4Cl$ over the temperature interval 5–300 K since the original (powder) measurements were made in the temperature interval 60–300 K.[4] In many cases, magnetic susceptibility measurements are necessary at low temperatures to observe deviation from normal Curie–Weiss behavior. We also decided to repeat the EPR study because, due to a poor signal-to-noise level in the original EPR measurements, a complete spectrum was not obtained and the conclusions are open to question.[4] A complete solution EPR spectrum of the complex and some of its adducts are reported at 4 K. We also obtained far-IR

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(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982, and references therein.
(2) Bennett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1.
(3) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599.
(4) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.
(5) Norman, J. G., Jr.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256.
(6) Clark, R. J. H.; Ferris, L. T. H. *Inorg. Chem.* **1981**, *20*, 2759.
(7) Martin, D. S.; Newman, R. A.; Vlasnik, L. M. *Inorg. Chem.* **1980**, *19*, 3404.