of intermediate range interactions between main group centers have recently been identified in other main group–transition metal clusters.[17] A fuller assessment of the situation here awaits the structural characterization of neutral **2**.

Electrical measurements show that [**2**][(TCNQ)$_2$] is an *n*-type semiconductor. Four probe conductivity measurements were obtained along the needle axis which is parallel to the long axis of the TCNQ molecules.[18] Plots of $-\ln(R)$ vs. kT from 300 to 220 K (5° intervals) give a band gap of 0.24 and 0.26 eV for two different crystals. These values are comparable to the band gap for PbTe (0.27 eV).[20] Thermoelectric power measurements at several different temperatures (T_{av} = 262.3 K), again along the needle axis, indicate that electrons are the majority carriers. Given the synthetic manipulability of metal sulfide clusters,[21] there is reason to expect that the electrical properties of this type of compound can be developed much further. The incentives for such an undertaking are accentuated by the extraordinary properties observed for those metal sulfide clusters prepared by traditional high-temperature methods.[22]

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Supplementary Material Available: Tables of positional and thermal parameters for [(MeCp)$_5$V$_5$S$_6$][(TCNQ)$_2$] (5 pages); a listing of structure factors for [(MeCp)$_5$V$_5$S$_6$][(TCNQ)$_2$] (17 pages). Ordering information is given on any current masthead page.

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Oxidative Decarbonation of an Acetylide Ligand

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Summary: The organometal acetylide bridged dicobalt complexes [Cp(CO)$_2$MC≡CPh][Co$_2$(CO)$_6$] with M = Fe or Ru undergo a nondestructive reaction with oxygen which results in the net loss of one acetylide carbon atom together with a CO ligand and the formation of the alkylidyne-bridged clusters (μ_3-PhC)Co$_2$MCp(CO)$_7$.

It is standard knowledge that most organometallic compounds have to be handled in the absence of air and that their applications involve reductive chemistry, i.e., the use of unsaturated compounds, CO, or H$_2$. Nondestructive oxidative reactions are rare, and only recently has it become obvious that ligand substitutions by oxidants lead to novel classes of compounds.[1] We believe that an extensive chemistry of oxidative ligand transformations has yet to be uncovered. In support of this assumption we report here an oxygen-induced ligand fragmentation.

In the course of cluster construction studies we investigated the trinuclear acetylide complexes **1a**[2] and **1b** which can be considered as metalloalkyne representatives of the well-known Co$_2$(CO)$_6$(μ-alkyne) class. After observing that these compounds are not completely destroyed when their solutions are exposed to air, we optimized their oxidative conversions and found they proceeded according to Scheme I, producing the alkylidyne-bridged MCo$_2$ clusters **2a** and **2b**. In a typical run over 8 h a slow stream of oxygen was bubbled for five 1-min periods into a solution of ca. 1 mmol of **1b** in 20 mL of *n*-hexane and 10 mL of dichloromethane. Filtration, concentration, and crystallization yielded about 50% of **2b**. **2a** was obtained analogously in about 20% yield. Both clusters are fully characterized including elemental analyses. Their identity could be deduced via spectral analogy[3] with that of the corresponding μ_3-MeC-bridged FeCo$_2$ cluster[4] and was confirmed for **2b** by a crystal structure determination.[5] The lack of quantitative conversion in these reactions is due not so much to uncontrolled destruction of the starting compounds **1** but to the fact that the product clusters **2** are quite air-sensitive themselves. Nevertheless this route is the best one so far for producing **2b**-type FeCo$_2$ clusters.[4]

The good yield of **2b** indicates that the **1** → **2** conversions cannot involve sacrificing 50% of the starting material, thereby generating CPh fragments or their precursors which then attack remaining **1**, or any similar destructive reaction step. On the other hand, the nonquantitative reactions prevent simple mechanistic conclusions. Qualitative gas analysis showed the gaseous reaction products to contain CO and CO$_2$ from which no conclusions can be drawn since this is not unusual for oxidations of metal carbonyls. Control experiments (heating of **1b** under Ar and treatment of **1b** with H$_2$O/Ar and with H$_2$O/O$_2$)[6] indicate that **1** → **2** is not a thermal interconversion and that water, which can cleave acetylide

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(3) IR data (C$_6$H$_{12}$, cm^{-1}): **2a**, 2082 s, 2040 vs, 2032 vs, 1992 w, 1984 w, 1919 w; **2b**, 2080 s, 2036 vs, 2030 vs, 1988 w, br, 1952 w, br. NMR data (CDCl$_3$, internal Me$_4$Si): **2a**, 7.5 (m, 5 H), 4.43 (s, 5 H); **2b**, 7.4 (m, 5 H), 4.82 (s, 5 H).

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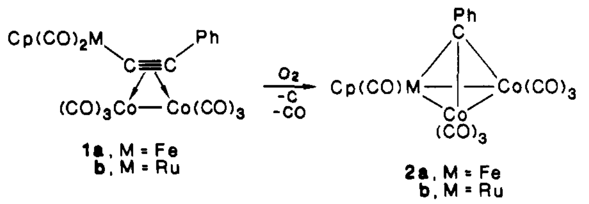
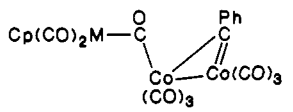
Scheme I

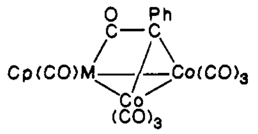


$C{\equiv}C$ bonds[7], is not involved in the reaction.

