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Reactivity of Chromium–Selenium Triple Bonds: The First Example of a Planar Cr_3Se Multiple-Bond System Generated via Selective Reduction[1]

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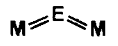
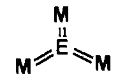
The recent spate of discoveries of generally applicable synthetic routes to complexes containing multiple bonds between transition metals and unsubstituted ("bare") main group elements has led, especially in the case of the more electropositive elements of groups 4–6, to a rapid accrual of new compounds of wide structural diversity.[3] Initial reactivity studies have revealed close relationships to the chemistry of metal–metal bonds.[3,4] All of the valence electrons of the main group elements often participate in bonding to transition metals resulting in an exceptionally unsaturated bonding situation, with the Cr_2Se complex **1** representing a prototypal example.[3]

According to cyclovoltammetric measurements,[5] complexes of type A, B, or C (E = S, Se, Te) often show two successive,

A

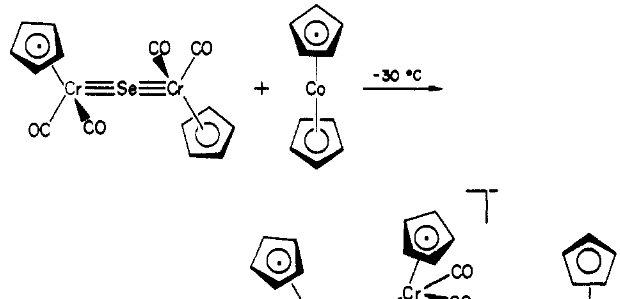


B



C

reversible or quasi-reversible one-electron reduction processes at medium scan speeds. The compound $(\mu\text{-Se})[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$ (**1**; type A, with E = Se) serves as an informative example. The cyclovoltammogram (DMF vs. SCE, v = 100 mV/s) shows nearly reversible half-wave potentials at $E_{1/2}(I) = -0.72$ V (ΔE = 65 mV) and $E_{1/2}(II) = -1.40$ V (ΔE = 70 mV) for the two-step reduction $\mathbf{1} \rightarrow [\mathbf{1}]^{-\cdot} \rightarrow [\mathbf{1}]^{2-}$. We now found that selective reduction of the Cr_2Se complex **1** with cobaltocene ($E_{1/2}$-$[Cp_2Co^+/Cp_2Co] = -0.77$ V; DMF)[6] in tetrahydrofuran/diethyl ether mixtures at −30 °C smoothly leads according to eq 1 to the novel ionic complex of composition $[Co(\eta^5\text{-}C_5H_5)_2]^+[(\eta^5\text{-}C_5H_5)_3Cr_3(CO)_6Se]^-$ (**2**).[7]



(1)

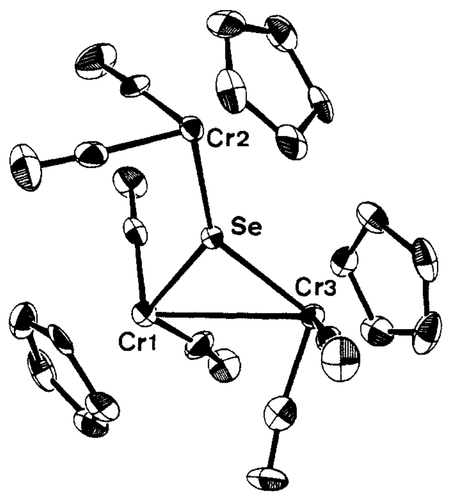
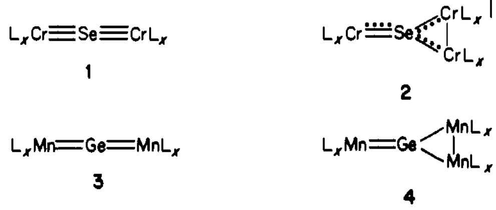


Figure 1. ORTEP view of the complex anion of compound **2** in the crystalline state (−50 °C). The complex crystallizes from tetrahydrofuran (THF)/diethyl ether mixtures at −78 °C with one molecule of THF and the cobaltocenium counterion. Selected bond angles (deg): Cr(1)–Se–Cr(2) 138.0 (2), Cr(1)–Se–Cr(3) 82.6 (1), Cr(2)–Se–Cr(3) 139.2 (2). The sum of the angles within the Cr_3Se core amounts to 359.9°.

