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[20] Cross-correlation contributions to relaxation can lead to easily detectable dynamic shifts (that is, splittings), in particular when paramagnetic species are involved,[21] but they should also contribute to the natural linewidth with an order of magnitude which is at least as large. In contrast, the experimentally measured proton natural linewidth is about 6 Hz in MLCs.

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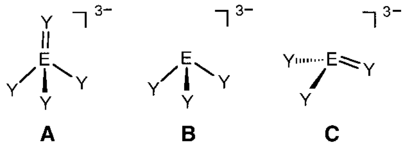
Novel Approach to Mixed Group 15/16 Element Ligands—Formation of Unusual Trichalcogenophosphonato Ligands in Mixed Fe/Cr Clusters**

Manfred Scheer,* Shubhangi B. Umbarkar,
Saurav Chatterjee, Rajiv Trivedi, and Pradeep Mathur*

Dedicated to Professor Henri Brunner
on the occasion of his 65th birthday

Complex chemistry of "naked" main group element ligands has been a fascinating area of research over the last few decades. Within this field, ligands consisting of different main group elements are scarce and are only well established between Group 15 and Group 16 elements.[1] Known synthetic approaches for obtaining such complexes make use of E_4Y_n cages (E = element from Group 15, Y = element from Group 16, $n = 3$, 4) or their metal salts, such as $M^I_3AsS_3$; another method is the chalcogenation of pnicogenido complexes. Recently Fenske et al. have used $SP(SSiMe_3)_3$ as a precursor to $(PS_4)^{3-}$ and $(P_2S_6)^{4-}$ ligands.[2]

While $EY_4{}^{3-}$ (type **A**; E = P, As; Y = S, Se) is established as a ligand in some complexes, the molecular structure of the complexed $EY_3{}^{3-}$ ligand (type **B**) has only been observed for E = As in $[Cp'_3Ti_2(\mu\text{-O})(\mu\text{-AsS}_3)]$ ($Cp' = \eta^5\text{-C}_5H_4Me$)[3] and for E = P in $[Pd_3(PS_4)(PS_3)(PEt_3)_4]$.[2b] So far complexes of type **C** ligands are unknown.



We report here a novel synthetic approach to mixed Group 15/16 element ligands by using the reaction of Group 15 element complexes with those of Group 16. This method leads to novel trichalcogenophosphonato ligands of type **C** (Y = S, Se). Our initial attempts to prepare mixed-metal clusters containing mixed chalcogenide/phosphorus bridging ligands centered on thermolysis and photolysis reactions between $[Fe_3(CO)_9(\mu_3\text{-}Y)_2]$ (Y = S (**1a**) or Se (**1b**)) and $[CpCr(CO)_2(\eta^3\text{-}P_3)]$ (**2**). Under such conditions, no new product was obtained; either the starting materials were

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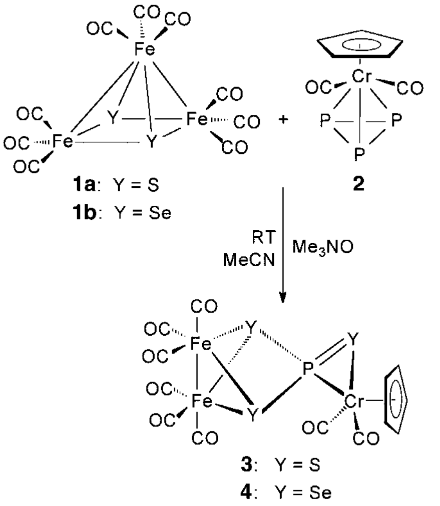
[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the German Academic Exchange Service (DAAD).

recovered intact or, after extended reaction periods, complete decomposition of **1** occurred. We therefore resorted to the use of trimethylamineoxide (Me_3NO) for labilization purpose, and from the reaction of **1** with **2** in acetonitrile, in the presence of Me_3NO, we could isolate the new complexes, $[\{Fe_2(CO)_6\}(\mu_3\text{-}Y_3P)\{CpCr(CO)_2\}]$ (Y = S (**3**) or Se (**4**)) [Eq. (1)].



(1)

The IR spectra of the products indicate the presence of only terminally bonded carbonyl groups, and the ^1H NMR spectra for both compounds show the signal for the Cp protons split into a small doublet due to coupling with the P atom. The ^{31}P NMR spectra show a singlet and, for **4**, two pairs of satellites due to different $^{31}P,^{77}Se$ couplings are also revealed. Mass spectra of both compounds showed molecular ion peaks and fragments arising from CO loss.

