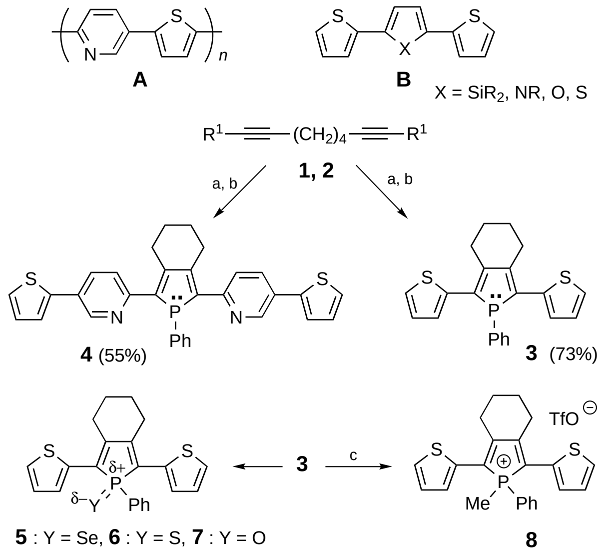
Electropolymerization of π-Conjugated Oligomers Containing Phosphole Cores and Terminal Thienyl Moieties: Optical and Electronic Properties**

Caroline Hay, Cédric Fischmeister, Muriel Hissler, Loic Toupet, and Régis Réau*

Dedicated to Professor Pierre H. Dixneuf
on the occasion of his 60th birthday

Thiophene-based π-conjugated oligomers and polymers have recently emerged as very promising organic devices for electronic and optical technologies.[1] The optoelectronic properties of these materials vary with the degree of extended conjugation and the inherent electron density of the π-conjugated backbone. A recent strategy to modulate these two parameters involves the synthesis of macromolecules featuring more than one type of conjugated-ring unit along the main chain.[2] Increased conjugation can be achieved in alternating copolymers such as **A** (Scheme 1) because of an intramolecular charge transfer (ICT) from the electron-donor thienyl to the electron-acceptor pyridinyl moieties.[3] The derivatives of **B**, the 2,5-bis(2-thienyl)heterocyclopentadienes, are not only versatile synthons for the preparation of copolymers,[2e, 4] but also act as well defined models suitable for studying the dramatic influence of the electronic properties of the central heteroatom and its effect on the degree of conjugation between the consecutive subunits. Silole derivatives of **B** (X = SiR$_2$) possess a higher degree of conjugation than thiophene and pyrrole analogues ($\Delta\lambda_{max} = 60$ nm) due to ICT involving the electron-accepting silicon-containing heterocyclopentadiene.[4e, 5] Phosphole-containing π-conjugated systems have been poorly investigated,[6] in spite of the phospholes possessing limited aromatic character and a reactive phosphorus atom,[7] which affords a family of chromophores with different electronic properties. Herein, we describe new chromophores featuring phosphole-based cores and terminal thienyl moieties, and the preparation of the first phosphole-containing polymers through electrooxidation.



Scheme 1. Synthesis of the chromophores featuring phosphole cores and terminal thienyl moieties. Synthesis: a) [Cp$_2$ZrCl$_2$], 2 BuLi, THF, −78 °C; b) PhPBr$_2$, THF; c) MeOTf. Cp = C$_5$H$_5^-$; OTf = OSO$_2$CF$_3$; R = alkyl, aryl; R^1 = 2-thienyl (**1**), 5-(2-thienyl)-2-pyridyl (**2**).

