also used to collect the intensity data. The diffractometer was run under the control of the NRCCAD software.[36] Crystal data for $[Cp_2Ti(\mu\text{-}Se)_2TiCp]_2(\mu\text{-}Se)\cdot 0.25(C_6H_5CH_3)$: M_r 1000.04 daltons; triclinic, $P\bar{1}$; $\lambda(\text{Mo K}\bar{\alpha}) = 0.710\,73$ Å; $a = 11.329$ (1), $b = 12.572$ (1), $c = 23.769$ (2) Å; $\alpha = 88.587$ (7), $\beta = 86.481$ (8), $\gamma = 89.217$ (7)°; $V = 3377.70$ Å^3; $Z = 4$; $D_{\text{calcd}} = 1.97$ Mg m^{-3}; $F(000) = 1922$; $\mu(\text{Mo K}\bar{\alpha}) = 0.99$ cm^{-1}. A total of 8799 reflections with a $2\theta \le 45°$ were measured by the ω–2θ scan technique, of which 6237 were judged as being observed by the criterium that $I > 2.5\sigma(I)$.

Preliminary positions for the metal and selenium atoms were derived by using MULTAN direct methods.[37] The positions of these atoms were used in the phasing of a Fourier synthesis, and the positions of all non-hydrogen atoms of the $[Cp_2Ti(\mu\text{-}Se)_2TiCp]_2(\mu\text{-}Se)$ unit were obtained by successive Fourier, difference Fourier, and partial refinement techniques. The structure was refined by standard methods,[38] minimizing the function $\sum w(\Delta F)^2$ with a weighting scheme of the form $w = 1/(\sigma(F)^2 + kF^2)$ with σ based on counting statistics. Scattering factors were taken from ref 39 and were corrected for both the real and the imaginary parts of the anomolous dispersion where appropriate. An absorption correction of an empirical nature[40] was made. The hydrogen atoms in the C_5H_5 rings were included with their positions calculated by using sp^2 hybridization at the C atom and a fixed C–H distance of 0.96 Å. The $C_6H_5CH_3$ molecule was disordered in a very complicated fashion, and only the six carbon atoms of the ring could be seen in difference Fourier maps. It is assumed that the CH_3 group is disordered over all six positions. This carbon was not included in the final refinement, which used anisotropic thermal parameters for the Ti and Se atoms and isotropic for the C atoms. The H atoms were fixed with a C–H distance of 0.96 Å and sp^2 hybridization at the C atom.

The total number of parameters was 416; the final R (= $\sum\Delta|F|/\sum|F|$) was 0.056, R_w(= $(\sum w(\Delta F)^2/\sum wF^2)^{1/2}$) was 0.092 and the goodness of fit (= $\sum w(\Delta F)^2$/(number of reflections – number of parameters)) 1.13. A final difference Fourier had a minimum residual intensity of –0.79 e Å^{-3} and a maximum of 1.72 e Å^{-3} in the region of the toluene of crystallization. The positional parameters for the non-hydrogen atoms of $[Cp_2Ti(\mu\text{-}Se)_2TiCp]_2(\mu\text{-}Se)$ are given in Table VII, the important distances in Table IV, the angles in Table V, and the planes in Table VI. Figure 1, which was drawn by ORTEP-II,[41] gives the numbering scheme.

Conclusions

The reactivities of $Cp'_2M(CO)_2$ in reaction with H_2A or N_2O lie in the order $Cp_2Ti(CO)_2 > Cp_2Zr(CO)_2 > Cp^*_2Ti(CO)_2 > Cp^*_2Zr(CO)_2$ and $H_2Se > H_2S > H_2O \simeq N_2O$. The reactivities are consistent with a mechanism in which initial loss of CO from $Cp'_2M(CO)_2$ is assisted by protonation. The primary product of the reactions is $[Cp'_2M(\mu\text{-}A)]_2$ unless steric factors prevent formation of this dimer, in which case the primary product is $Cp'_2M(AH)_2$. For $[Cp_2Ti(\mu\text{-}Se)]_2$ further reaction with H_2Se gives $[Cp_2Ti(\mu\text{-}Se)_2TiCp]_2(\mu\text{-}Se)$ which is an intermediate in the formation of the clusters $[CpTi]_mSe_n$.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