Single-crystal X-ray structure analyses were carried out for **3** and **4**. They are isostructural and crystallize with two independent molecules in the unit cell. Both molecules are similar in their structural parameters and a representative molecular structure of one of the molecules is shown in Figure 1.[4] The structure consists of a butterflylike $[Fe_2(CO)_6Y_2]$ unit and a $[CpCr(CO)_2Y]$ moiety; these are connected by a μ_4-P bridge which is bonded to the three chalcogenides and one Cr atom. The structures of **3** or **4** can be considered as the metal-substituted derivatives of a trithio- or triselenophosphonate, respectively, in which the P atom is bonded to a Cr atom and reveals two different chalcogen bonding modes. One P–Y bond in both compounds is shorter than the other two (P–S: 1.9761(10) in contrast to 2.1152(10) and 2.1202(10) Å; P–Se: 2.132(13) in contrast to 2.286(16) and 2.282(16) Å) and comparable to the P–Y double bond distances reported in the literature: 1.949 Å (av) in P_4S_5,[5] 1.949 Å (av) in $[Cp_4Fe_4(P_2S_2)_2]$,[6] 2.116 Å (av) in P_4Se_5,[7] and 2.101 Å (av) in $[Cp_4Fe_4(P_2Se_2)_2]$.[6] The other P–Se bond lengths in **4** are also comparable to the P–(μ_2-Se) and P–(μ_3-Se) bond lengths in $[Fe_4Se_2(\mu\text{-}Se_2PC\mathit{t}Bu)(CO)_{11}]$.[8] The three-membered Cr–P–Y subunit in **3** and **4**, which arises from the side-on coordination of the trithio- or triselenophosphonato ligand has been observed in the compounds $[Cp_4Cr_4(CO)_9(P_4Y_3)]$, which were obtained from the thermolysis of $[Cp_2Cr_2(CO)_6]$ with P_4Y_3 (Y = S,[9] Se[10]). The structures of $[Cp_4Cr_4(CO)_9(P_4Y_3)]$ also feature a $CpCr(CO)_2$ fragment connected to a P=Y subunit (Y = S, Se) with comparable P–Y bond lengths but longer Cr–P bond lengths (2.282 Å (av) for $[Cp_4Cr_4(CO)_9(P_4S_3)]$ and 2.29 Å (av) for $[Cp_4Cr_4(CO)_9(P_4Se_3)]$) than those in **3** (2.2148(9) Å) and **4** (2.218(8) Å). Assuming that the PY_3 ligand contributes three electrons to the Cr atom and six electrons to the Fe_2 unit, the 18-electron count for all three metal centers in **3** and **4** is satisfied.

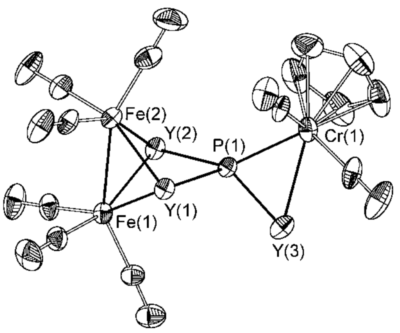


Figure 1. Representative molecular structure from the X-ray crystal structure analyses of **3** and **4** (molecule A, showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: **3** (Y = S): Cr(1)-P(1) 2.2125(9), Cr(1)-S(3) 2.5514(12), P(1)-S(3) 1.9783(10), P(1)-S(1) 2.1188(10), P(1)-S(2) 2.1204(10), Fe(1)-S(1) 2.2706(9), Fe(1)-S(2) 2.4704(9), Fe(2)-S(1) 2.2801(9), Fe(2)-S(2) 2.2790(8); Cr(1)-P(1)-S(3) 74.77(4), P(1)-S(3)-Cr(1) 56.80(3), P(1)-Cr(1)-S(3) 48.43(3), S(1)-P(1)-S(2) 85.84(4), P(1)-S(1)-Fe(1) 89.86(4), P(1)-S(1)-Fe(2) 86.66(4), P(1)-S(2)-Fe(1) 86.66(4), P(1)-S(2)-Fe(2) 86.65(4). **4** (Y = Se): Cr(1)-P(1) 2.218(2), Cr(1)-Se(3) 2.6859(18), P(1)-Se(3) 2.132(2), P(1)-Se(1) 2.2815(19), P(1)-Se(2) 2.2861(18), Fe(1)-Se(1) 2.3887(12), Fe(1)-Se(2) 2.3915(13), Fe(2)-Se(1) 2.3936(12), Fe(2)-Se(2) 2.4024(11); Cr(1)-P(1)-Se(3) 76.22(7), P(1)-Se(3)-Cr(1) 53.33(6), P(1)-Cr(1)-Se(3) 50.44(6), Se(1)-P(1)-Se(2) 85.31(7), P(1)-Se(1)-Fe(1) 89.97(5), P(1)-Se(1)-Fe(2) 86.43(6), P(1)-Se(2)-Fe(1) 89.79(6), P(1)-Se(2)-Fe(2) 86.12(5).