Besides 2,5-bis(2-thienyl)phosphole **3** (Scheme 1), a phosphorus-containing derivative of **B**, the mixed oligomer **4** was chosen as a target, since **4** should possess alternating donor and acceptor units as phospholes are generally considered electron-rich heterocyclopentadienes.[8] Derivatives **3** and **4** were prepared through an intramolecular coupling of diynes **1**[9a] and **2**[9b] via a zirconacyclopentadiene intermediate[5, 10] and addition of PhPBr$_2$ (Scheme 1). Phospholes **3** and **4** are obtained as air-stable orange solids after purification by flash chromatography on alumina (yields: **3**: 73 %; **4**: 55 %). Their NMR spectra show typical resonance patterns and the simplicity of the ^{13}C NMR spectra indicates a symmetric structure.[11] The endocyclic phosphole carbon atoms give two signals at low field, whereas only one set of signals is observed for the two substituents at the 2,5 positions. The proposed structures were confirmed by X-ray analysis performed on the free phosphole **3** (Figure 1) and W(CO)$_5$-coordinated **4**[12]

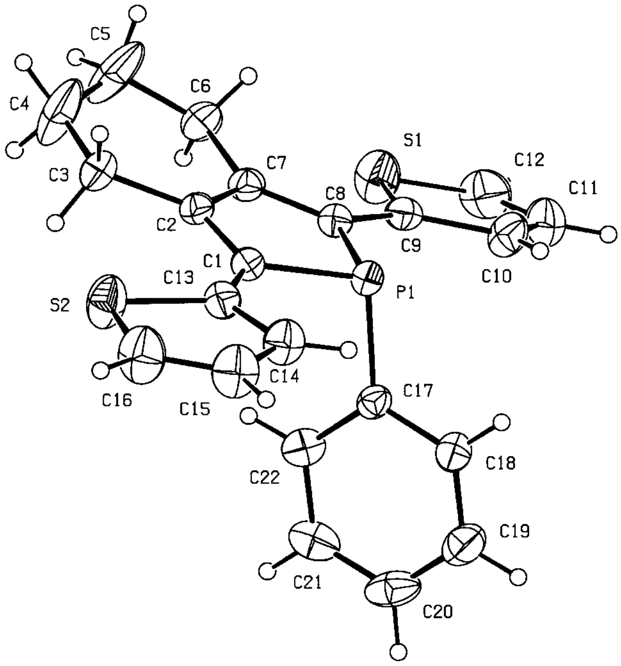


Figure 1. X-ray structure analysis of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.817(4), C1-C2 1.336(6), C2-C7 1.465(7), C7-C8 1.356(6), C1-C13 1.436(6), C8-C9 1.457(6); C1-P1-C8 90.9(2), C1-P1-C17 104.3(2), C8-P1-C17 104.1(2).

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[*] Prof. R. Réau, C. Hay, Dr. C. Fischmeister, Dr. M. Hissler
Organométalliques et Catalyse
Chimie et Electrochimie Moléculaires
UMR 6509, CNRS-Université de Rennes
Campus de Beaulieu, 35042 Rennes Cedex (France)
Fax: (+33) 2-99286939
E-mail: regis.reau@univ-rennes.1.fr

Dr. L. Toupet
UMR 6626, CNRS-Université de Rennes
Campus de Beaulieu, 35042 Rennes Cedex (France)

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(Figure 2).[13] In both cases, the thienyl rings exhibit a statistical disorder (90–60 % for the prevailing conformations), a feature which is typical for linear oligomers that bear terminal thiophene rings.[3a, 4d, 14] For both compounds, the twist angles between two adjacent rings are small (**3**: 16.7(5)° and 12.5(5)°; [W(CO)$_5$(**4**)]: 1.8(16)–18.3(17)°) and allow an extended π conjugation. The C–C links between the rings (**3**: 1.436(6)–1.457(6) Å; [W(CO)$_5$(**4**)]: 1.444(12)–1.476(12) Å) and the endocyclic C2–C7 bond (**3**: 1.465(7) Å; [W(CO)$_5$(**4**)]: 1.466(13) Å) are relatively short, whereas the endocyclic P–C bond lengths (**3** and [W(CO)$_5$(**4**)]: 1.817(4)–1.822(9) Å) approach that of a P–C single bond (1.84 Å). These solid-state data are in favour of an extended delocalisation path involving the dienic moiety of the phosphole rings and the two thienyl or 5-(2-thienyl)pyridyl units.