Registry No. $Cp_2Ti(CO)_2$, 12129-51-0; H_2Se, 7783-07-5; $[Cp_2Ti(\mu\text{-}Se)]_2$, 113725-89-6; $[Cp_2Ti(\mu\text{-}Se)_2TiCp]_2(\mu\text{-}Se)$, 113704-80-6; $[CpTi]_6Se_8$, 113747-40-3; $[CpTi]_5Se_6$, 113747-41-4; $[CpTi]_4Se_4$, 113704-85-1; $Cp^*_2Ti(CO)_2$, 11136-40-6; $Cp^*_2Ti(SeH)_2$, 113704-81-7; $Cp^*_2Ti(\mu\text{-}Se)]_2$, 113704-82-8; $Cp_2Zr(CO)_2$, 59487-85-3; $[Cp_2Zr(\mu\text{-}Se)]_2$, 100581-44-0; $Cp^*_2Zr(CO)_2$, 61396-31-4; $[Cp^*_2Zr(\mu\text{-}Se)]_2$, 113704-83-9; $[Cp_2Ti(\mu\text{-}Se)_2TiCp]_2(\mu\text{-}Se)\cdot 0.25(C_6H_5CH_3)$, 113704-84-0; H_2O, 7732-18-5; H_2S, 7783-06-4; N_2O, 10024-97-2.

Supplementary Material Available: Tables of hydrogen atom positions, thermal parameters, and equations of some mean planes and comprehensive lists of bond distances and angles (21 pages); a table of $|F_o|$ and $|F_c|$ (57 pages). Ordering information is given on any current masthead page.

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Communications

C–F Bond Activation and Vicinal Defluorination by $(OC)_3Mn^-$

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Summary: C–F bond activation and vicinal defluorination of $F_2C{=}CF_2$, $F_2C{=}CHF$, $FCH{=}CHF$, and F_3CCF_3 were accomplished in the gas phase by reactions with $(OC)_3Mn^-$. The product ions were shown to have the general structure $F_2Mn(XC_2Y)^-$ where X and Y are F or H.

The large dissociation energies of C–F bonds in fluorinated alkanes ($D^0(CF_3CF_2\text{–}F) = 126.8 \pm 1.8$ kcal mol^{-1})[1] and alkenes ($D^0(CH_2{=}CH\text{–}F) = 118.7$ kcal mol^{-1})[2] are associated with the low reactivity of these compounds under various conditions. For example, a number of organometallic d^{10} Ni(0), Pd(0), and Pt(0) complexes readily react with vinyl halides to yield oxidation adducts via their π-complexes[3] (eq 1)[4] with the oxidative insertion occurring

$$L_2Pt(CF_2{=}CFBr) \rightarrow cis\text{-}L_2Pt(Br)(CF{=}CF_2) \quad (1)$$

$$L = Ph_3As$$

exclusively in the non-CF bond. In the vicinal dehalo-

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genations of *vic*-dihaloalkanes and -alkenes to olefins and alkynes, respectively, the conversions are not useful with *vic*-difluorides.[5] Any reagent which will effect oxidative insertion into C–F bonds must overcome this thermodynamic stability by producing strong new bonds to fluorine and carbon for a net exothermic reaction.[6] We wish to report preliminary results which demonstrate that in the gas phase $(OC)_3Mn^-$ effects the unique vicinal defluorination of the fluorinated alkenes C_2F_4, C_2HF_3, and 1,2-$C_2H_2F_2$ and the perfluoroalkane C_2F_6 to yield the metal complex negative ions with the general structure of $F_2Mn(XC_2Y)^-$ where X and Y are F or H.

Our studies are carried out in a previously described flowing afterglow (FA) apparatus.[7] The method for generating a mixture of $(OC)_5Mn^-$ (m/z 195), $(OC)_4Mn^-$ (m/z 167), and $(OC)_3Mn^-$ (m/z 139) by dissociative electron attachment to $Mn_2(CO)_{10}$ using energetic electrons has been reported.[8] While $(OC)_5Mn^-$ did not react with the above fluorinated ethylenes or ethane ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}), $(OC)_4Mn^-$ reacted slowly with C_2F_4 ($k = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) yielding the adduct and (adduct–CO) product negative ions (eq 2).[9-11] However,

