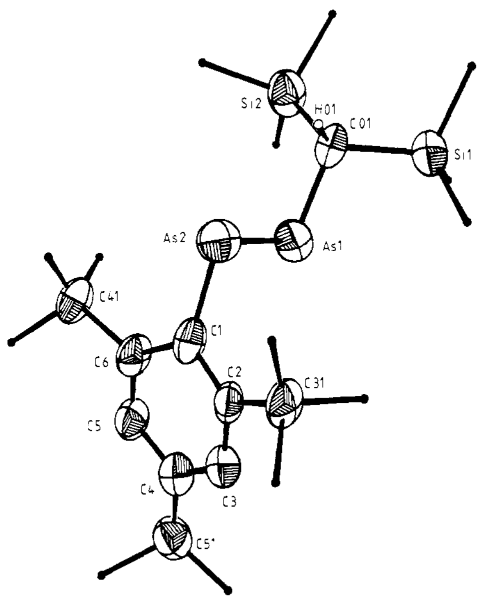
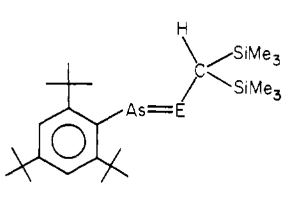


Figure 1. View of the $(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)As{=}AsCH(SiMe_3)_2$ (4) molecule. The methyl carbons are of reduced size for clarity. Important parameters: As(1)–As(2) 2.224 (2), As(1)–C(01) 1.976 (10), As(2)–C(1) 1.946 (10) Å; As(2)–As(1)–C(01) 99.9 (3)°, As(1)–As(2)–C(1) 93.6 (3)°.



4, E = As
7, E = P

found, 554.1745) and UV spectroscopy (λ_{max} 255 (ϵ 12660), 368 (ϵ 6960), and 449 nm (ϵ 180)) Confirmation of the structure of **4** was provided by a single-crystal X-ray diffraction study.[5] Like the congeneric diphosphenes, $[(Me_3Si)_3C]_2P_2$ (**5**)[6] and $(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)_2P_2$ (**6**),[1a] **4** adopts a trans geometry (Figure 1) and the skeletal atoms (C(01), As(1), As(2), and C(1)) are planar within experimental error (0.017 Å). The arsenic–arsenic distance in **4** (2.224 (2) Å) is the shortest such distance reported[7,8] and is consistent with the value of $\sim$2.3 Å that Dahl et al.[7a,b] have suggested for the arsenic–arsenic double bond. The bond angles at arsenic (99.9 (3)° at As(1); 93.6 (3)° at As(2)) are appreciably smaller than the bond angles at phosphorus in the diphosphenes **5** (108.5 (4)° av)[6] and **6** (102.8 (1)°),[1a] reflecting both the tendency to increasing p character in the ligand bonds as group 5A in descended and possibly a decrease in steric forces resulting from a lengthened double bond.

The primary arsine, **3**, also proved useful for the synthesis of a phosphaarsene (RP=AsR). Thus, treatment of an equimolar quantity of **3** and $(Me_3Si)_2CHPCl_2$[3] in THF solution at 0 °C in the presence of a 5% excess of DBU afforded orange-crystalline $(Me_3Si)_2CHP{=}As(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ (**7**) (mp 118–120 °C) after purification as per **4**. Compound **7** was characterized spectroscopically: HRMS, M^+ calcd 510.2248, found 510.2256; UV λ_{max} 254 (ϵ 10440), 354 (ϵ 8400), and 431 (ϵ 220). The 32.384-MHz $^{31}P\{^1H\}$ NMR spectrum exhibited a very low-field resonance (s, δ 533), which is characteristic of double-bonded phosphorus compounds.[1]

Acknowledgment. Generous financial support from the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. 1, 86528-35-0; **2**, 86528-36-1; **3**, 86528-37-2; **4**, 86528-38-3; **7**, 86528-39-4; $2,4,6\text{-}(t\text{-}Bu)_3C_6H_2Li$, 35383-91-6; $AsCl_3$, 7784-34-1; AsF_3, 7784-35-2; $(Me_3Si)_2CHAsCl_2$, 76505-21-0; $(Me_3Si)_2CHPCl_2$, 76505-20-9.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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[4] No unsupported arsenic–arsenic double bonds have been reported previously. Metal complexes of the type RAs–AsR–M are known, however. See: (a) Elmes, P. S.; Leverett, P.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1971**, 747. (b) Huttner, G.; Schmid, H.-G.; Frank, A.; Oraina, O. *Angew. Chem., Int. Ed. Engl.* **1976**, *158* 234.