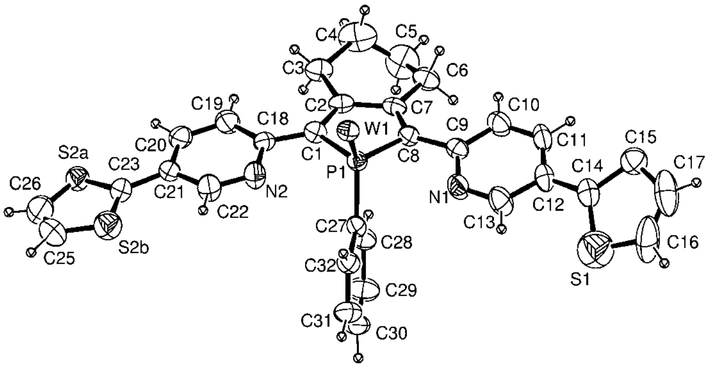

Figure 2. X-ray structure analysis of [W(CO)$_5$(**4**)]. Hydrogen atoms and carbonyl ligands have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-C1 1.822(9), C1-C2 1.362(12), C2-C7 1.466(13), C7-C8 1.341(12), C1-C18 1.444(12), C8-C9 1.476(12), C12-C14 1.445(14), C21-C23 1.469(13), P1-W1, 2.534(2); C1-P1-C8 90.7(4), C1-P1-C27 104.3(4), C8-P1-C27 104.4(4).

The absorption maximum in the UV/Vis spectrum of compound **4** (λ_{max} = 427 nm) is at a notably longer wavelength than that recorded for 2,5-bis(2-dipyridyl)phosphole (λ_{max} = 390 nm[15]) and clearly indicates an extended π conjugation. The fluorescence spectrum of this oligomer shows an emission maximum at 570 nm, which reveals a large Stokes shift ($\Delta\lambda$ = 143 nm). Remarkably, **3** shows an absorption at 412 nm, a wavelength only slightly shorter than that of **4**[16] but considerably longer than those observed for the related derivatives of **B** that feature central electron-rich rings, such as pyrrole derivatives (X = N–CH$_3$, λ_{max} = 322 nm)[4d] or group 16 heterocyclopentadienes (λ_{max} = 366 (X = O),[2e] 356 nm (X = S)[5b]). This unexpected, relatively high value for λ_{max} is within the range recorded for 2,5-bis(2-thienyl)siloles (X = SiPh$_2$, λ_{max} = 418 nm), which possess an unusually low HOMO–LUMO gap due to ICT.[5] This surprising analogy between silicon- and phosphorus-containing heterocyclopentadienes[17] should be even more pronounced for σ^4,λ^4-phospholes, which have no aromatic character and feature an electropositive tetrahedral heteroatom. We prepared electrically neutral σ^4,λ^4-phospholes with polarised $P^{\delta+}$=$Y^{\delta-}$ bonds (Y = O, S, Se) and cationic σ^4,λ^4-phospholes in order to evaluate the influence of the electron density of the phosphorus atom on the optical and electronic properties of the chromophore **B**. Derivative **3** was treated with selenium, elemental sulfur, bis(trimethylsilyl)peroxide, and methyl trifluorosulfonate affording σ^4,λ^4-phospholes **5** (91 % yield), **6** (93 % yield), **7** (95 % yield), and **8** (95 % yield), respectively (Scheme 1). The λ_{max} of derivatives **5**–**8** are red shifted with respect to that of **3** and, suggesting ICT, this effect is weak for the $P^{\delta+}$=$Y^{\delta-}$ derivatives **5**–**7** and stronger for the phospholium salt **8** (Table 1). Compounds **5**–**8** have comparable high energy absorptions, comparable with those of reported chromophores **B** bearing a central thiophene-*S*-oxide unit (λ_{max} = 424–428 nm).[10c] The tuning of the emission properties through derivativation is more pronounced. Oxidation of the phosphorus atom causes a bathochromic shift of λ_{em} in the fluorescence spectra ($\Delta\lambda_{em}$ = 46–92 nm; Table 1) and a notable increase of the Stokes shifts (**3**: $\Delta\lambda$ = 89 nm; **5**–**8**: $\Delta\lambda$ = 116–151 nm). The wavelenghts of the emission bands of chromophores **3**–**8** cover a range of approximately 92 nm.

