

Molybdenum Chalcogenobenzimidato Complexes: Radical Synthesis and Nitrile Extrusion via β -EPh (E = S, Se, and Te) EliminationArjun Mendiratta,[†] Christopher C. Cummins,^{*,†} Olga P. Kryatova,[‡] Elena V. Rybak-Akimova,[‡] James E. McDonough,[§] and Carl D. Hoff[§]

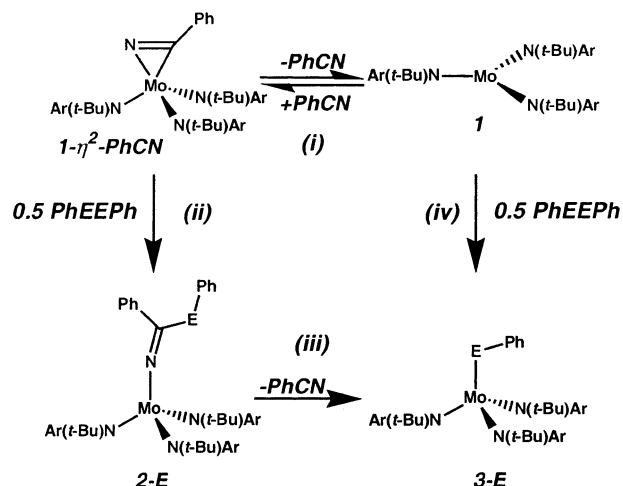
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Received September 11, 2003

Molybdenum chalcogenobenzimidates of formula $(\text{Ph}[\text{PhE}]\text{C}=\text{N})\text{Mo}(\text{N}[\text{t-Bu}]\text{Ar})_3$ (Ar = 3,5- $\text{C}_6\text{H}_3\text{Me}_2$) have been obtained by treatment of $\text{Mo}(\text{N}[\text{t-Bu}]\text{Ar})_3$ sequentially with benzonitrile and 0.5 equiv of PhEEPPh (E = S, Se, and Te). Molecular structure determinations have been carried out for the S and Se variants. The Te variant extrudes PhCN forming structurally characterized $(\text{PhTe})\text{Mo}(\text{N}[\text{t-Bu}]\text{Ar})_3$ with facility assessed via stopped-flow kinetic measurements, while the Se and S analogues exhibit increasing stability. Quantum chemical calculations and solution calorimetry have been employed as an aid to interpretation of the PhCN extrusion reaction.

The observation¹ that aqueous Hg(II) promotes hydrolysis of $[\text{H}_2\text{N}=\text{C}(\text{SMe})\text{Ph}][\text{I}]$ to provide PhCN is suggestive that nitrile release from the thioimide skeleton may be facilitated by thiophilic metals. In general, coordination complexes of organic chalcogenoimide derivatives ($\text{N}=\text{C}[\text{ER}^1]\text{R}^2$, E = S, Se, or Te) are rare. To our knowledge the only example of chalcogenoimide coordination to a transition metal is the complex $\text{Re}(\text{SAr})(\text{N}=\text{C}[\text{SAr}]\text{Me})_2(\text{PPh}_3)_2$ (Ar = 2- $[\text{Me}_3\text{Si}]\text{C}_6\text{H}_4$),² formed upon addition of an acetonitrile solution of $\text{ReCl}_3(\text{PPh}_3)_2(\text{CH}_3\text{CN})$ to an excess of thiol HSAr and triethylamine. A related reaction exemplifying nitrile insertion into a metal thiolate bond is that between Et_2AlSEt and acetonitrile to provide $\text{Et}_2\text{Al}(\text{N}=\text{C}[\text{SEt}]\text{Me})$.³ With the present work we define a radical pathway for the formation of molybdenum chalcogenobenzimidates, obtain the first

Scheme 1



examples known for selenium and tellurium, and explore the facility with which they extrude benzonitrile (Scheme 1).

Recently we characterized in detail a variety of organonitrile adducts with molybdenum trisamides $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ (Ar = 3,5- $\text{C}_6\text{H}_3\text{Me}_2$; R = *t*-Bu (**1**), *i*-Pr (**1b**)).⁴ The indicated adduct chemistry was exceptionally rich with η^1 , η^2 , and certain bis- η^1 organonitrile adducts having proved amenable to characterization. Herein we show that such adducts are exploitable as reactive intermediates.