[5] Crystal data for **4**: $C_{25}H_{48}As_2Si_2$, M = 554.17, triclinic, space group $P\bar{1}$ (No. 2) (by refinement); a = 9.955 (9), b = 10.393 (7), c = 15.159 (5) Å; α = 89.56 (4)°, β = 85.39 (6)°, γ = 78.31 (9)°; U = 1530 (3) Å^3, D_c = 1.199 g cm^{-3}, Z = 2, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 22.6 cm^{-1}. From a total of 5046 unique reflections, measured on an Enraf-Nonius CAD-4 diffractometer over the range $2.0 \leq 2\theta \leq 50.0°$, 2508 ($I > 2.5\sigma(I)$) were used to solve (Patterson and difference Fourier) and refine (full matrix, least squares) the structure of **4**. No absorption correction was applied. All non-hydrogen atoms were refined by using anisotropic thermal parameters while H(01) was positionally refined with a fixed isotropic temperature factor. Refinement with unit weights converged smoothly to give final residuals R = 0.0807, R_w = 0.1062. Since the crystal quality was relatively poor, the percentage of observed data was somewhat low, causing rather high residuals and some difficulties with the refinement of one carbon atom (C(33)).

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Elemental Sulfur and Selenium Induced Intramolecular Carbyne–Carbyne Coupling in Trinuclear Bis(carbyne) Cobalt Clusters. A Novel Entry into Metalladithiolenes and Metalladiselenolenes

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Sulfur is not only an undesirable pollutant in coal[1] and petroleum[2] but is also detrimental to fuel-related catalytic processes, such as hydrocarbon reforming[2] and Fischer–Tropsch synthesis.[3] While homogeneous transition-metal complexes have been studied as potential models[4] for hydrodesulfurization processes[5] and for sulfur–sulfur interactions,[6] none have specifically probed the reactivity of sulfur with respect to carbon-based potential surface analogues. We report that μ_3-η^1-carbyne ligands couple intramolecularly in the coordination sphere of trinuclear cobalt clusters when exposed to elemental sulfur (and selenium) to provide a

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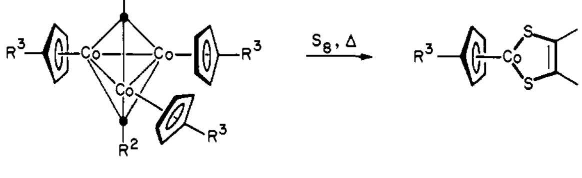
novel, efficient synthetic entry into η^5-cyclopentadienylcobaltadithiolenes and selenolenes.

We have demonstrated that $[\mu_3\text{-}\eta^1\text{-}CR^1][\mu_3\text{-}\eta^1\text{-}CR^2][CpCo]_3$ clusters (**1**), Cp = η^5-C_5H_5, undergo electrophilic H–D[7] (and



1 **2**

a $R^1 = R^2 = C_6H_5$; $R^3 = H$
b $R^1 = C_6H_5$; $R^2 = C_6D_5$; $R^3 = H$
c $R^1 = C_6H_5$; $R^2 = CH_2CH_3$; $R^3 = H$
d $R^1 = R^2 =$ *n*-Bu; $R^3 = H$
e $R^1 = R^2 = CO_2CH_3$; $R^3 = H$
f $R^1 = R^2 = C_2Si(CH_3)_3$; $R^3 = H$
g $R^1 = R^2 = C_6H_5$; $R^3 = CH_3$