Table 1. UV/Vis, fluorescence, and electrochemical data for **3**–**8**.

Compound	3	4	5	6	7	8
λ_{max} [nm][a]	412	427	423	432	434	442
lg ε	3.94	4.53	4.09	3.98	3.97	3.87
λ_{em} [nm][b]	501	570	547	548	556	593
E_{pa} [V][c]	+1.01	+1.10	+1.28	+1.27	+1.26	+1.52

[a] In THF. [b] Maximum wavelength in emission spectra; in THF. [c] Sample concentration 1 mM; solution 0.1 M LiClO$_4$ in MeCN; scan rate 100 mV s^{-1}. Oxidation potential (versus standard calomel electrode (SCE)) measured against a ferrocene internal standard ($E_{p1/2}$ = 0.5 V versus SCE, ΔE_p = 70 mV).

Electropolymerization of **B** derivatives is usually accomplished by oxidation proceeded by coupling of cation radicals.[4c] Indeed, derivatives **3** and **5**–**8** were oxidized irreversibly and with anodic potentials clearly related to the electron density of the central phosphole rings (Table 1). The anodic peak potentials (E_{pa}) range from +1.01 V for σ^3,λ^3-phosphole **3** to +1.52 V for cation **8**, whereas compounds **5**–**7** show intermediate E_{pa} values (+1.27 V). Derivatives **5**–**8** are oxidized at higher potentials than **4** bearing the terminal thienylpyridyl groups (+1.10 V, irreversible). These data in total clearly show that the optical and electronic properties of phosphorus-containing chromophores **B** are considerably influenced by the properties of the central phosphorus atom.

No films formed on the surface of the platinum working electrode after oxidation of monomers **3** and **4** (containing a σ^3,λ^3-phosphole unit) or of cation **8**. In contrast, films formed on the electrode surface with compounds **5**–**7** (a typical polymerization voltammogram is shown in Figure 3 a). Repeated scan cycling results in increased activity of the electrode surface, which is indicative of electroactive polymer growth. Interestingly, the polymers formed have E_{pa} values (Figure 3 b) dependent on the nature of the Y chalcogen substituent (E_{pa} = +1.63 (Y = Se), +1.54 (Y = S), +1.38 V (Y = O)). It should be noted that to deposit films, applied potentials must lie between those of the monomer and of the corresponding polymer. This behaviour is probably related to the fact that the radical cations involved in the polymerization[4c] are not stabilized by delocalisation on the positively charged phosphole rings.

