Reaction of Group 15 Trichlorides ECl_3 with the Anion $[Mo_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$; Synthesis and Characterization of the First Complexes Featuring a Hetero μ,η^2-PE ligand (E = As, Sb)[**]

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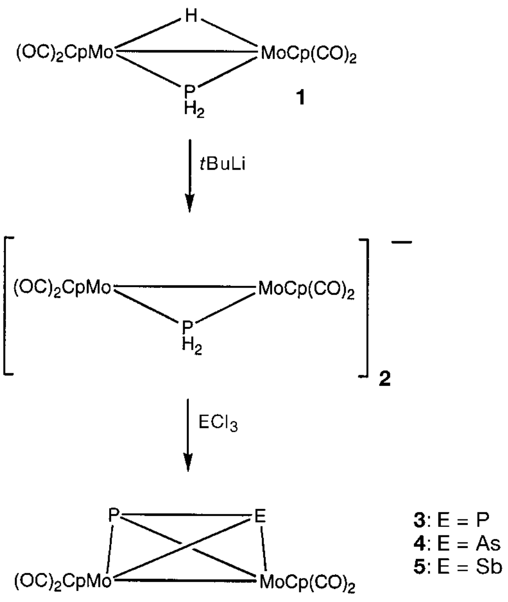
The synthesis of organometallics containing naked Group 15 ligands has been a fruitful area of research for a number of years. The E_2 ligand is particularly well known, having been observed in a wide range of complexes for both phosphorus and arsenic, and with rather fewer examples for antimony and bismuth.[1] In contrast to this plethora of homocomplexes, to our knowledge there have been no reported examples of structurally characterized complexes featuring heteroligands such as PAs or PSb; indeed, there are very few reports of structural characterization of the P–Sb bond at all.[2] We now report that the reaction of the anion $[Mo_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (**2**) with ECl_3 (E = P, As, Sb) affords the tetrahedrane complexes $[Mo_2Cp_2(CO)_2(\mu,\eta^2\text{-}PE)]$ (**3**, E = P; **4**, E = As; **5**, E = Sb) in moderate yields, presumably with concomitant elimination of one equivalent of LiCl and two equivalents of HCl.

Reaction of a THF solution of $[Mo_2Cp_2(CO)_4(\mu\text{-}H)(\mu\text{-}PH_2)]$ (**1**), prepared by the literature method,[3] with 1 equivalent of *t*BuLi leads to an immediate color change from orange to purple and essentially quantitative formation of $[Mo_2Cp_2(CO)_4(\mu\text{-}PH_2)]^-$ (**2**). Treatment of this solution with one equivalent of ECl_3 (E = P, As, Sb) results in a color change back to orange (Scheme 1). Chromatography on silica with 1:1 hexane:dichloromethane as eluent affords a small quantity of **1** and the air stable derivatives **3**–**5** as the only isolated products. Complex **3** was identified by comparison of its IR spectrum to that reported in the literature.[4] The new complexes **4** and **5** were identified by IR and NMR spectroscopy, mass spectrometry, and microanalysis. Complexes **4** and **5** have been the subject of single-crystal X-ray diffraction analyses.[5] The complexes crystallize in the space group *P*2/*c* with two crystallographically distinct molecules in the unit cell, like the diarsenic analogue $[Mo_2Cp_2(CO)_4(\mu,\eta^2\text{-}As_2)]$ (**6**)[6] but unlike the diphosphorus complex $[Mo_2Cp_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ (**3**).[4] The molecular structures of **4** and **5** are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are given in Table 1. The PAs ligand of **4** shows a 50:50 disordering over the two sites; the interatomic separation of 2.2324(13) Å is intermediate between those observed for the diphosphorus and diarsenic complexes.[4, 6] Similar behavior is observed for the PSb ligand in **5**, where the separation is observed to be 2.4699(14) Å. The Mo–Mo bond lengths of 3.0191(9) Å in **4** and 3.0563(11) Å in **5** are comparable with 3.038 Å in **6**[6] and 3.021 Å in **3**[4] and indicative of a single



Scheme 1. Synthesis of **3**–**5**.

