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]

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).

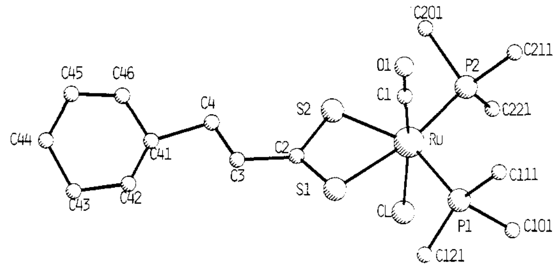
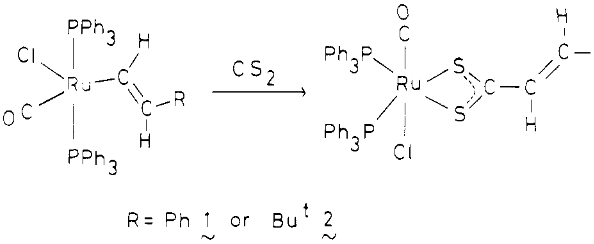


Figure 1. Molecular structure of compound 1 showing the atomic numbering scheme (phenyl groups are omitted for clarity). Selected bond distances (Å): Ru–P(1) = 2.43 (2), Ru–P(2) = 2.39 (2), Ru–Cl = 2.47 (2), Ru–S(1) = 2.52 (2), Ru–S(2) = 2.35 (2), Ru–C(1) = 1.81, O(1)–C(1) = 1.02, S(1)–C(2) = 1.65 (4), 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).



(1)

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 ^1H 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}; ^1H 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}; ^1H 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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An interesting aspect of complexes 1 and 2 is the relative position of the two phosphine ligands. In dithioformate complexes $MX(S_2CH)(CO)(PR_3)_2$ (M = Ru or Os, X = Cl or Br, and R = Ph, Ph_2Me, or $PhMe_2$), the cis isomer is formed in a first step but the trans isomer is observed after lengths of heating in benzene.[2] Moreover, the cis and trans isomers were detected in phosphoniodithiocarboxylate complexes $[RuH(CO)(S_2CPR_3)(PCy_3)_2][BPh_4]$ (R = Cy or Et) synthesized at moderated temperatures.[3] The cis isomer of complex $IRCl_2(S_2CH)(PPh_3)_2$ was also obtained from the reaction of (trans chlorides) $IrCl_2(PPh_3)_3$ with carbon disulfide in boiling benzene, but the cis → trans isomerization was not observed.[2] From spectroscopic data of the crude complexes 1 and 2 only one isomeric form seems to be formed even in solution at room temperature after several days. In order to determine the relative position of the phosphines and to confirm the nature of the dithiocarboxylate ligand in complexes 1 and 2, a X-ray diffraction study was undertaken.[12] Suitable single crystals of 1 were obtained from a CH_2Cl_2/MeOH solution.

The molecular structure of 1 is shown in Figure 1. One important feature of the molecule is the cis disposition of the two phosphines with a P(1)–Ru–P(2) angle of 108.4°. The two phosphorus, the ruthenium, and the two sulfurs are in a plane forming with C(1) and Cl a very distorted octahedral geometry around of the metallic center. The C(1)–O(1) distance is very short (1.02 Å), perhaps influenced by the nearly trans position of the Cl ligand (170.6 (3)°). A similar situation was observed in the complex $OsCl(CO)(HC{=}CHPh)(P\text{-}i\text{-}Pr_3)_2$.[13] The ruthenium–sulfur distances are different (2.52 (2) and 2.35 (2) Å) as well as the ruthenium–phosphorus bonds (2.43 (2) and 2.39 (2) Å).