other)[8] exchange and deck shifts in double-deck systems involving simultaneous carbyne–carbyne coupling and decoupling.[9] These processes were viewed as possible models for surface-catalyzed transformations of hydrocarbon fragments.[10] Whereas the metal core in **1** is extraordinarily air stable,[8] we now find that an unprecedented reaction with excess (>0.75 equiv S_8) elemental sulfur[11] ($CHCl_3$, Δ, 48 h) degrades the cluster to the metalladithiolenes **2** in mostly quantitative yield.[12] The only other identifiable product is the known $(CpCo)_3S_2$[13] (ca. 33% yield based on Co). Selenium results, albeit more slowly, in the metalladiselenolenes analogous to **2**. Metalladichalcogenes are interesting molecules because of their unusual modes of bonding, electrochemistry, and reactivity.[14] Few examples exist containing selenium or cobalt,[14] and synthetic approaches have mainly relied on the use of appropriate dichalcogen-containing precursors (dithiolates, dithietenes, etc.).[14] Some systems are accessible by direct reaction of alkynes with metal sulfides and selenides.[15]

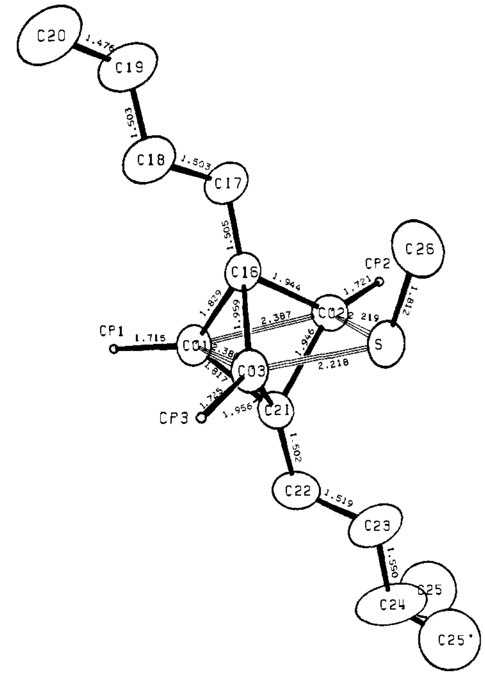
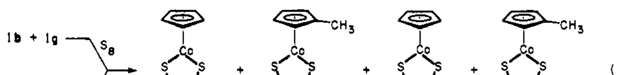


Figure 1. ORTEP drawing of **3** including selected bond lengths (Å). CP1, CP2, and CP3 are the centroids of the cyclopentadienyl ligands. Ellipsoids are scaled to represent 50% probability surface. There is some disorder at the terminus of one of the butyl substituents.

The selective preparation of **2c** from **1c** and, more rigorously, **2b** from **1b** clearly indicates that *intramolecular carbyne–carbyne coupling* has occurred during the reaction. This is only the second unambiguous example of such a process[9] and the first to be induced by an external reagent.

Mechanistically, considering the nucleophilic nature of **1**,[7,8] we suggest that sulfur attacks the cluster as an electrophile, possibly edge on, as observed for proton in **1d**[8] and for sulfur in other systems.[16] Consistent with this notion, dimethyl(methylthio)sulfonium tetrafluoroborate[17] converts **1d** (CH_3NO_2, room temperature, 1 h) to the corresponding edge-thiolated salt **3**[12] (Figure 1). One notes that in **3** the distances between Co_2–Co_3 (2.738 Å) are no longer bonding, whereas those from $Co_{2,3}$ to Co_1 are unchanged.[18] Moreover, the carbyne–cobalt bonds to $Co_{2,3}$ lengthen, but those of Co_1 shorten relative to **1**.[18] Treatment of **3** with sulfur furnishes **2d** (30%).

A crossover experiment involving a mixture of **1b** and **1g** showed complete scrambling ($CHCl_3$, Δ, 48 h), (1). However, a control



(1)

experiment (**2b** + **2g**, $CHCl_3$, Δ, 48 h) revealed the occurrence of the known[14a] but mechanistically obscure exchange between the metalladithiolenes, (1). Exchange could occur in three ways: (1) by Cp transfer[19] [treatment of **2g** with Cp anion (THF, Δ, 24 h) gave **1g**], (2) CpCo transfer (equivalent to enedithiolate exchange),[20] and (3) alkyne crossover [**2a** reacts with dimethyl acetylenedicarboxylate to give **2e** (CH_2Cl_2, Δ)].