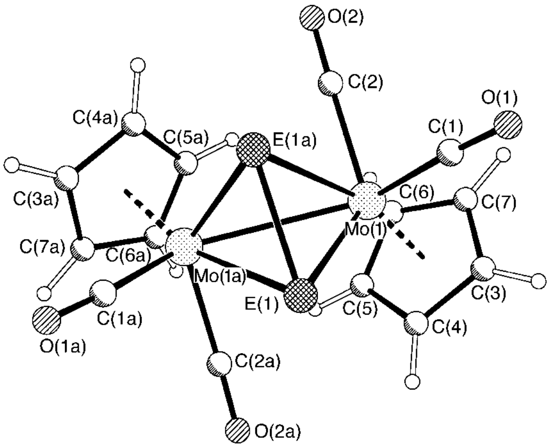


Figure 1. Molecular structure of **4**. E represents a P or an As atom.

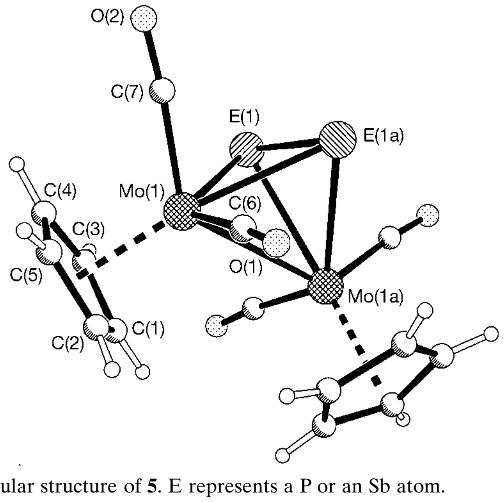


Figure 2. Molecular structure of **5**. E represents a P or an Sb atom.

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Table 1. Selected bond lengths [Å] and angles [°] for **4** and **5**.[a]

	4	**5**
Mo(1) – Mo(1a)	3.0191(9)	3.0563(11)
E(1) – E(1a)	2.2324(13)	2.4699(14)
Mo(1) – E(1)	2.6428(9)	2.6942(9)
Mo(1a) – E(1a)	2.6428(9)	2.6942(9)
Mo(1a) – E(1)	2.5468(10)	2.7972(9)
Mo(1) – E(1a)	2.5468(10)	2.7972(9)
E(1)-Mo(1)-E(1a)	50.91(3)	53.42(3)
E(1)-Mo(1)-Mo(1a)	55.92(2)	57.80(2)
E(1a)-Mo(1)-Mo(1a)	52.96(2)	54.59(2)
E(1a)-E(1)-Mo(1)	66.67(3)	65.42(2)
E(1a)-E(1)-Mo(1a)	62.32(2)	61.16(2)
Mo(1)-E(1)-Mo(1a)	71.12(3)	65.42(2)

[a] Two independent, but not significantly different, molecules reside in the unit cell. Values given refer to one molecule only.

Mo – Mo bond, as required for agreement with the eighteen-electron rule.

Complexes featuring hetero-Group 15 ligands of this type have not previously been prepared. We are currently investigating the range of naked-ligand and related complexes preparable from the μ-PH$_2$ species in this manner and comparing their reactivity to the reactivity of the known homocomplexes with Group 15 ligands.

Experimental Section

All reactions were performed under an atmosphere of dry oxygen-free nitrogen with solvents freshly distilled from the appropriate drying agent.

Synthesis of **5**: To a solution of **1** (0.497 g, 1.062 mmol) in THF (40 mL) was added *t*BuLi (0.63 mL of 1.7 M solution in pentane, 1.01 equiv.). The solution immediately became purple. SbCl$_3$ (0.244 g, 1.070 mmol) was added,and the mixture stirred for 2 min. The solution became deep orange. The solvent was removed under reduced pressure. The residue was redissolved in the minimum quantity of dichloromethane and applied to the base of TLC plates. Elution with hexane:dichloromethane (1:1) afforded orange **1** (0.096g, 0.205 mmol, 19 %) and red-orange **5** (0.241g, 0.410 mmol, 39 %). Similar treatment of **1** with PCl$_3$ or AsCl$_3$ result in the isolation of **3** and **4** in 29 % and 33 % yields, respectively. Selected spectroscopic data: [IR ($\tilde{\nu}_{CO}$ cm^{-1}) recorded in dichloromethane solution; ^{1}H NMR and ^{31}P NMR recorded in CDCl$_3$ solution; ^{31}P NMR chemical shifts recorded relative to P(OMe)$_3$ at $\delta = 0.0$ with positive shifts downfield. For conversion to 85 % H$_3$PO$_4$ as a reference, $\delta = 146.2$ should be added to the values given; calculated microanalytical values in parentheses]. **3**: $\tilde{\nu}_{C0}$ 1965vs, 1913vs; ^{31}P NMR $\delta = -188.5$, s. **4**: $\tilde{\nu}_{C0}$ 1959vs, 1908vs; ^{1}H NMR $\delta = 5.17$, s; ^{31}P NMR $\delta = -111.5$, s; FAB MS 541 [M^++1], 484, 457, 428 [$M^+ - n$CO, $n = 2-4$]; microanalysis C 30.96 (31.08), H 1.76 (1.85). **5**: $\tilde{\nu}_{CO}$ 1949vs, 1900vs; ^{1}H NMR $\delta = 5.14$, s; ^{31}P NMR $\delta = -50.6$, s; FAB MS 588 [M^++2), 532, 504 [$M^+ - n$CO, $n = 2$,3]; microanalysis C 28.45 (28.65), H 1.64 (1.72), P 5.31 (5.28)