Chart I. Isolobal and Isoelectronic Relationships between Compounds **1**, **2**, **3**, and **4** [$L_x = (\eta^5\text{-}C_5H_5)(CO)_2$]



As determined by an X-ray diffraction study,[8] the diamagnetic complex anion of this compound contains a strictly planar Cr_3Se unit, in which both the exo- and endocyclic Cr–Se bonds (227.9 (2) and 233.2 (2)/234.5 (2) pm, respectively) show significant multiple-bond character, whereas the Cr–Cr distance (308.8 (2) pm) corresponds to a single bond. This anion hence represents an unprecedented coordination mode for substituent-free sixth main group elements[3] (Figure 1).

The structure of the new Cr_3Se complex can be rationalized as follows: as the linear Cr_2Se complex **1** is isoelectronic with the Mn_2Ge compound **3** (same bonding situation within Cr_2Se

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(1) Paper 26 of the series "Multiple Bonds Between Main Group Elements and Transition Metals". This work was supported by the German Federal Ministry of Research, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the HOECHST Aktiengesellschaft, and the Chemische Werke Hüls AG. Paper 25: Herrmann, W. A.; Rohrmann, J. *Chem. Ber.* **1986**, *119*, 1437.

(2) (a) Technische Universität München. (b) Universität Frankfurt.

(3) For a recent review, see: Herrmann, W. A. *Angew. Chem.* **1986**, *98*, 57; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56.

(4) For a comprehensive monograph, see: Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

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(7) **Experimental Procedure.** A solution (−30 °C) of 1.00 g (5.29 mmol) of $Co(\eta^5\text{-}C_5H_5)_2$ in 10 mL of THF was added to a solution (−30 °C) of 0.82 g (1.93 mmol) of $(\mu\text{-Se})[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$ (**1**) in 5 mL of THF and 30 mL of diethyl ether, which, over a period of time, resulted in a gradual color change from red brown to dark green followed by slow precipitation. After approximately 25 days at low temperature, ca. 500 mg (50% based on chromium) of **2** were isolated as shiny black crystals, which could be recrystallized from THF/diethyl ether (2 + 1 volume ratio). The compound is readily soluble in THF and acetone to give dark green solutions but is insoluble in diethyl ether. The solutions are extremely air and thermal sensitive. The crystals decompose gradually at room temperature. **Spectroscopic Data.** IR (cm^{-1}, ν_{CO}; KBr) 1920 s, 1864 vs, 1820 s, 1805 s; (THF) 1920 m, 1875 vs, 1853 vs, 1829 m, 1816 m. ^1H NMR (270 MHz, $[D_6]$acetone, −80 °C) δ $(Co(\eta^5\text{-}C_5H_5)_2{}^+)$ 5.93 (s, 10 H), $((\eta^5\text{-}C_5H_5)_3Cr_3(CO)_6Se^-)$ 5.20 (s, 5 H; *exo*-$CpCr(CO)_2$, see text), 4.74 and 4.57 (2 × s, 2 × 5 H; *endo*-$CpCr(CO)_2$, see text). Correct elemental analyses have been obtained.

