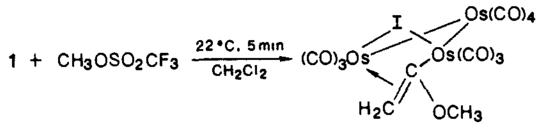
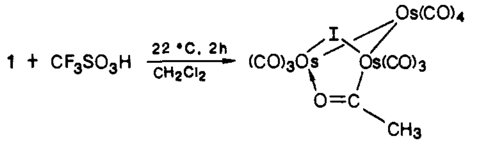
Reaction of **1** with *electrophiles* follows a different course. Addition of $CH_3OSO_2CF_3$ to **1** gives alkylation of the ketene carbonyl oxygen to form the σ,π-vinyl cluster **4**,[15] eq 2. An X-ray diffraction study on a disordered crystal of **4** showed the assigned structure to be correct, but a satisfactory refinement was not obtained.[16] The ^1H NMR spectrum of **4** shows the expected methoxy and methylene protons at δ 3.85 (s, 3 H) and δ 5.10 (d, 1 H, J_{HH} = 4.92 Hz), 5.06 (d, 1 H), respectively. The −80 °C ^{13}C NMR spectrum of **4** shows separate resonances attributed to the 10 inequivalent carbonyl ligands in the assigned structure, but upon warming, these broaden, coalesce, and then sharpen into six resonances at 25 °C. We attribute this to a fluxional process in which the σ,π-vinyl ligand exchanges between the front two osmium atoms in a "windshield wiper" motion similar to that seen in other σ,π-vinyl compounds.[17]



(2)

4 (70%)

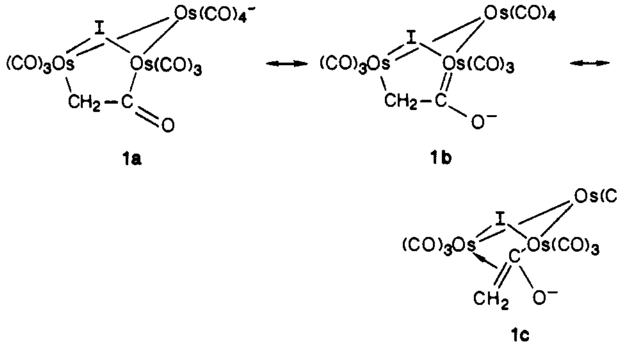
Addition of acid to **1** converts the ketene ligand into a μ-acetyl ligand in the known cluster **5**,[11,18] eq 3. This reaction proceeds through the formation of an intermediate species, indicated by the immediate dark to light-orange color change followed by slow formation of the yellow color of **5**. The intermediate has an IR spectrum[19] similar to that of the σ,π-vinyl cluster **4**, and we suggest a similar structure in which protonation initially occurs on the ketene oxygen to give a hydroxyvinyl ligand which subsequently tautomerizes to the acetyl form in **5**.



(3)

5 (72%)

The reactions of **1** with the *nucleophiles* CH_3^- and CH_3O^- to give the cluster enolates **2** and **3** are similar to established reactions of nucleophiles with free ketenes,[1] organic carbonyls,[20] and metal acyl complexes.[21] The reactions of **1** with the *electrophiles* H^+ and CH_3^+ imply that important contributing resonance forms for **1** are the oxycarbene (**1b**) and oxyvinyl (**1c**) structures drawn below. Oxycarbene resonance forms are known to be important for anionic metal acyl complexes and contribute to the ease with which these are alkylated at the carbonyl oxygen to yield metal carbenes.[21] Oxyvinyl structures such as **1c** have not been previously considered. The facile alkylation and apparent protonation of the ketene oxygen in the **1** → **5** and **1** → **6** transformations indicate the importance of resonance forms **1b**/**1c** as does the unusually low ketene ν(CO) band of **1** at 1551 cm^{-1}.[3b]



1a **1b**

1c

These and other studies[2-5] indicate that coordinated ketene ligands have a rich derivative chemistry and may prove to be of synthetic utility if it can be shown that coordinated ketene ligands undergo organic reactions different from those of free ketene. Our further studies in this area will emphasize the reactions of **1** and related type II ketene complexes with more sophisticated organic nucleophiles and electrophiles so as to begin to define the synthetic utility of these ligands.