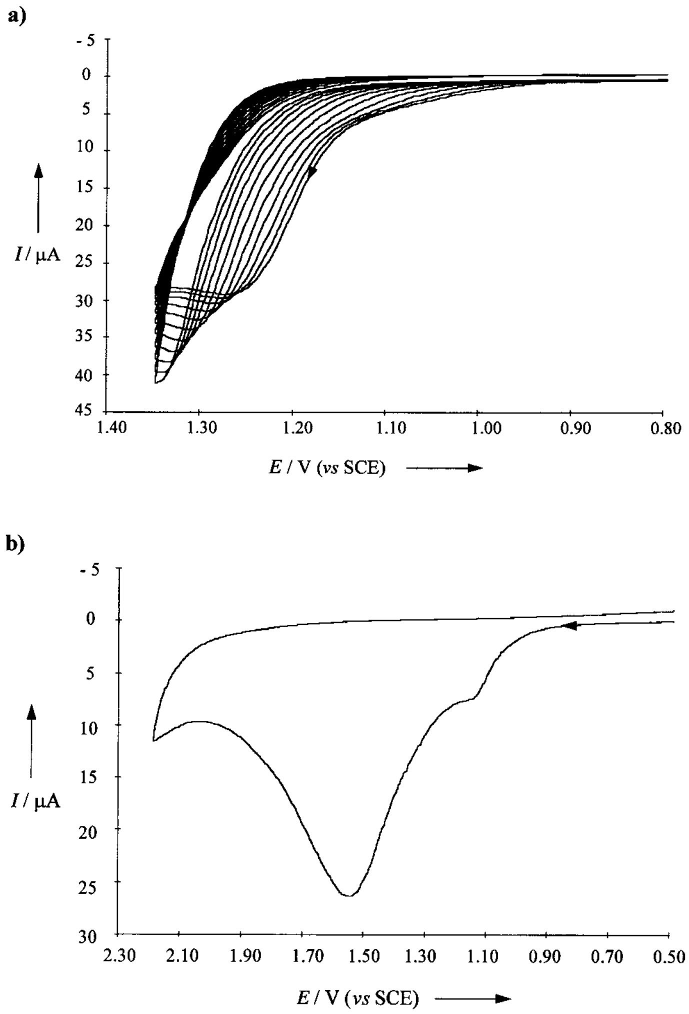

Figure 3. a) Anodic polymerization of **6** and b) anodic cyclic voltammogram of the corresponding polymer using a 0.03 cm^2 Pt button electrode in 0.1 mM $LiClO_4$ in MeCN solution at scan rate of 100 $mV\,s^{-1}$.

In conclusion, we have prepared a new family of mixed donor–acceptor molecules with chromophores possessing tunable optical and electronic properties that may be modified via chemical procedures. The unprecedented electropolymerization of phosphole-containing derivatives opens the route to a range of new materials upon functionalization of the initial σ^3,λ^3-phosphole cores. Metal-containing polymers are now important targets.[18]

Experimental Section

A solution of BuLi in hexanes (5.32 mL, 1.6 M, $-78\,^{\circ}C$) was added to a solution of $[Cp_2ZrCl_2]$ in THF (1.18 mg, 4.06 mmol, 40 mL). The mixture was allowed to warm to $-60\,^{\circ}C$ and a solution of **1** in THF (1.0 g, 3.70 mmol, 40 mL) was added dropwise. The mixture warmed to room temperature and neat $PhPBr_2$ (0.84 mL, 4.07 mmol) was added. The solution was stirred for 4 h and the solvent removed under vacuum. Phosphole **3** was isolated by flash column chromatography on basic alumina (THF, $R_f = 0.7$) as an orange solid (1.02 g, 73 %, m.p. 205 °C (dec.)).

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[11] Selected physical data: **3**: ^{13}C NMR (75.469 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 23.1$ (s, CH_2), 29.3 (s, CH_2), 124.8 (d, $J(P,C) = 2.0$ Hz, SCH), 125.6 (d, $J(P,C) = 10.2$ Hz, SCHCH*C*H), 126.8 (s, SCH*C*H), 128.7 (d, $J(P,C) = 9.2$ Hz, phenyl C_{meta}), 129.6 (s, phenyl C_{para}), 133.5 (d, $J(P,C) = 13.3$ Hz, phenyl C_{ipso}), 133.9 (d, $J(P,C) = 19.5$ Hz, phenyl C_{ortho}), 135.7 (s, P*C*CCH_2), 139.7 (d, $J(P,C) = 22.1$ Hz, S*C*CP), 144.4 (d, $J(P,C) = 9.1$ Hz, PC*C*CH_2); ^{31}P NMR (81.014 MHz, CD_2Cl_2, 25 °C, 80 % H_3PO_4): $\delta = +12.7$ (s); HR-MS (EI): *m*/*z*: calcd: 378.0651; found: 378.0666 $[M]^+$. **4**: ^{13}C NMR (75.469 MHz, C_6D_6, 25 °C, TMS): $\delta = 23.2$ (s, CH_2), 29.8 (s, CH_2), 123.3 (d, $J(P,C) = 10.2$ Hz, py CH), 123.6, 125.2, 128.0 (3 × s, thienyl CH), 128.6 (d, $J(P,C) = 7.8$ Hz, phenyl C_{meta}), 129.2 (s, phenyl C_{para}), 132.5 (s, py CH), 133.6 (d, $J(P,C) = 14.0$ Hz, phenyl C_{ipso}), 134.3 (d, $J(P,C) = 18.8$ Hz, phenyl C_{ortho}), 141.0 (s, thienyl C_{ipso}), 144.4 (d, $J(P,C) = 3.9$ Hz, P*C*CCH_2), 146.5 (d, $J(P,C) = 1.5$ Hz, NCH), 149.08 (d, $J(P,C) = 9.4$ Hz, PC*C*CH_2), 154.9 (d, $J(P,C) = 20.3$ Hz, NC_{ipso}), NCC_{ipso} is not observed; ^{31}P NMR (81.014 MHz, C_6D_6, 25 °C, 80 % H_3PO_4): $\delta = +11.3$ (s); HR-MS (FAB): *m*/*z*: calcd: 533.1274; found: 533.1275 $[M+H]^+$.