(8) Black crystals from THF/diethyl ether (−78 °C). Space group $P2_1/n$; a = 1314.4 (5) pm, b = 1635.7 (5) pm, c = 1625.1 (8) pm, β = 102.71 (3)°, $V = 3408 \times 10^6$ pm^3, Z = 4; $F(000)$ 1728, d(calcd) = 1.68 g cm^{-3}, μ = 24.2 cm^{-1}; Syntex $P2_1$ diffractometer, Mo Kα radiation, graphite monochromator, ω scan ($\Delta\omega$ = 1.0 deg/min; $2° \leq \theta \leq 24°$), t(max) = 60 s; h(0/15), k(0/18), l(−18/18); 5821 observed reflections, of which 4327 have $F_o \geq 2.5\sigma(F_o)$. The structure was solved by direct methods; all non-hydrogen atoms were refined anisotropically, hydrogen atoms were calculated from ideal positions and included in structure factor calculations; 437 parameters in two blocks; R = 0.065, R_w = 0.053. Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (Germany), by quoting the depository number CSD 51882, the names of the authors and the journal citation.

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and Mn_2Ge cores)[3,9] so is the Cr_3Se anion of **2** isoelectronic with the neutral Mn_3Ge compound **4** (Chart I).

The central selenium atom provides formally all available valence electrons for bonding to the three $(\eta^5\text{-}C_5H_5)Cr(CO)_2$ fragments ($d^5\text{-}ML_5$); the latter are isolobal with CH and CH_2^+ fragments, so that a structural relationship with *exo*-methylenecyclopropane exists for the anion of **2** as well as for the neutral compound **4** on account of the isolobal mapping Se $\underset{\smile}{\leftrightarrow}$ C^{2-} $\underset{\smile}{\leftrightarrow}$ CH^- (for **2**) and Ge $\underset{\smile}{\leftrightarrow}$ C as well as $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ $\underset{\smile}{\leftrightarrow}$ CH_2 (for **4**).[10]

The ^1H NMR spectra of the Cr_3Se complex **2** shows that the molecule is fluxional in solution. At −80 °C three well-resolved C_5H_5 signals appear, two of which broaden as the temperature is raised and form a single resonance at −40 °C. This observation is in agreement with a cis/trans isomerization of the dinuclear fragment $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$. The appearance of *one* sharp signal for the exocyclic $(\eta^5\text{-}C_5H_5)Cr(CO)_2$ moiety within the entire temperature range and at exactly the same chemical shift indicates that free rotation of this fragment occurs about the associated CrSe bond on the NMR time scale, which indicates the presence of triple bond contributions to this entity.[9]

Compound **2** is extremely sensitive to oxygen. Thus, upon exposure to air the starting material **1** is rapidly produced, albeit not quantitatively. The complex is stable in solution only at temperatures well below ambient but rapidly decomposes at room temperature to give the selenium-free salt $[Co(\eta^5\text{-}C_5H_5)_2]^+$-$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^-$[11a] and the cubane-type cluster compound $(C_5H_5)_4Cr_4Se_4$[11b] (X-ray structure analyses).

The formation of the diamagnetic polynuclear anion of the ionic complex **2** from a one-electron reduction of a diamagnetic starting material is a special case of what may turn out to be a new area for synthetic endeavor: the study of the secondary reactions of the initially formed radical anions.

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(9) Cf.: Kostic, N. M.; Fenske, R. F. *J. Organomet. Chem.* **1982**, *233*, 337.

(10) Review: Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1983**, *21*, 711.

(11) (a) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Riede, F.; Ziegler, M. L.; Sergeson, G. *Chem. Ber.*, in press. (b) Black crystals, insoluble in all common organic solvents. IR (cm^{-1}, KBr) 3102 w, 1872 m, 1431 m, 1005 m, 802 vs.

γ-Silicon Stabilization of Carbonium Ions

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Silyl substitution on the γ-carbon has recently been shown experimentally to have large effects on the stability of carbocation intermediates.[1] Further, these effects are strongly orientation dependent. In this paper, we offer an explanation of these results based on theoretical calculations on some model compounds.