The available evidence suggests that the inner carbon atom in 1, i.e., the one which is attached to three metal atoms, is the one which is attacked by oxygen, and the resulting CO unit is lost subsequently by decarbonylation. In view of the possibilities of alkyne ligand scissions with[7] and without[8] chemical attack at the alkyne C atoms two types of possible reaction intermediates come into mind. Adhering to the 18-electron rule **3** could result from $C{\equiv}C$ scission followed by oxidation whereas **4** would represent initial oxidation and loss of one CO ligand. Although at the moment this mechanism is purely speculative, in both cases the emergence of the CPh ligand which has to become μ_3 bridging can be visualized.



3



4

Cluster model systems related to surface-catalyzed CO interconversions have focused on the deoxygenation of CO ligands forming carbide species[9] which then undergo C–C couplings[10]. The reactions presented herein represent the reversal of such sequences and underline our proposition that by variation of its metal constituents a polymetallic system can be tuned such that it supports organic reactions in its ligand sphere in both possible directions.[11] Further work will elucidate the course of the reaction by isotopic labeling studies and test the possible generalization of this approach.

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Registry No. [1]a, 104575-70-4; **1b**, 104575-71-5; **2a**, 89253-31-6; **2b**, 104575-72-6; Co, 7440-48-4; Fe, 7439-89-6; Ru, 7440-18-8.

(6) In a typical control experiment **1b** (42 mg, 0.07 mmol) was kept at 40 °C for $4^1/_2$ h in 15 mL of the original reaction solvent (hexane/dichloromethane, 2:1) under an argon atmosphere without any reaction. Addition of 1 mL of deoxygenated and Ar-saturated water and vigorous stirring for 12 h did not lead to any change. When a slow stream of O_2 was subsequently bubbled through the solution for 30 s and stirring was continued, TLC tests indicated the beginning formation of **2b** after 30 min and the complete disappearance of **1b** after 5 h. Chromatography over silica gel then yielded 15 mg (39%) of **2b**.

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Reductive Distortion of Azobenzene by an Organosamarium(II) Reagent To Form $[(C_5Me_5)_2Sm]_2(C_6H_5)_2N_2$: An X-ray Crystallographic Snapshot of an Agostic Hydrogen Complex on an Ortho-Metalation Reaction Coordinate[1]

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Summary: $(C_5Me_2)_2Sm(THF)_2$ reacts with $C_6H_5N{=}NC_6H_5$ in toluene to form $[(C_5Me_5)_2Sm](C_6H_5)NN(C_6H_5)[Sm(C_5Me_5)_2]$ characterized by X-ray crystallography and spectroscopic techniques. The complex crystallizes from toluene at −30 °C in space group $P2_1/n$ with a = 10.855 (7) Å, b = 20.435 (5) Å, c = 21.686 (9) Å, β = 106.68 (4)°, and D_{calcd} = 1.48 g cm^{-3} for Z = 4 dimers. The $(C_5Me_5)_2Sm$ groups are coordinated to the NN unit (NN distance = 1.25 (1) Å) in a trans manner with Sm–N distances of 2.40 (1) and 2.41 (1) Å. The C_6H_5 groups are attached to the NN unit in a trans geometry with C–N distances of 1.56 (2) and 1.61 (1) Å. The above four groups are arranged asymmetrically around the NN unit such that the two samarium atoms are closer to one of the phenyl rings than to the other. Short (phenyl ortho hydrogen)–samarium distances of 2.29 and 2.34 Å are observed.

The soluble divalent organosamarium(II) complex $(C_5Me_5)_2Sm(THF)_2$[3] previously has been found to display unusual reductive chemistry with CO[4] and with CO/alkyne combinations.[5] We report here that this reducing agent also can react with nitrogen-containing substrates in a unique way. With azobenzene, it is possible to trap an unusual complex displaying agostic metal hydrogen interactions[6] which may be related to ortho-metalation reaction pathways.[7,8]

Addition of $C_6H_5N{=}NC_6H_5$ (0.032 g, 0.177 mmol) to purple $(C_5Me_5)_2Sm(THF)_2$ (0.200 g, 0.354 mmol) in 10 mL of toluene in a nitrogen-filled glovebox resulted in an immediate color change to dark blue. After the solution was stirred 6 h, the solvent and THF were removed by rotary evaporation to give a dark blue complex identified as $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$ (0.179 g, 90%) by analytical[9] and X-ray methods[10] (eq 1).

(1) Reported in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985.

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(9) Complexometric metal analysis. Calcd for $SmNC_{26}H_{35}$: Sm, 29.37. Found: Sm, 28.6. A complete elemental analysis (Analytische Laboratorien) was incomplete (Sm, 27.95; C, 57.28; H, 6.13; N, 2.39) but gave a reasonable elemental ratio of Sm:N:C:H = 1:0.92:26:33. UV–vis (15.5 mg in 100 mL of toluene): 600 (br, ϵ 1300), 372 (shoulder, ϵ 5300) nm. UV–vis (4.65 mg in 100 mL of toluene): 272 (ϵ 22000), 210 (ϵ 16000) nm.

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