[12] The UV/Vis spectra of oligomer **4** in the free state and in the coordination sphere of $W(CO)_5$ have similar λ_{max}. Single crystal X-ray diffraction studies of complex $[W(CO)_5(\mathbf{3})]$ (to be published) revealed minor modifications of the geometric data compared to the free phosphole **3**.

[13] X-ray structural analysis. **3**: $C_{22}H_{19}S_2P$, 0.40 × 0.35 × 0.33 mm, hexagonal, space group $R\bar{3}$, $a = 33.059(5)$, $c = 9.001(2)$ Å, $V = 8519(3)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.328$ mg m^{-3}, $2\theta_{max} = 54°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, ω scan, 293 K, 2319 measured reflections, 2307 independent, observed $I > 2\sigma(I)$, Lorentz and polarization correction ($\mu = 3.67$ cm^{-1}), 227 refined parameters with $R1 = 0.0582$ and $wR2 = 0.1649$, max./min. residual electron density 0.335/−0.304 e Å^{-3}. **4**: $C_{37}H_{25}N_2O_5PS_2W$, 0.45 × 0.40 × 0.40 mm, monoclinic, space group $C2/c$, $a = 26.378(7)$, $b = 22.272(2)$, $c = 15.479(7)$ Å, $\beta = 123.99(2)°$, $V = 7540.4(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.571$ mg m^{-3}, $2\theta_{max} = 54°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, ω scan, 293 K, 8218 measured reflections, 8044 independent, observed $I > 2\sigma(I)$, Lorentz and polarization correction ($\mu = 33.31$ cm^{-1}), 437 refined parameters with $R1 = 0.0573$ and $wR2 = 0.1615$. After Lorentz and polarization corrections with HELENA, the structures were solved with SIR-97, and refined with SHELX93 by full-matrix least squares on F^2. Programs: HELENA: A. L. Spek, **1997**, Utrecht University, The Netherlands; SIR-97: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1998**, *31*, 74; SHELX93: G. M. Sheldrick, **1993**, Universität Göttingen, Germany. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137515 and -137516. 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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[16] Theoretical calculations in order to understand the effect of the central phosphorus atom on the relative properties of 2,5-bis(2-pyridyl)- and 2,5-bis(2-thienyl)phospholes are in progress.

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The First Structurally Characterized Metal–SeH Compounds: $[LAl(SeH)_2]$ and $[L(HSe)AlSeAl(SeH)L]$**

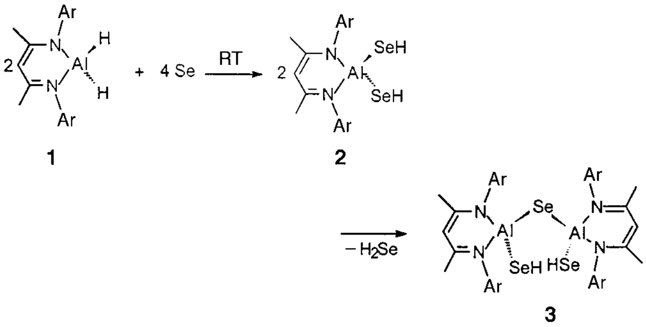
Chunming Cui, Herbert W. Roesky,* Haijun Hao, Hans-Georg Schmidt, and Mathias Noltemeyer