Sequential room-temperature treatment of **1** (0.05 M in Et_2O solvent) with 1.0 equiv of PhCN and 0.5 equiv of PhEEPPh (E = S or Se) is found to furnish cleanly the corresponding chalcogenobenzimidates $(\text{Ph}[\text{PhE}]\text{C}=\text{N})\text{Mo}(\text{N}[\text{t-Bu}]\text{Ar})_3$ according to reactions i and ii in Scheme 1; these dark blue compounds, **2-S** and **2-Se**, were isolated in yields of 64% and 70%, respectively, and were characterized structurally by single-crystal X-ray diffraction methods. The molecular structure of **2-S** is shown in Figure 1;⁵ **2-Se** is found to be isomorphous (Figure S1, Supporting Information).⁶

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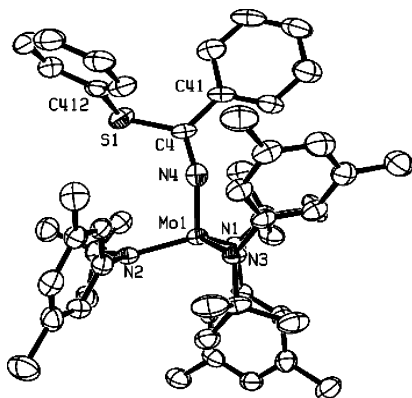


Figure 1. X-ray crystal structure of 2-S drawn with thermal ellipsoids at 50% probability. One of two independent molecules in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): Mo1–N1 1.963(4), Mo1–N2 1.988(4), Mo1–N3 1.965(4), Mo1–N4 1.794(5), N4–C4 1.317(6); Mo1–N4–C4 164.3(4), C4–S1–C412 103.6(3).

The possibility that 2-E (E = S, Se) formation is a consequence of the direct reaction of **1** with PhEPh to produce thiolate or selenolate complexes 3-E (reaction iv) followed by PhCN insertion (reverse of reaction iii) is ruled out by control experiments in which 3-S and 3-Se were treated with 10 equiv of PhCN under the synthesis reaction conditions and found to undergo no reaction.

Interestingly, use of PhTeTePh in the above synthesis did *not* result in tellurobenzimidate 2-Te formation. Specifically, sequential room-temperature treatment of **1** (0.05 M in Et₂O) with 1.0 equiv of PhCN and 0.5 equiv of PhTeTePh led exclusively to phenyltelluroate PhTeMo[N(*t*-Bu)Ar]₃ (3-Te) formation. Nitrile was not incorporated. A possible explanation was that 2-Te, formed as a short-lived intermediate, underwent facile conversion to 3-Te via PhCN expulsion (reaction iii in Scheme 1). Alternatively, PhTeTePh underwent direct reaction with **1** to provide 3-Te despite the presence of PhCN (reaction iv).

The direct reaction of **1** with PhTeTePh (reaction iv, E = Te) was found by stopped-flow kinetic studies to be a facile process ($\Delta H^\ddagger = 11.6 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -141 \text{ J K}^{-1} \text{ mol}^{-1}$) first order in each reactant. Forest green 3-Te is prepared readily by this reaction in synthetically useful quantities and has been the subject of a structural investigation (Figure S2, Supporting Information).⁷ As a complement to these kinetic and synthetic investigations, thermodynamic measurements employing solution calorimetry were carried out on reaction iv for E = S, Se, and Te. The enthalpies of reaction were found to be $-31.6(8)$, $-31.4(1)$, and $-24.0(3) \text{ kcal mol}^{-1}$, respectively.