Exposure of **2g** to $CpCo(Se_2C_2R_2)$, *R* = *n*-Bu (mp 72–73 °C),

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[12] All new compounds gave satisfactory analytical and/or spectral data. Compound **2a**: purple crystals, 100%; mp 113–114 °C; *m/e* 366 (M^+, 73.6), 188 (100); ^1H NMR (C_6D_6, 250 MHz) δ 4.71 (s, 5 H), 6.95 (m, 6 H), 7.45 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 79.6, 127.1, 127.9, 129.0, 142.2, 168.8; IR (KBr) 1598, 1490, 1440, 755, 690 cm^{-1}. **2c**: purple crystals, 100%; mp 110–111 °C. **2d**: purple crystals, 100%; mp 62–64 °C. **2e**: violet crystals, 98%; mp 112–114 °C. **2f**: aquamarine crystals, 32%; mp 115–116 °C. **2g**: blue crystals, 100%; mp 165–166 °C. **3**: black plates, 90%; mp >300 °C; *m/e* 557 (M^+, 1.68), 189 (100); ^1H NMR (CD_3CN, 250 MHz) δ 1.21 (s, 3 H), 1.28 (t, $J = 8$ Hz, 3 H), 1.36 (t, $J = 7.2$ Hz, 3 H), 2.05 (m, 4 H), 2.53 (m, 2 H), 2.99 (m, 2 H), 4.81 (s, 10 H), 5.08 (s, 5 H) 5.27 (m, 4 H); X-ray, crystal size 0.21 × 0.23 × 0.32 mm, monoclinic Laue symmetry, space group $P2_1/C$, $a = 8.8230$ (6) Å, $b = 20.3331$ (25) Å, $c = 15.3307$ (14) Å, $V = 2699$ Å^3, 25 °C, $\mu_{calcd} = 19.36\ cm^{-1}$, radiation graphite monochromatized Mo Kα, scan range $3° \leq 2\theta \leq 45°$, 3916 reflections collected, 3525 unique with $F^2 > 3\sigma(F^2)$, $R = 0.0332$, $R_w = 0.0493$.

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the selenium analogue of **2d**, gave (C_6D_6, 90 °C, sealed NMR tube) exchange products (mass and NMR spectral analysis) in which the chalcogen had *remained attached* to the alkyne fragment, ruling out option 3. Similar reaction of $CpRh[S_2C_2(C_6H_5)_2]$ (20%;[21] mp >250 °C), the rhodium analogue of **2a**, with $CH_3C_5H_4Co(S_2C_2R_2)$, R = *n*-Bu (30%;[21] mp 116–118 °C), produced only CpRh and $CH_3C_5H_4Co(S_2C_2R_2)$ products. Thus, option 2 is operating, probably through the intermediacy of bridging metalladichalcogene dimers.[14a,22]

Finally, in as much as one may regard metal clusters as potential surface analogues,[23] we note that a calculation has predicted accelerated bond scission in alkynes on surfaces covered by chalcogens.[24] Our system provides, at least formally, a homogeneous example of the reverse transformation.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC-03-76SF00098, and in part by the NSF (CHE 82-00049). K.P.C.V. is a Camille and Henry Dreyfus Teacher-Scholar (1978–1983). The crystal structure analysis was carried out by Dr. F. J. Hollander, U.C. Berkeley X-ray Crystallographic Facility. Thanks are due to Johnson and Matthey for a gift of rhodium chloride hydrate.

Supplementary Material Available: A listing of positional and thermal parameters and tables of bond lengths and angles derived from crystallographic analysis of **3** (5 pages). Ordering information is given on any current masthead page.

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Nucleophilic Displacement with a Selectively Solvated Nucleophile: The System $OH^-\cdot H_2O + CH_3Br$ at 300 K

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When the familiar nucleophilic displacement reaction[3-6] between OH^- and CH_3Br is run in the gas phase for the selectively solvated nucleophile $OH^-\cdot H_2O$, the major product at 300 K is Br^- (reaction 1a). This reaction, for solved ions in the gas phase, is *not* the corresponding reaction found for solvated ions in solution.

$$OH^-\cdot H_2O + CH_3Br \rightarrow CH_3OH + Br^- + H_2O \quad \Delta H^\circ = -31\ \text{kcal/mol} \quad (1a)$$

$$\rightarrow CH_3OH + Br^-\cdot H_2O \quad \Delta H^\circ = -43\ \text{kcal/mol} \quad (1b)$$