Extensive theoretical and experimental results[2,3] have shown that the stabilization of H^- exchange between carbocations

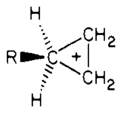
$$RCH_2^+ + HCH_3 \rightarrow RCH_3 + HCH_2^+$$

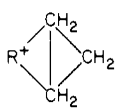
caused by silyl in the α-position is more effective than hydrogen by about 17 kcal/mol but less effective than methyl by about the same amount. Because α-silyl destabilizes an alcohol by about 7 kcal/mol, silyl is less stabilizing than methyl by 6–8 kcal/mol for OH^- exchange between cations. These α effects are regarded as inductive and hyperconjugative.

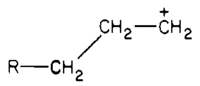
Wierschke et al.[2] have recently published a theoretical study of β-silyl. They concluded that the inductive effect was about equivalent to that of methyl but that the SiC bond was much more effective at hyperconjugative stabilization of the adjacent $\text{-}CH_2^+$ than was a CC bond. This was deduced from the strong orientation dependence of the stabilization energy which was maximum for a coplanar arrangement of the empty p orbital on the $\text{-}CH_2^+$ and the SiC bond.

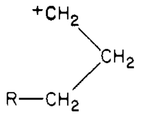
In γ-substituted compounds, one is always comparing hyperconjugation with a CC bond vs. hyperconjugation with CH bonds, so a strong dependence of the hyperconjugation on substituent is unexpected. Also, a γ substituent seems too far removed from the α site to exert much of an inductive effect. Nevertheless the experimental data show a large orientational dependence for γ-trimethylsilyl stabilization.

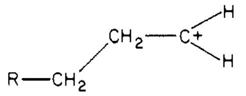
We have calculated RHF energies with various basis sets and symmetry-constrained geometry optimization. The symmetry constraints allow us to examine model conformations typical of the more constrained molecules studied experimentally. We have considered H, CH_3, SiH_3, and Li γ substitution of the propyl carbocation and alcohol. The alcohol was in a planar, all trans configuration with respect to RCCCOH. Several configurations were considered for each cation. The labels in Table I correspond to


cor (C_s)


edg (C_s)


tra-per (C_s)


cis-per (C_s)


tra-pla (C_s)

Here -per refers to a terminal CH_2^+ group perpendicular to the C–C–C mirror plane while -pla refers to a terminal CH_2^+ group lying in the C–C–C mirror plane. A few of the most critical optimized angles and bond lengths are included in Table I.

The stabilization energies (SE) in Table I for the different propyl cations were computed relative to the trans-perpendicular conformation. In the process of doing this calculation, we found that the 3-21G geometry, reported in The Carnegie-Mellon Archive,[4] was not fully optimized. The 1-propyl cation potential surface is unusually flat, so large geometry changes are possible with little change in energy. This is apparent in the small energy change in going from the trans-perpendicular structure, through the corner-protonated form, to the cis-perpendicular structure.[5] Because the surface is so flat, the results are also very basis set dependent with corner protonated lowest for 3-21G, trans perpendicular lowest for 6-31G, and cis perpendicular lowest for 6-31G*. In the latter case no trans-perpendicular stationary energy could be found. The flatness of the energy surface makes one anticipate that chemical substitution will also produce large changes in geometry.

For the other compounds in Table I, the stabilization energy is defined as the RHF energy for OH^- exchange with the *corresponding* conformation of propyl.

$$R(CH_2)_3^+ + H(CH_2)_3OH \rightarrow R(CH_2)_3OH + H(CH_2)_3^+$$

Cis-perpendicular silyl and trans- and cis-perpendicular lithium

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(4) Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 2nd ed.; 1981. Starting with the geometry reported there, we reproduced their energy and gradient. Further optimization with a tighter criteria for convergence led to the structure reported here. The main change was that the C_α–C_γ distance increased from 2.05 to 2.12 Å while the maximum gradient component decreased from 0.000 288 to 0.000 117.

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