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this research and the National Science Foundation for contributing funds toward the purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Tables of atomic positional parameters, bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates for **2**; crystallographic details and an ORTEP drawing of molecule A of **4** (8 pages). Ordering information is given on any current masthead page.

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[15] **4**: IR (pentane) 2105 (w), 2068 (s), 2054 (m), 2020 (s), 2014 (sh), 2001 (sh), 1995 (m), 1979 (w) cm^{-1}; MS (EI) (^{190}Os), *m/z* 1034 M^+, plus fragments corresponding to loss of 10 CO's and CH_3; ^{13}C NMR ($CDCl_3$, 22 °C) (22 °C) δ 199.4 (s, 1 C, *C*(OCH_3)CH_2), 179.0 (s 2 C, CO), 178.4 (s, 1 C, CO), 178.3 (s, 1 C, CO), 175.0 (s, 2 C, CO), 174.4 (s, 2 C, CO), 164.6 (s, 2 C, CO), 35.9 (t, C(OCH_3)CH_2, J_{CH} = 153 Hz); (CD_2Cl_2, −80 °C, metal carbonyls) δ 179.5, 179.1, 178.6, 178.2, 176.2, 175.2, 174.8, 173.9, 164.8, 164.7. Anal. Calcd for $C_{13}H_5O_{11}IOs_3{\cdot}C_5H_{12}$: C, 19.53; H, 1.54. Found: C, 19.30; H, 1.58.

[16] See supplementary material.

[17] (a) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *94*, C43. (b) Lee, K. W.; Brown, T. L. *Organometallics* **1985**, *4*, 1030 and references cited therein. (c) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.; Naceur, J. B.; Mentzeen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123 and references cited therein. (d) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Rosenberg, E.; Anslyn, E. V. *Inorg. Chim. Acta* **1986**, *111*, 95.

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[19] ν(CO) (CH_2Cl_2): 2114 (w), 2105 (w), 2064 (vs), 2055 (sh), 2029 (sh), 2018 (s), 1999 (sh) cm^{-1}.

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Transfer of Perfluoroalkyl Groups between Metals: Preparation of the Anionic Perfluoroalkyl Metal Complex $Ag[CF(CF_3)_2]_2^-$

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Despite the large number of transition-metal organofluorine compounds and the importance of fluorocarbons as specialty chemicals, little is known about the fundamental chemical reactivity of metal-bonded fluorocarbons.[1] We have initiated a systematic exploration of the reaction chemistry of metal-bonded fluorocarbons. We quickly discovered an exception to the common belief that transition-metal-mediated transformations of fluorocarbons are prevented by the low lability of metal-bonded perfluoroalkyl groups. The silver perfluoroalkyl $(CF_3)_2CFAg(CH_3CN)$ is heterolytically labile, existing in dynamic equilibrium in solution with solvated Ag^+ and the new anionic perfluoroalkyl metal complex $Ag[CF(CF_3)_2]_2^-$. Equilibrium 1 demonstrates the

$$2(CF_3)_2CFAg(CH_3CN) \overset{K_{eq}}{\rightleftharpoons} Ag^+ + Ag[CF(CF_3)_2]_2^- \quad (1)$$

facile transfer of perfluoroalkyl groups between metals in solution and provides a synthetic route to the first isolable anionic perfluoroalkyl metal complex.

The perfluoroalkyl complex $(CF_3)_2CFAg(CH_3CN)$ is prepared by reaction of AgF with $CF_3CF{=}CF_2$ in acetonitrile.[2] The ^{19}F

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[1] (a) Bruce, M. I.; Stone, F. G. A. *Prep. Inorg. React.* **1968**, *4*, 177–235. (b) Morrison, J. A. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 293. (c) Clark, H. C. *Adv. Fluorine Chem.* **1963**, *3*, 19. (d) *Organofluorine Chemicals and Their Industrial Applications*; Banks, R. E., Ed.; Ellis Horwood: Chichester, 1979.