Dedicated to Professor Jürgen Troe on the occasion of his 60th birthday

Aluminum compounds containing Group 16 elements have been widely studied due to their important applications in chemical vapor deposition (CVD) and catalysis.[1] We have recently shown that organoaluminum dihydrides are very useful precursors for preparing aluminum chalcogenides of the formula $[(RAlE)_n]$ (R = organic ligand; E = S, Se, Te; n = 2,4).[2] A few novel intramolecularly stabilized aluminum chalcogenides, $[\{[N(SiMe_3)C(Ph)C(SiMe_3)_2]AlE\}_2]$[2a] and $[(ArAlE)_2]$ (Ar = 2,6-$(Et_2NCH_2)_2C_6H_3$, 2-Et_2NCH_2-6-MeC_6H_3; E = Se, Te),[2b] have been synthesized. We became interested in employing the same synthetic route using other ligand systems with the aim of studying the mechanism of the reaction and synthesizing monomeric aluminum chalcogenides [RAlE]. Previously we predicted that this reaction proceeds through hydroselenide (SeH) or hydrotelluride (TeH) intermediates.[2] Barron et al. and Oliver et al. discussed the same intermediates for the reaction of Group 13 trialkyl compounds with H_2Se.[3] However, no stable compounds of Group 13 elements with the SeH ligand have been isolated so far. In fact, only a few transition metal complexes (Co, Cr, Fe, Ir, Mn, Pt, Re, Ta, Ti) containing the SeH ligand (both terminal and bridging) are known, but they have not been structurally characterized.[4] Herein we report on the first stable aluminum SeH compounds with the β-diketiminato ligand.

Reaction of the β-diketimine LH (L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-$iPr_2C_6H_3$)[5] with $AlH_3 \cdot NMe_3$ at room temperature in n-hexane leads to the dihydride $[LAlH_2]$ (**1**; see Scheme 1) in high yield. The IR spectrum shows typical asymmetric and symmetric absorptions[6] for Al–H at 1832 and 1795 cm^{-1}, and the mass spectrum gives the highest peak at $[M^+ - H]$, indicating the formation of a monomeric dihydride. Compound **1** is related to $[\{(iPr)_2(ati)\}AlH_2]$ (ati = 2-aminotroponimine), which has a monomeric structure in the solid state.[6b]

Compound **1** reacts smoothly with two equivalents of elemental selenium at room temperature to afford $[LAl(SeH)_2]$ (**2**) in modest yield (Scheme 1). It is noteworthy that **2** is formed even when only one equivalent of Se is used for the reaction. Compound **2** is not stable in solution (n-hexane, THF) over a longer period of time at room temperature, and it slowly eliminates H_2Se to give pale yellow $[L(HSe)AlSeAl(SeH)L]$ (**3**). Compound **3** can also be obtained by the reaction of **1** with two equivalents of Se at 60 °C.



Scheme 1. Synthesis of **2** and **3**. Ar = 2,6-$iPr_2C_6H_3$.

Compounds **2** and **3** have been characterized by multinuclear NMR spectroscopy, mass spectrometry as well as elemental analysis. The ^1H NMR spectra of **2** and **3** show a high-field singlet at $\delta = -2.82$ and -2.83, respectively, which

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[*] Prof. Dr. H. W. Roesky, Dipl.-Chem. C. Cui, H. Hao, H.-G. Schmidt, Dr. M. Noltemeyer
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-393373
E-mail: hroesky@gwdg.de

[**] L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-$iPr_2C_6H_3$. This work was supported by the Deutsche Forschungsgemeinschaft