Formation of the new clusters formally involves the following: conversion of $[Fe_3(CO)_9(\mu_3\text{-}Y)_2]$ into an open $[Fe_2(CO)_6(\mu_2\text{-}Y)_2]$ butterfly unit and loss of a P_2 unit from $[CpCr(CO)_2P_3]$ to form a $[CpCr(CO)_2P]$ fragment, which abstracts one Y atom from $[Fe_3(CO)_9(\mu_3\text{-}Y)_2]$ such that an intermediate of the form $[CpCr(CO)_2PY]$ is obtained. New bond formation between the two Y atoms in another $[Fe_2(CO)_6(\mu_2\text{-}Y)_2]$ moiety and the P atom in the $[CpCr(CO)_2PY]$ unit yields **3** and **4**.

The results show the high synthetic potential of the novel approach to the production of mixed Group 15/16 element ligand complexes. Through the reaction between complexes of Group 15 and Group 16 elements complexes revealing novel coordination modes can be obtained. We are presently extending this approach to obtain different mixed Group 15/16 ligand complexes as well as investigating other methods for the activation of the starting materials, such as photolysis and ultrasonic activation.

Experimental Section

3 and **4**: In a typical preparation, a solution of trimethylamineoxide (44 mg, 0.6 mmol) in acetonitrile was added dropwise to an acetonitrile solution (50 mL) of $[CpCr(CO)_2(\eta^3\text{-}P_3)]$[12] (0.052 g, 0.2 mmol) and either $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$[11] (0.290 g, 0.6 mmol) or $[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$[11] (0.34 g, 0.6 mmol) with constant stirring at room temperature under an argon atmosphere. The solution was stirred for 30 min at room temperature and was closely monitored by thin layer chromatography. The solvent was removed under vacuum and the residue was dissolved in dichloromethane. The solution was filtered through Celite to remove the insoluble material and the solution was subjected to chromatographic workup using silica gel thin layer chromatography plates. Elution with n-hexane yielded a single brown band which contained **3** (30 mg, 25%) or **4** (46 mg, 32%).

Compound **3**: IR (n-hexane): $\tilde{\nu}(\mathrm{CO}) = 2083(\mathrm{s}), 2050(\mathrm{vs}), 2014(\mathrm{vs}), 1999(\mathrm{m}), 1919(\mathrm{m})\ \mathrm{cm}^{-1}$; EI-MS (70 eV, 180 °C): m/z (%): 579.7 (6) [M^+], 523.7 (24) [$M^+ - 2\,\mathrm{CO}$], 439.9 (26) [$M^+ - 5\,\mathrm{CO}$], 411.6 (9) [$M^+ - 6\,\mathrm{CO}$], 383.7 (22) [$M^+ - 7\,\mathrm{CO}$], 355.7 (100) [$M^+ - 8\,\mathrm{CO}$], 292.7 (52) [$M^+ - 8\,\mathrm{CO} - \mathrm{PS}$], 227.7 (25) [$M^+ - 8\,\mathrm{CO} - \mathrm{PS} - \mathrm{Cp}$]; ^{1}H NMR (250.113 MHz, 298 K, $\mathrm{CDCl_3}$, TMS): $\delta = 4.90$ (d, $^3J(\mathrm{P,H}) = 1.8$ Hz, 5H); ^{31}P NMR (101.256 MHz, 298 K, $\mathrm{CDCl_3}$, 85% $\mathrm{H_3PO_4}$ ext.): $\delta = 260.7$; m.p. 136–137 °C; elemental analysis (%) calcd for $\mathrm{C_{13}H_5CrFe_2O_8PS_3}$: C 26.9, H 0.86; found: C 26.2, H 1.3.

Compound **4**: IR (n-hexane): $\tilde{\nu}(\mathrm{CO}) = 2075(\mathrm{s}), 2042(\mathrm{vs}), 2006(\mathrm{vs}), 1991(\mathrm{m}), 1985(\mathrm{s}), 1920(\mathrm{m})\ \mathrm{cm}^{-1}$; EI-MS (70 eV, 180 °C): m/z (%): 721.8 (7) [M^+], 665.8 (20) [$M^+ - 2\,\mathrm{CO}$], 581.7 (21) [$M^+ - 5\,\mathrm{CO}$], 497.8 (100) [$M^+ - 8\,\mathrm{CO}$], 432.7 (12) [$M^+ - 8\,\mathrm{CO} - \mathrm{Cp}$], 321.8 (34) [$M^+ - 2\,\mathrm{Fe} - 8\,\mathrm{CO} - \mathrm{Cp}$]; ^{1}H NMR (250.113 MHz, 298 K, $\mathrm{CDCl_3}$, TMS): $\delta = 4.88$ (d, $^3J(\mathrm{P,H}) = 2.01$ Hz, 5H); ^{31}P NMR (101.256 MHz, 298 K, $\mathrm{CDCl_3}$, $\mathrm{H_3PO_4}$ ext.): $\delta = 235.1$ (s, $J(\mathrm{P,Se}) = 95.9$ and 269 Hz); m.p. 142–143 °C; elemental analysis (%) calcd for $\mathrm{C_{13}H_5CrFe_2O_8PSe_3}$: C 21.6, H 0.69; found: C 21.5, H 1.15.