Table I. Rate Constants and Heats of Reaction

reactants	ΔH°, kcal/mol[a]	k, cm^3/(molecule s) × 10^{10} SIFT (300 K)[b]	FA (300 K)[c]	ICR[d]
$OH^- + CH_3Br$	−55.7	17	10 ± 2	19
$OH^-\cdot H_2O + CH_3Br$	−30.7	11	6.3 ± 2.5	
$OH^-\cdot(H_2O)_2 + CH_3Br$	−14.3		0.02 ± 0.01	
$OH^-(H_2O)_3 + CH_3Br$	+0.7[e]		<0.002	
$OH^- + CH_3Cl$	−47.5	13	15	16

[a] Estimated for the channel $OH^-\cdot(H_2O)_n + CH_3X \rightarrow CH_3OH + nH_2O + X^-$. [b] Estimated accuracy ±50%. [c] Flowing afterglow measurements, ref 4 and 5. [d] Ion cyclotron resonance measurements, ref 3a. [e] The uncertainty in the thermochemistry (~2 kcal/mol) is enough that this could be exothermic.

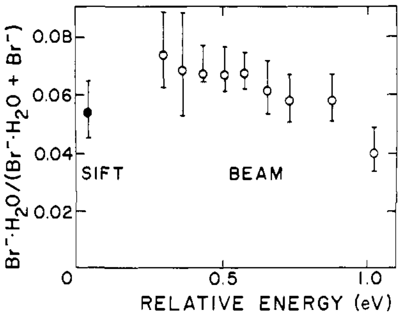

Figure 1. Fraction of $Br^-\cdot H_2O$ in the products as a function of relative energy. Open circles, beam results; filled circle, SIFT result (300 K).

$$OH^-\cdot(H_2O)_n + RX \rightarrow ROH + nH_2O + X^- \quad \text{gas phase} \quad (2a)$$

$$\rightarrow ROH + X^-\cdot(H_2O)_n \quad \text{solution} \quad (2b)$$

This result belies[7] the attractive and plausible notion that solvated-ion reactions bridge the gap between the reactions of unsolvated ions in the gas phase and of fully solvated ions in solution.[5]

Two different techniques have been used here: a selected ion flow tube (SIFT) at 300 K[8,9] and a double mass spectrometer[10] at relative energies down to ~0.3 eV. Solvated ions were produced by electron bombardment of water vapor (~10^{-2} torr). Table I summarizes rate constant data for the reaction of hydroxide ions, hydrated and unhydrated, with methyl halides; our measurements[11] agree acceptably with published values.

The high yield of Br^- (~95%) is seen not to be the consequence of collision-induced dissociation of $Br^-\cdot H_2O$ in the flow-tube sampling orifice, since the beam results, taken under single collision conditions, are identical (Figure 1).[12] Nor does the yield of Br^- result from the unimolecular decomposition of vibrationally excited $Br^-\cdot H_2O$. First, we find for other nucleophilic displacement reactions involving solvated ions little or no solvation of the leaving group.[13] Second, increasing the relative translational energy does not increase the $Br^-/Br^-\cdot H_2O$ ratio (Figure 1).[14]

Br^- is thus identified as the principal *primary* product. Solvate

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(11) Microcanonical rate constants, evaluated from the beam data at the lowest energies, e.g., Figure 1, also show agreement.

(12) Discrimination in the beam experiment, resulting from the kinematics, would favor collection of $Br^-\cdot H_2O$.

(13) Supported by limited supplementary studies on higher hydrates and other substrates (CH_3Cl). Hierl, P. M., Paulson, J. F., Henchman, M., manuscript in preparation.

(14) Contrast the strongly exothermic reaction $OH^-\cdot(H_2O)_2 + CO_2 = HCO_3^-\cdot H_2O + H_2O$ (ΔH° = −60 kcal/mol) where the product ratio $HCO_3^-\cdot H_2O/HCO_3^-$ falls from ~10 at ~0.1 eV to ~0.01 at ~1 eV relative energy (Hierl, P. M.; Paulson, J. F., manuscript in preparation).

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