It is interesting to note that the shorter Ru–S distance is pseudotrans to the longer Ru–P distance and vice versa, suggesting a trans effect between the ligands. The related dithiocarbamate ligands frequently are not symmetrically bonded to metals.[14] The S(1)–Ru–S(2) angle (72.4 (7)°) is similar to those observed in other octahedral (dithioformato)ruthenium complexes.[15,16] The rest of the dithiocarboxylate ligand was easily identified by spectroscopic techniques (IR and ^1H NMR), but in the crystallographic study of 1, the C(3)–C(4) double bond appears significantly short (1.252 (1) Å) compared with others.[7]

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Registry No. 1, 113161-98-1; 2, 113161-99-2; Ru(CO)Cl(HC=CHPh)$(PPh_3)_2$, 109800-33-1; Ru(CO)Cl(HC=CH-*t*-Bu)$(PPh_3)_2$, 113161-97-0; CS_2, 75-15-0.

Supplementary Material Available: Tables of final atomic coordinates and final anisotropic thermal parameters for $Ru(CO)Cl(S_2CHC{=}CHC(C_6H_5))(P(C_6H_5)_3)_2$ (5 pages); a listing of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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[12] Crystal data: $C_{46}H_{37}ClOP_2S_2Ru$; M_r 867.6; monoclinic; $a = 15.09$ (2), $b = 16.531$ (5), $c = 17.96$ (2) Å; $\beta = 106.18$ (12)°; $V = 4302.7$ (8) $Å^3$ (by least-squares refinement on a CAD-4 diffractometer for 25 automatically centered reflections, $\lambda = 0.7107$ Å); space group *Cc*; $Z = 4$; $D_{calcd} = 1.28$ g cm^{-3}; poor crystal (0.1 × 0.1 × 0.2 mm); $\mu(Mo\ K_\alpha) = 11.7$ cm^{-1}. Data collection and processing. Intensity data were recorded by the w–2θ scan technique. A total of 7747 reflections with $1 < \theta < 25°$ were measured; 1300 were considered observed ($I > 2\sigma(I)$). No measurable intensities were obtained at high resolution. Absorption corrections were made (Walker, N.; Stuart, P. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158–166). Structure Determination. Ru atom was located from a Patterson map. The other atoms except hydrogens were found in successive Fourier syntheses. The hydrogen atoms were located by geometrical calculations. Because of the low resolution, it was impossible to refine the whole of structure and part of the atoms were fixed. Anisotropic temperature factors were applied to Ru, P, Cl, and S. Unit weights were applied to every reflection (Martínez-Ripoll, M.; Cano, F. H. PESOS, Instituto Rocasolano, CSIC, Madrid). The refinement converged at $R = 0.10$ ($R_w = 0.109$) for observed reflections only. Calculations were performed with the XRAY70 System (Stewart, J. M.; Kundell, F. A.; Baldwin, J. C. The XRAY70 System, Computer Science Center, University of Maryland, College Park, MD, 1974). Atomic scattering dispersion correction factors for Ru, P, Cl, and S were chosen from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. 4. The molecule plot was drawn with PLUTO (Motherwell, S.; Clegg, B. PLUTO, Program for plotting molecular and crystal structures, 1978, Cambridge Data Center, Cambridge England).

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Sterically Accelerated Carbon–Carbon Bond Formation at Hafnium: Formation and Structure of $Hf(\eta^5\text{-}C_7H_{11})[N(SiMe_2CH_2PR_2)_2]$ (R = *i*-Pr) via Coupling of Coordinated Allyl and Butadiene Fragments

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Summary: A unique coupling of an allyl and a butadiene ligand occurs within the coordination sphere of hafnium to generate an $\eta^5\text{-}C_7H_{11}$ fragment. The reaction is accelerated by the presence of bulkier ancillary phosphines.

Carbon–carbon bond-forming reactions are probably the single most important transformation in synthetic organic methodology.[1] Of particular interest are such reactions that occur in the coordination sphere of a transition-metal complex since the resulting stereoselectivity of the process can often be fine-tuned by changes in the ancillary ligands at that metal center.[2] In the course of examining the fundamental chemistry of "lower" oxidation states of the group 4 metals, we discovered a simple C–C coupling/rearrangement reaction at hafnium which is accelerated by increasing the steric bulk of the ancillary ligand.

Since phosphine donors are relatively rare[3] as ancillary ligands for early metal complexes, we have developed a mixed donor system of the formula $^-N(SiMe_2CH_2PR_2)_2$ which binds in a tridentate fashion to zirconium and

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