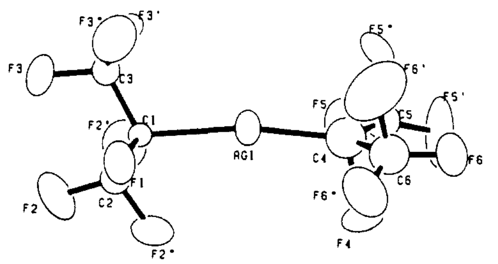

Figure 1. ORTEP view of the bis(perfluoroisopropyl)silver anion. Important parameters: Ag(1)–C(1) = 2.191 (17), Ag(1)–C(4) = 2.015 (35), F(1)–C(1) = 1.419 (21), F(4)–C(4) = 1.737 (33) Å, ∠C(1)–Ag(1)–C(4) = 170 (1)°, ∠Ag(1)–C(1)–F(1) = 108 (1)°, ∠Ag(1)–C(4)–F(4) = 108 (1)°.

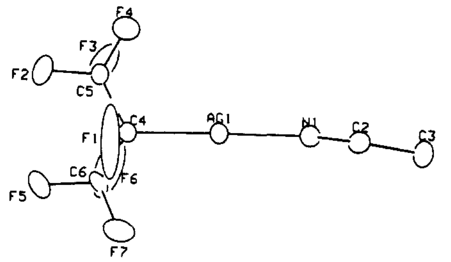

Figure 2. ORTEP view of $(CF_3)_2CFAg(CH_3CN)$. Important parameters: Ag(1)–Ag(1) = 3.206, Ag(1)–N(1) = 2.083 (7), Ag(1)–C(4) = 2.104 (11), N(1)–C(2) = 1.124 (11), F(1)–C(4) = 1.702 (83) Å. (Hydrogens have been omitted for clarity.)

NMR spectrum in THF-d_8 at 293 K shows resonances for $(CF_3)_2CFAg(CH_3CN)$ at −68.9 ppm (d of d, $J_{F-F} = 12$, $J_{Ag-F} = 14$ Hz, 6 F, $AgCF(CF_3)_2$) and −211.8 ppm (binomial septet, $J_{F-F} = 12$ Hz, $AgCF(CF_3)_2$, relative to $CFCl_3$). A second set of resonances was found at −68.4 and −215.2 ppm in a 6:1 intensity ratio and account for approximately 50% of the total intensity of the spectrum. This second set of resonances was assigned to a new anionic perfluoroalkyl metal complex, $Ag[CF(CF_3)_2]_2^-$, based on the following observations. The spectra were highly solvent-dependent. In acetonitrile, the ionic species predominated over $(CF_3)_2CFAg(CH_3CN)$, the equilibrium constant being 13 at 298 K, with no concentration dependence over the range 0.044–0.44 M in total silver. In THF-d_8, K_{eq} was 0.20 at 298 K, while in the noncoordinating solvents, CD_2Cl_2 and toluene-d_8, $(CF_3)_2CFAg(CH_3CN)$ is the sole detectable species in solution with no evidence for formation of the anion.

Tetraalkylammonium salts of the anion were isolated by addition of 0.5 equiv of $R_4N^+Br^-$ to acetonitrile solutions of $(CF_3)_2CFAg(CH_3CN)$. Following removal of precipitated AgBr, $R_4N^+Ag[CF(CF_3)_2]_2^-$ (R = methyl or ethyl) was crystallized from CH_2Cl_2/ether/pentane mixtures. Similarly, Ag[cryptofix 2.2.2]$^+Ag[CF(CF_3)_2]_2^-$ (cryptofix 2.2.2 = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$) was prepared by addition of 0.5 equiv of the cryptofix ligand to acetonitrile solutions of $(CF_3)_2CFAg(CH_3CN)$ followed by recrystallization from CH_2Cl_2/ether/pentane mixtures. The photochemical and thermal instability of these salts precluded elemental analyses and structure determination by X-ray crystallography, but the ^{19}F NMR spectra of these compounds are all identical in both CD_2Cl_2 and THF-d_8 with resonances at −68.4 ppm (t, $J = 12$ Hz, $AgCF(CF_3)_2$, 6 F) and −215.2 ppm (d of heptets, $J_{Ag-F} = 18$, $J_{F-F} = 12$ Hz, $AgCF(CF_3)_2$, 1 F, relative to $CFCl_3$).