$$\underset{m/z\ 167}{(OC)_4Mn^-} + C_2F_4 \xrightarrow[\text{He}]{0.51} \underset{m/z\ 267}{(OC)_4Mn(C_2F_4)^-} \tag{2a}$$

$$\underset{m/z\ 167}{(OC)_4Mn^-} + C_2F_4 \xrightarrow{0.49} \underset{m/z\ 239}{(OC)_3Mn(C_2F_4)^-} + CO \tag{2b}$$

when $F_2C{=}CF_2$ was added to a flow containing $(OC)_3Mn^-$, we observed a rapid decay of the m/z 139 ion signal ($k = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) with exclusive formation of the (adduct-3CO) product anion at m/z 155 (eq 3). With

$$\underset{m/z\ 139}{(OC)_3Mn^-} + F_2C{=}CF_2 \rightarrow \underset{m/z\ 155}{Mn(C_2F_4)^-} + 3CO \tag{3}$$

$F_2C{=}CHF$ ($k = 4.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and FHC=CHF (cis/trans mixture, PCR/SCM Chemicals) ($k = 8.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) as the neutral reactants, the corresponding (adduct-3CO) product anions at m/z 137 and 119, respectively, were also exclusively generated (eq 4 and 5).

$$\underset{m/z\ 139}{(OC)_3Mn^-} + F_2C{=}CHF \rightarrow \underset{m/z\ 137}{Mn(C_2HF_3)^-} + 3CO \tag{4}$$

$$\underset{m/z\ 139}{(OC)_3Mn^-} + FHC{=}CHF \rightarrow \underset{m/z\ 119}{Mn(C_2H_2F_2)^-} + 3CO \tag{5}$$

This reaction type was extended to the perfluoroalkane CF_3CF_3 and the results are shown in eq 6. Since the

$$\underset{m/z\ 139}{(OC)_3Mn^-} + CF_3CF_3 \rightarrow \underset{m/z\ 155}{Mn(C_2F_4)^-} + 2CO + COF_2 \tag{6}$$

reductive elimination of F_2 from an intermediate complex is unlikely to be exothermic, we suggest that COF_2 is an expelled neutral.[9,12] Although the rate constant for this reaction ($k = 9.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}) was more than 2 orders of magnitude *less* than the rate constants measured with the fluoroethylenes, the exclusive product anion at m/z 155 was believed to be the same ion formed in eq 3. The considerably slower reaction with C_2F_6 implies that the fast reactions of the 14-electron $(OC)_3Mn^-$ with the fluorinated alkenes occur by initial π-coordination.

This process of trisdecarbonylation was new in our experience with the ion–molecule chemistry of $(OC)_3Mn^-$.[8,13-15] The kinetic and product results of the reactions with the fluorinated ethylenes require a large reaction exothermicity. It is, therefore, most unlikely that the product ions of reactions 3–5 are simple π-complexes which may be the process occurring in eq 2. To determine the structures of these (adduct-3CO) product ions in eq 3–5, the further ion–molecule reactions of the m/z 155, 137, and 119 anions with SO_2 were carried out (eq 7–9, with the nature of the bonding to the $C_2F_xH_{4-x}$ (x = 2–4) unit unspecified).[10] In all three of these reactions, we observe formation of a fragmented product negative ion at m/z 157 which is the result of ejection of the corresponding acetylene molecule, C_2F_2, C_2HF, and C_2H_2, respectively, from the initially formed excited adducts.[9]

$$\underset{m/z\ 155}{Mn(C_2F_4)^-} + SO_2 \xrightarrow[\text{He}]{0.94} \underset{m/z\ 219}{(O_2S)Mn(C_2F_4)^-} \tag{7a}$$

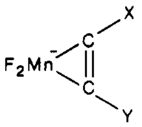
$$\underset{m/z\ 155}{Mn(C_2F_4)^-} + SO_2 \xrightarrow{0.06} \underset{m/z\ 157}{(O_2S)MnF_2^-} + C_2F_2 \tag{7b}$$

$$\underset{m/z\ 137}{Mn(C_2HF_3)^-} + SO_2 \xrightarrow[\text{He}]{0.27} \underset{m/z\ 201}{(O_2S)Mn(C_2HF_3)^-} \tag{8a}$$

$$\underset{m/z\ 137}{Mn(C_2HF_3)^-} + SO_2 \xrightarrow{0.73} \underset{m/z\ 157}{(O_2S)MnF_2^-} + C_2HF \tag{8b}$$

$$\underset{m/z\ 119}{Mn(C_2H_2F_2)^-} + SO_2 \rightarrow \underset{m/z\ 157}{(O_2S)MnF_2^-} + C_2H_2 \tag{9}$$