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[5] Crystal data for **4**: C$_{14}$H$_{10}$AsMo$_2$O$_4$P, $M = 539.99$, monoclinic, space group *P*2/*c*, $a = 13.497(4)$ Å, $b = 7.479(4)$ Å, $c = 15.852(3)$ Å, $\beta = 96.03(2)°$, $V = 1591.3(10)$ Å^3 (by least-squares refinement on diffractometer angles from 25 centered reflections, $30 < 2\theta < 40°$), $T = 196(2)$ K, graphite-monochromated Mo$_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $Z = 4$, $\rho_C = 2.254$ Mg m^{-3}, $F(000) = 1032$, orange block, $0.40 \times 0.25 \times 0.25$mm, μ(Mo$_{K\alpha}$) = 3.752 mm^{-1}, semiempirical absorption correction based on ψ scans, relative transmission 0.837 – 1.000, Rigaku AFC5R diffractometer, $\omega - 2\theta$ scans, data collection range $5.16 < 2\theta < 54.96°$, $-17 \leq h \leq 17$, $0 \leq k \leq 9$, $-20 \leq l \leq 20$, 3 standard reflections showed no significant variation in intensity. Of 7614 reflections measured, 3655 independent ($R_{int} = 0.047$) used in all subsequent calculations. Solution by direct methods (SHELXL PLUS[7]) and subsequent Fourier syntheses, anisotropic full-matrix least-squares refinement on F^2 (SHELXL 93[8]), hydrogen atoms included by means of the riding model. Final $wR(F^2)$ on all data 0.168, conventional $R(F)$ 0.029 for 3030 observed reflections [$I > 2\sigma(I)$] weighting scheme $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$ and x and y are constants adjusted by the program, 199 parameters, GOF = 1.075, maximum $\delta/\sigma = 0.001$, maximum $\Delta\rho = 0.796$, minimum $\Delta\rho$ -1.179 e Å^{-3}. Crystal data for **5**: C$_{14}$H$_{10}$Mo$_2$O$_4$PSb, $M = 586.82$, monoclinic, space group *P*2/*c*, $a = 13.535(3)$ Å, $b = 7.640(2)$ Å, $c = 15.848(3)$ Å, $\beta = 95.09(2)°$, $V = 1632.3(6)$ Å^3 (by least-squares refinement on diffractometer angles from 25 centered reflections, $20 < 2\theta < 30°$), $T = 180(2)$ K, graphite-monochromated Mo$_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, $Z = 4$, $\rho_C = 2.388$ Mg m^{-3}, $F(000) = 1104$, orange block, $0.42 \times 0.30 \times 0.25$mm, μ(Mo$_{K\alpha}$) = 3.266 mm^{-1}, semiempirical absorption correction based on ψ scans, relative transmission 0.873 – 1.000, Rigaku AFC5R diffractometer, $\omega - 2\theta$ scans, data collection range $5.16 < 2\theta < 55.02°$, $0 \leq h \leq 17$, $0 \leq k \leq 9$, $-20 \leq l \leq 20$, 3 standard reflections showed no significant variation in intensity. Of 3912 reflections measured, 3758 independent ($R_{int} = 0.045$) used in all subsequent calculations. Solution by direct methods (SHELXL PLUS[7]) and subsequent Fourier syntheses, anisotropic full matrix least squares refinement on F^2 (SHELXL 93[8]), hydrogen atoms included by means of the riding model. Final $wR(F^2)$ on all data 0.1029, conventional $R(F)$ 0.0369 for 3029 observed reflections [$I > 2\theta(I)$] weighting Scheme $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$ and x and y are constants adjusted by the program, 200 parameters, GOF = 1.073, maximum $\Delta/\sigma = 0.001$, maximum $\delta\rho = 1.120$, minimum $\Delta\rho = -1.240$ e Å^{-3}.

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