Germaine Edition: DOI: 10.1002/ange.201500173
German Edition: DOI: 10.1002/ange.201500173

Yttrium–Arsenic Complexes

Yttrium Complexes of Arsine, Arsenide, and Arsinidene Ligands**

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Abstract: Deprotonation of the yttrium–arsine complex \([\text{Cp}^\prime_2\text{Y(AsH)}_2\text{Mes}]\) (1) (\(\text{Cp}^\prime = \eta^5-\text{C}_5\text{H}_5\text{Me}, \text{Mes} = \text{mesityl}\)) by \(\text{nBuLi}\) produces the \(\mu\)-arsenic complex \([\text{Cp}^\prime_2\text{Y(\mu-AsH)}_2\text{Mes}]/\). (2). Deprotonation of the As–H bonds in \(2\) by \(\text{nBuLi}\) produces \([\text{Li(thf)}_2]_2[\text{Cp}^\prime_2\text{Y(\mu-AsMes)}]/\text{Li}], [\text{Li(thf)}_2]_2[3], in which the diatomic \(3\) contains the first example of an arsinidene ligand in rare-earth metal chemistry. The molecular structures of the arsenic, arsenide, and arsinidene complexes are described, and the yttrium–arsenic bonding is analyzed by density functional theory.

Rare-earth metal compounds containing soft heteroatom donor ligands have attracted considerable interest in recent years.[1–6] The combination of Lewis acidic \(M^+\) cations with heavy p-block donor atoms results in a hard–soft mismatch that can lead to unusual bonding properties and to distinct reactivity. Within this context, rare-earth metal complexes of anionic phosphorus donor ligands such as phosphide (\(\text{RP}^\text{−}\)) have been extensively studied.[7] A key development occurred in 2008, when a lutetium phosphinidene (\(\text{RP}^\text{−}\)) complex was structurally characterized and its phosphinidene transfer reactivity towards aldehydes and ketones demonstrated.[8] Phosphinidene complexes of other rare-earth metals were subsequently reported, and their phosphinidene transfer chemistry and small-molecule activation reactions described.[9–14] Despite the increased activity in rare-earth metal phosphinidene chemistry, the area is considerably underdeveloped relative to transition metal phosphinidene chemistry.[15] A terminally bonded phosphinidene ligand remains a key target in rare-earth metal chemistry, although a uranium complex of such a ligand was reported recently.[16]

The chemistry of rare-earth metal complexes with arsenic donor ligands is almost entirely unexplored: arsenide (\(\text{R}_2\text{As}^\text{−}\)) complexes are rare,[17–22] and arsinide (\(\text{RAs}^\text{−}\)) ligands are unknown in rare-earth metal chemistry. The development of synthetic routes to rare-earth metal arsinidene complexes could lead to more novel reactivity, such as arsinide transfer, and would also furnish new opportunities for using arsenic ligands to influence the electronic structure and magnetism of lanthanide(III) complexes. With these possibilities in mind, we now report the first example of a rare-earth metal arsinidene complex.

Our strategy involved the initial synthesis of a primary arsine complex of yttrium to establish the metal–arsenic bond, followed by deprotonation of the \([\text{YAsH}_2\text{R}]\) unit to give corresponding yttrium–arsenic and yttrium–arsinidene complexes. Thus, adding one stoichiometric equivalent of mesitylarsine to \(\text{Cp}^\prime\text{Y}\) in toluene led to the formation of \([\text{Cp}^\prime_2\text{Y(AsH)}_2\text{Mes}]\) (1) (\(\text{Cp}^\prime = \eta^5-\text{C}_5\text{H}_5\text{Me}, \text{Mes} = \text{mesityl}\)), which was crystallized as colorless blocks in 88% yield (Scheme 1). To obtain the yttrium arsenide complex, 1 was dissolved in toluene and one equivalent of \(\text{nBuLi}\) was added. The ensuing work-up allowed isolation of the trinuclear \(\mu\)-arsenic complex \([\text{Cp}^\prime_2\text{Y(\mu-As(H)}_2\text{Mes}]/\text{toluene} (2\text{-toluene})\) in 59% yield. Deprotonation of 2 by \(\text{nBuLi}\) in \(\text{thf}\), followed by crystallization from the same solvent, resulted in formation the heterobimetallic yttrium–lithium \(\mu\)-arsinidene complex \([\text{Li(thf)}_2]_2[(\text{Cp}^\prime_2\text{Y(\mu-AsMes)}]/\text{thf}, [\text{Li(thf)}_2]_2[3]\)-thf, as orange crystals in 73% yield.