The results of the ion–molecule reaction induced decompositions of the three (adduct-3CO) product anions with SO_2 strongly suggest that the structures of these ions at m/z 155, 137, and 119 are of the general form $F_2Mn(XC_2Y)^-$ (1) where X and Y are F or H. The increases in the branching fractions for the ligand substitution process in eq 7b, 8b, and 9 suggest that the relative binding energies of the acetylenes in these complex negative ions is $C_2F_2 > C_2HF > C_2H_2$. The absence of further reaction of the product ions at m/z 155, 137, and 119 in eq 3–5 with the excess fluorinated alkenes present or with higher



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[10] Observation of a total adduct is assumed to require collisional stabilization of the initially formed excited adduct with the helium buffer gas to remove the excess energy. The flow parameters (P_{He} = 0.7 Torr and $\bar{v}$ = 58 mol s^{-1}) used in generating $(OC)_{3,4}Mn^-$ cannot be significantly varied to determine P_{He} effects on product distributions.

[11] The slow reaction of $(OC)_4Mn^-$ with C_2F_4 forming the adduct and (adduct–CO) in eq 2 is similar to the results of C_2F_4 reacting with the complexes $(OC)Fe(NO)_2^{\bullet-}$, $(OC)_2Co(NO)^{\bullet-}$, and $(\eta^3\text{-}C_3H_5)Co(CO)_2^{\bullet-}$; Schell, P. L. Ph.D. Thesis, Kansas State University, 1986.

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concentrations of the olefin substrate added to the flow suggests that the fluoride and acetylene ligands serve as multielectron donors with 16- or 18-electron configurations at Mn in these complexes.

We speculate that the reactions of the 14-electron complex $(OC)_3Mn^-$ with the fluorinated olefins occur by initial π-coordination yielding the excited 16-electron adducts $[(CO)_3Mn(\pi\text{-}C_2F_xH_{4-x})^-]^*$ (2) where $x = 2$–4. The major difference in the adduct 2 ($x = 4$) and the product ion at m/z 239 in reaction 2b is the larger internal energy in 2. This could result in (a) C–F bond activation in 2 which proceeds to give $F_2Mn(C_2F_2)^-$ or (b) CO ligand loss yielding an intermediate 14-electron complex negative ion which ultimately forms the product. In spite of these uncertainties, the oxidative insertions into the two *vic*-CF bonds must be sufficiently exothermic to effect loss of the two or three CO ligands yielding the product ions 1. Experiments designed to clarify the mechanism and to determine the generality of vicinal dehalogenation with different halides and metal complex negative ions are underway.

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Insertion of Carbon Disulfide into Ruthenium–Alkenyl Bonds. Formation of an Alkenedithiocarboxylate Ligand

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Summary: CS_2 reacts with complexes $Ru(CO)Cl(HC{=}CHR)(PPh_3)_2$ (R = Ph or *t*-Bu) to give products $Ru(CO)Cl(S_2C(H)C{=}CHR)(PPh_3)_2$ (R = Ph (**1**) and *t*-Bu (**2**)). The insertion products contain an alkenedithiocarboxylate ligand coordinated through two sulfur atoms. The structure of **1** has been established by an X-ray diffraction study.

Insertion of carbon disulfide into transition-metal–hydrogen[2] and –phosphorus bonds[3] are common, leading to formation of dithioformate and phosphoniodithiocarboxylate ligands. Metal–carbon bonds are less reactive toward this molecule, but in some cases a coupling between carbon disulfide and an alkyl ligand is observed.[4] In general, the coordination chemistry of carbon disulfide provides an attractive entry into the chemistry of sulfur-containing coordinated ligands.[5,6]