Received: August 10, 2000 [Z15615]

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[4] Crystal structure analysis of **3** and **4**: STOE IPDS area-detector diffractometer with $\mathrm{Ag_{K\alpha}}$ radiation ($\lambda = 0.56087$ Å) for **3** and $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å) for **4**. The structures were solved by direct methods using SHELXS-86,[13a] and refined by full matrix least squares on F^2 using SHELXL-93,[13b] with anisotropic displacement for non-H atoms. H atoms were placed in idealized positions and refined isotropically using a riding model. **3**: $\mathrm{C_{26}H_{10}Cr_2Fe_4O_{16}P_2S_6}$, $M_r = 1160.04$, crystal size $0.40 \times 0.20 \times 0.03$ mm, monoclinic, space group $P2_1/n$, $a = 7.5570(15)$, $b = 21.477(4)$, $c = 24.213(5)$ Å, $\beta = 96.11(3)°$, $V = 3907.5(13)$ Å^3, $T = 213(2)$ K, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.972\ \mathrm{Mg\,m^{-3}}$, $\mu(\mathrm{Ag_{K\alpha}}) = 12.66\ \mathrm{cm^{-1}}$; 14890 independent reflections ($2\theta_{\max} = 52°$, $R_{\mathrm{int}} = 0.0669$), 505 parameters, $wR_2 = 0.1400$; R_1 (10513 with $F_o = 4\sigma\ (F_o)) = 0.0483$. **4**: $\mathrm{C_{26}H_{10}Cr_2Fe_4O_{16}P_2Se_6}$, $M_r = 1441.44$, crystal size $0.30 \times 0.15 \times 0.01$ mm, monoclinic, space group $P2_1/n$, $a = 7.5355(2)$, $b = 21.868(2)$, $c = 24.809(3)$ Å, $\beta = 96.16(3)°$, $V = 4172.4(10)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho_{\mathrm{calcd}} = 2.295\ \mathrm{Mg\,m^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 72.31\ \mathrm{cm^{-1}}$; 8095 independent reflections ($2\theta_{\max} = 52°$, $R_{\mathrm{int}} = 0.0816$), 505 parameters, $wR_2 = 0.1164$; R_1 (5107 with $F_o = 4\sigma\ (F_o)) = 0.0480$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148123 and CCDC-146124. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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About the Chemistry of Phosphorus Suboxides**

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While the molecular phosphorus subsulfides $\mathrm{P_4S_3}$, $\mathrm{P_4S_4}$, and $\mathrm{P_4S_5}$ are well known,[1] various attempts to prepare the corresponding molecular phosphorus suboxides have failed so far. In its polymeric form phosphorus suboxide "$\mathrm{P_4O}$" was already mentioned in 1832[2] but in molecular form $\mathrm{P_4O}$ has been detected only in rare gas matrices.[3] Using IR spectroscopy combined with ab initio calculations[4] it was possible to identify the geometries of three different isomers of $\mathrm{P_4O}$. The energetically most favorable isomer of $\mathrm{P_4O}$ possesses a planar five-membered ring (isomer **I** in Table 1), while a terminal (isomer **III** in Table 1) and a bridged-bonded isomer (isomer **II** in Table 1), which are closely related to the tetrahedral structure of the $\mathrm{P_4}$ molecule, were found to lie much higher in energy.[4]

While the structure of $\mathrm{P_4O}$ is known, very little is known about its chemistry. For the other phosphorus suboxides $\mathrm{P_4O}_n$ ($n = 2$–5), even structural information is missing. The question why phosphorus subsulfides have been prepared, but analogous oxides could not be isolated is generally answered by the statement that P–O bonds are more stable than P–S bonds, however, detailed thermodynamical data of phosphorus suboxides are not known. In order to extract a building-up

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[**] The authors thank J. Clade, A. Tellenbach, and M. Jansen (Max-Planck-Institut, Stuttgart) for many fruitful discussions. This work was supported by the Deutsche Forschungsgesellschaft (Sonderforschungsbereich 334) and the Fonds der Chemischen Industrie. Service and computer time from the HRLZ Jülich were essential for the present study.