Stopped-flow kinetic studies subsequently were carried out using premixing of **1** with a *large excess* (>40 equiv, 12 mM) of PhCN, followed by mixing with PhTeTePh, to push equilibrium i far to the left (as drawn in Scheme 1) and thus

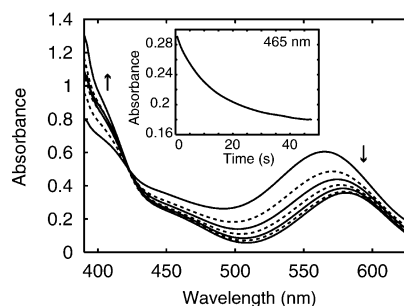


Figure 2. Spectral changes upon mixing toluene solutions containing Mo[N(*t*-Bu)Ar]₃ (0.3 mM) and PhCN (12 mM) with Ph₂Te₂ (0.15 mM) at -40°C . Formation of 2-Te is complete in 50 s.

favor reaction ii over reaction iv. Interestingly, this procedure when carried out in the -50 to $+5^\circ\text{C}$ temperature range produced a long-lived species assigned as tellurobenzimidate 2-Te with a diagnostic UV–vis spectral feature at 585 nm (see Figure 2). This reaction was found to be a clean second-order process (first order in each reactant) with activation parameters $\Delta H^\ddagger = 15.8 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -121 \text{ J K}^{-1} \text{ mol}^{-1}$. The procedure for generating 2-Te was adapted further for preparative-scale purposes. Specifically, addition of 0.5 equiv of PhEPh to a solution of **1** (30 mg in THF, 0.02 M) premixed with 60 equiv of PhCN (ca. 1 M) provided a solution of 2-Te suitable for ¹²⁵Te NMR studies; 2-Te is associated with a single ¹²⁵Te NMR signal of chemical shift +699 ppm, which compares favorably to the value of +617 ppm determined computationally⁸ for (H[PhTe]C=N)Mo-(NH₂)₃.^{9,10} In contrast, 3-Te (modeled as (NH₂)₃MoTePh) is calculated to exhibit a singlet at +1572 ppm, although we have been unable thus far to observe such a signal. While the requirement for excess PhCN in the synthesis of 2-Te has hampered its isolation as a solid, we feel that the observed spectral data allow confidence in its assignment.

We next investigated the ability of compounds 2-E (E = S, Se, Te) to extrude benzonitrile (reaction iii in Scheme 1). Although heating a benzene-*d*₆ solution of 2-S (80 °C, 12 h) elicited no reaction, complex 2-Se exhibited a slow reaction at 37 °C in which known selenolate 3-Se¹¹ was detected by ¹H NMR spectroscopy. Unfortunately, 3-Se itself decomposes to a mixture of unknown products at temperatures $\geq 37^\circ\text{C}$, obviating a kinetic study of the 2-Se $\rightarrow$ 3-Se + PhCN conversion.

Fortunately, such complications did not arise in the case of 2-Te. Upon heating THF/PhCN solutions of 2-Te (gener-

(5) X-ray crystallographic data for 2-S: $T = 193(2) \text{ K}$, monoclinic, $P2_1/n$, $a = 20.534(2) \text{ Å}$, $b = 24.450(2) \text{ Å}$, $c = 21.635(2) \text{ Å}$, $\alpha = 90^\circ$, $\beta = 111.261(2)^\circ$, $\gamma = 90^\circ$, $V = 10122.5(18) \text{ Å}^3$, $Z = 4$, $R1 = 0.0621$, $wR2 = 0.1505$.

(6) X-ray crystallographic data for 2-Se: $T = 193(2) \text{ K}$, monoclinic, $P2_1/n$, $a = 20.534(2) \text{ Å}$, $b = 24.450(2) \text{ Å}$, $c = 21.635(2) \text{ Å}$, $\alpha = 90^\circ$, $\beta = 111.261(2)^\circ$, $\gamma = 90^\circ$, $V = 10122.5(18) \text{ Å}^3$, $Z = 4$, $R1 = 0.0799$, $wR2 = 0.1592$.

(7) X-ray crystallographic data for 3-Te: $T = 193(2) \text{ K}$, triclinic, $P\bar{1}$, $a = 11.1740(12) \text{ Å}$, $b = 18.1215(19) \text{ Å}$, $c = 20.134(2) \text{ Å}$, $\alpha = 91.445(2)^\circ$, $\beta = 90.692(2)^\circ$, $\gamma = 90.663(2)^\circ$, $V = 4075.0(7) \text{ Å}^3$, $Z = 2$, $R1 = 0.0566$, $wR2 = 0.1521$.