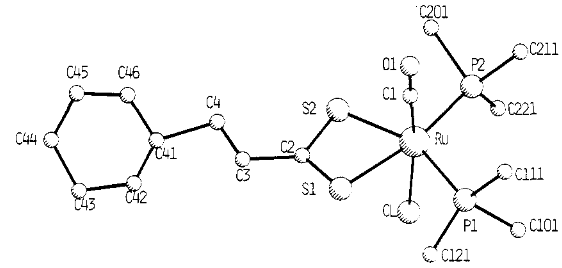
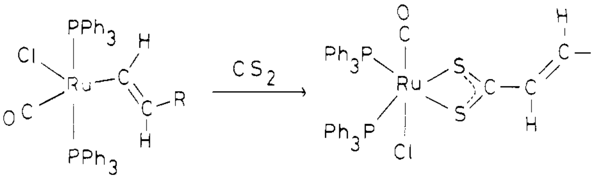


Figure 1. Molecular structure of compound 1 showing the atomic numbering scheme (phenyl groups are omitted for clarity). Selected bond distances (Å): Ru–P(1) = 2.43 (2), Ru–P(2) = 2.39 (2), Ru–Cl = 2.47 (2), Ru–S(1) = 2.52 (2), Ru–S(2) = 2.35 (2), Ru–C(1) = 1.81, O(1)–C(1) = 1.02, S(1)–C(2) = 1.65 (4), S(2)–C(2) = 1.83 (5), C(2)–C(3) = 1.56, C(3)–C(4) = 1.25. Selected angles (deg): S(1)–Ru–S(2) = 72.4 (7), Cl–Ru–C(1) = 170.6, P(1)–Ru–S(2) = 154.5 (7), P(2)–Ru–S(1) = 169.2 (6), P(1)–Ru–P(2) = 108.3 (6).

Recently we have shown that $Ru(CO)ClH(PPh_3)_3$ reacts with nonactivated alkynes to give unsaturated, five-coordinated alkenyl complexes of type $Ru(CO)Cl(R'C{=}CHR)(PPh_3)_2$.[7] When R′ = H, dimethyl acetylenedicarboxylate inserts into the ruthenium–alkenyl σ bond to give complexes that contain a butadienyl ligand with a subsequent additional coordination through a ketonic oxygen atom of one methyl carboxylate group.[8] This type of coordination was also observed in insertion reactions of activated mono- and disubstituted acetylenes into $Ru(CO)ClH(PPh_3)_3$.[9] These previous results suggest that the ruthenium–alkenyl σ bond is very reactive toward unsaturated molecules other than alkynes, possibly also toward CS_2. Indeed, alkenyl complexes $Ru(CO)Cl(HC{=}CHR)(PPh_3)_2$ react with carbon disulfide to form complexes of type $Ru(CO)Cl(S_2CCH{=}CHR)(PPh_3)_2$ which contain a vinyldithiocarboxylate ligand coordinated through two sulfur atoms (eq 1).



(1)

R = Ph **1** or Bu^t **2**

In a typical reaction, $Ru(CO)Cl(HC{=}CHR)(PPh_3)_2$ (R = Ph or *t*-Bu) and slight excess of carbon disulfide were heated at reflux in dichloromethane for 2 days under an atmosphere of nitrogen. After concentration, a solid precipitated on addition of Et_2O. Recrystallization from $CH_2Cl_2/MeOH$ gave orange crystals of 1 (R = Ph) or yellow crystals of 2 (R = *t*-Bu).[10] The IR spectra of the products exhibit one terminal carbonyl stretching vibration and one band at 955 and 971 cm^{-1}, respectively, characteristic of ν(CS) in chelating dithiocarboxylate ligands.[11] The ^{1}H NMR spectra show two doublets expected for monosubstituted alkenyl groups not bonded to the metal with two hydrogens in trans configuration (J = 15.5 Hz for 1 and 16 Hz for 2).

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(10) For **1**: IR (KBr) ν(CO) 1940, ν(CS) 955 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.6–7.3 (Ph + H), 6.9 (d, J = 15.5 Hz, H) ppm. Anal. Calcd for $C_{46}H_{37}RuOClS_2P_2$: C, 63.62; H, 4.26. Found: C, 63.40; H, 4.43. For **2**: IR (KBr) ν(CO) 1943, ν(CS) 971 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.5–7.0 (C_6H_5), 6.7 (d, J = 16 Hz, H), 6.2 (d, J = 16 Hz, H), 1.0 (s, *t*-Bu) ppm. Anal. Calcd for $C_{42}H_{41}RuOClS_2P_2$: C, 61.19; H, 4.98. Found: C, 60.93; H, 5.01.

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