The complex ion $Ag[CF(CF_3)_2]_2^-$ was also isolated as the $Rh[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2^+Ag[CF(CF_3)_2]_2^-$ salt which was sufficiently light stable to permit a single-crystal X-ray diffraction study.[3] This structure (Figure 1) is the first example of an anionic perfluoroalkyl metal complex. The overall geometry is essentially linear and the two isopropyl groups are rotated about the C–Ag–C axis such that the CF bonds are nearly perpendicular.[4] This structure is very similar to that of the parent molecule $(CF_3)_2CFAg(CH_3CN)$ (Figure 2).[5] The two-coordinate neutral complex $(CF_3)_2CFAg(CH_3CN)$ likewise shows a linear arrangement of the ligating atoms and the silver. Additionally, the silver atoms in $(CF_3)_2CFAg(CH_3CN)$ align in an infinite array with a separation of 3.206 (1) Å.

The temperature dependence of equilibrium 1 was measured by NMR in acetonitrile solution at 0.44 M in total silver concentration. Plots of log K_{eq} vs. $1/T$ were linear over the range 248–298 K. The enthalpy and entropy for equilibrium 1 are −3.61 ± 0.31 kcal/mol and −6.9 ± 1.2 eu, showing that the free energy for equilibrium 1 is small at moderate temperatures. Equilibrium 1 was shifted toward $(CF_3)_2CFAg$(solvate) by addition of a 10-fold excess of $AgBF_4$ to THF-d_8 solutions of Ag(cryptofix 2.2.2)$^+Ag[CF(CF_3)_2]_2^-$; no detectable $Ag[CF(CF_3)_2]_2^-$ remained in these solutions. Doubtlessly the state of solvation of Ag^+ and $(CF_3)_2CFAg(CH_3CN)$ play a large role in the equilibrium. Equilibrium 1 is formally analogous to the well-documented equilibria of the silver halides (equation 2);[6] in the present case

$$2AgX \rightleftharpoons Ag^+ + AgX_2^- \qquad (2)$$

the perfluoroalkyl groups behave as pseudohalogens. Lewis base adducts of silver halides are invariably aggregates with halogens bridging silver atoms.[7] Regarding the perfluoroalkyl groups as pseudohalogens, the perfluoroalkyl exchange in equilibrium 1 may proceed by way of structures in which the perfluoroalkyl groups bridge silver atoms, analogously to the silver halide structures.[7]

The stability of the anionic perfluoroalkyl metal complex with respect to elimination of fluoride ion is remarkable. Long-lived anionic perfluoroalkyl complexes are otherwise restricted to perfluoroalkyl groups lacking fluorine α to the metal.[8] Furthermore, of the perfluoroalkyl carbanions, only the tertiary carbanions are isolable.[9] Presumably, the stability of the silver complex is a mark of a high degree of covalency of the metal–perfluoroalkyl bond. We have clearly demonstrated the kinetic lability of these groups with regard to transfer of perfluoroalkyl groups between silver ions in solution.

Acknowledgment. We thank Dr. S. D. Ittel for valuable discussions and G. E. Barkley for technical assistance.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, structure factors, and thermal parameters for $Rh[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2^+Ag[CF(CF_3)_2]_2^-$ and for $(CF_3)_2CFAg(CH_3CN)$ (18 pages). Ordering information is given on any current masthead page.

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(3) Space group *Pba*2; $a = 21.142$ (3) Å, $b = 22.262$ (2) Å, $c = 11.877$ (2) Å, $Z = 4$, $T = -70$ °C. The structure (413 parameters) was refined to 2891 data (1.8° ≤ 2θ ≤ 55.0°) with $F_o^2 \geq 3\sigma(F_o^2)$, gathered on an Enraf-Nonius CAD4 diffractometer. Discrepancy indices were $R = 0.065$, $R_w = 0.053$, and error-of-fit = 1.50.

(4) This structure is similar to those of $Ag[C(Si(CH_3)_3)_3]_2^-$ and the β-disulfone complex AgR_2^- (R = 1,3-dithiane 1,1,3,3-tetraoxide). See, respectively: Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1984**, 870–871. DeMember, J. R.; Evans, H. F.; Wallace, F. A.; Tariverdian, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 5647–5652.

(5) Space group *P*2*na*; $a = 6.297$ (3) Å, $b = 6.890$ (3) Å, $c = 19.930$ (10) Å, $Z = 2$, $T = -70$ °C. The structure (126 parameters) was refined to 1232 data (2.0° ≤ 2θ ≤ 55.0°) with $F_o^2 \geq 3\sigma(F_o^2)$, gathered on an Enraf-Nonius CAD4 diffractometer. Discrepancy indices were $R = 0.038$, $R_w = 0.037$, and error-of-fit = 1.51.

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