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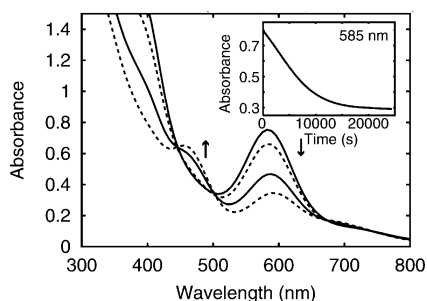


Figure 3. Spectral changes accompanying the 2-Te $\rightarrow$ 3-Te + PhCN conversion in THF/PhCN solution ($T = 35\text{ }^{\circ}\text{C}$, total time = 6 h).

ated as described above) to $35\text{ }^{\circ}\text{C}$, clean benzonitrile extrusion could be observed. As shown in Figure 3, UV-vis monitoring of this process indicated that 2-Te is quantitatively converted to 3-Te (note isosbestic points at 448 and 495 nm) with a first-order kinetic profile ($k_{\text{obs}} = 1.2(1) \times 10^{-4}\text{ s}^{-1}$). While we cannot conclusively rule out a bimolecular mechanism, the observed first-order kinetics strongly suggest that 2-Te converts to 3-Te through a unimolecular β -X elimination process.

Relative to β -H elimination, β -X elimination remains poorly studied, and the majority of well-defined systems involve group 10 metals.^{12–17} Prominent among early metal examples is Buchwald's observation that Cp_2ZrHCl (Schwartz's reagent) reacts with ethyl vinyl ether to yield $\text{Cp}_2\text{Zr}(\text{Cl})\text{OEt}$ and ethylene, presumably via 1,2 insertion of the olefinic unit followed by β -OEt elimination.¹⁸ No intermediates could be observed in this system, but Wolczanski measured first-order β -OR elimination kinetics for the more hindered $(\text{silox})_3\text{Ta}(\text{H})\text{CH}_2\text{CH}_2\text{OR}$ system.¹⁹ Although, to the best of our knowledge, nitrile release from well-defined halo- or chalcogenoimide complexes has not previously been documented, Glushkova and co-workers have presented limited evidence for the formation of d^0 early-metal chloroimide complexes through nitrile *insertion* into M–Cl bonds ($M = \text{Ti},^{20} \text{Nb},^{21} \text{Ta},^{22,23} \text{W}^{24}$).

Quantum chemical calculations⁸ carried out on the model system $\text{H}(\text{HE})\text{C}=\text{NMol}_3$ ($L_3 = (\text{NHMe})(\text{NH}_2)_2$) suggest that

HCN elimination to provide HEMol_3 complexes is an enthalpically uphill process by ca. 15 kcal mol^{-1} for all three E: S, Se, and Te.²⁵ We find on going from S to Se and Te that *both* the E–C and the E–Mo bond dissociation enthalpies (BDEs) diminish progressively, resulting in the cancellation that yields the same value as a function of E for the HCN elimination reaction. Calculated E–C BDEs are 61, 51, and 43 kcal mol^{-1} , while calculated Mo–E BDEs are 76, 68, and 51 kcal mol^{-1} . Complexation of HCN by MoL_3 to provide $(\eta^2\text{-HCN})\text{MoL}_3$ is a process calculated to be enthalpically favorable by 30 kcal mol^{-1} . We conclude, tentatively, that the observed conversion of 2-E to 3-E (E = Se, Te) is entropically driven.

The radical route presented here has allowed the synthesis of molybdenum chalcogenobenzimidates featuring S, Se, and Te, the latter two being the first of their kind. Preliminary investigations of the ability of these compounds to extrude benzonitrile indicate increasing facility on going from S to Se to Te; this observation is consistent with the trend toward weaker bond strengths to carbon as one descends the periodic table in the p-block.²⁶ We are currently exploiting the synthetic route elaborated here in order to synthesize chalcogenobenzimidates more amenable to detailed kinetic investigation of the nitrile extrusion process.

Acknowledgment. We are grateful to the National Science Foundation for their support of this work (CRC-0209977, CHE-9988806, and a predoctoral fellowship to A.M.). Joshua S. Figueroa is acknowledged for assistance with X-ray crystallography.

Supporting Information Available: Complete synthetic procedures and characterization data for all new compounds, tables of crystal structure data in CIF format, experimental details of the stopped-flow kinetic measurements and solution calorimetry, and details of the density functional calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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