Scheme 1. Synthesis of the complexes described herein.
The molecular structure of the yttrium arsenic complex 1 (Figure 1) features a Y1–As1 bond of length 3.0945(6) Å, and a Y1-As1-C19 angle of 122.55(7)°. The three Cp’ ligands are η²-coordinated to yttrium, with Y–C bond lengths in the range 2.672(3)–2.746(3) Å (average 2.706 Å). The IR spectrum of 1 shows characteristic As–H stretches at 2120 and 2154 cm⁻¹ (Supporting Information, Figure S9). The ¹H NMR spectrum of 1 in [D₆]benzene (Supporting Information, Figure S2) features a resonance corresponding to the arsine protons at δ(H) = 3.12 ppm, the mesityl methyl groups occur at δ(H) = 2.08 and 2.18 ppm, and the mesityl aromatic protons occur at δ(H) = 6.67 ppm. The Cp’ methyl group occurs at δ(H) = 1.95 ppm and the Cp’ CH protons occur at δ(H) = 5.86 and 5.77 ppm. The ¹H NMR spectrum of 1 shows no evidence for free arsine. The only rare-earth metal arsine complex reported to date contains a macrocyclic amidoxime ligand coordinated to yttrium, with Y–As bond lengths in the range 2.9545(7)–2.9968(7) Å. Complex 1 is therefore the first rare-earth metal complex of a primary arsine ligand. The molecular structure of the yttrium arsenide 2 (Figure 2) consists of a central Y₈As₈ chair-like ring, with each yttrium ligated by two μ-arsenide ligands and two η²-Cp’ ligands. The Y–As bond lengths in 2 are in the range 2.977(2)–3.019(2) Å (average 2.998 Å), and therefore they are, on average, approximately 0.10 Å shorter than the Y–As bond in 1, which is due to the stronger electrostatic attraction between yttrium and the arsenide ligand. The As-Y-As bond angles are in the range 88.66(5)°–96.26(5)°. The Y–C bond lengths in 2 are 2.59(1)–2.67(1) Å, and the average Y–C distance of 2.63 Å is approximately 0.08 Å shorter than in 1. The Y-As-Y angles in 2 are 130.56(5), 135.09(6), and 135.66(6)°, and each arsenic center carries an exo mesityl substituent. The As–H stretching vibrations were observed in the IR spectrum at 2120 and 2154 cm⁻¹ (Supporting Information, Figure S9).

The ¹H–¹³C HSQC spectrum of 2toluene at 298 K reveals that two proton environments at δ(H) = 2.51 and 2.60 ppm, with relative integrals of 1:2, do not engage in ¹J coupling to carbon, which identifies them as the As–H protons and indicates that there are two magnetically inequivalent arsine environments. The ¹H NMR spectrum of 2toluene features four resonances in the range δ(H) = 6.78–6.94 ppm and 5.84–6.51 ppm, which correspond to the six mesityl CH protons and the 24 Cp’ CH protons, respectively (Supporting Information, Figures S3–S5). The various CH₃ environments occur in the range δ(H) = 1.72–2.66 ppm.

Complex 2 is the first rare-earth metal complex of a primary arsine ligand; however, several crystallographically characterized rare-earth metal complexes of secondary arsenide ligands have been reported. Activation of AsH₃ by the lutetium–lithium methyl complex [Cp₄Lu(μ-CH₃)₂Li(tmeda)] (tmeda = N,N’,N’-tetramethylethlenediamine), which resulted in the formation of the arsenide-bridged species [Cp₄Lu(μ-AsPh₃)₂Li(tmeda)] [¹⁷] Activation of As–H bonds by samarium(II) reduction has also been used to access arsine complexes such as [Cp₆SmAsPh₃], which features a terminally bonded [Ph₃As]⁻ arsenide ligand [¹⁹,²⁰]. Lanthanide(II) arsine and arsyl complexes can be accessed by salt metathesis reactions of LnI₂ with alkali-metal arsenide salts; for example, Mes₃AsK reacts with SmI₂ to give trans-[Mes₃As₂Sm(THF)]₂ [²¹,²²].

The structure of the arsindene-ligated complex dianion 3 (Figure 3) also consists of a central chair-like Y₈As₈ core, with three arsindene ligands bridging the yttrium centers.
The lithium cation caps the core of the structure and bonds to the three arsenic donors, such that the arsine ligands adopt an overall \( \mu_2 \)-bridging mode. The Y–As bond distances in 3 are 2.8574(6)–2.8893(7) Å (average 2.8722 Å), making them shorter on average than the Y–As bonds in 2 by more than 0.12 Å. It is also noteworthy that the Y–Y separations in 2 are 5.465–5.548 Å, whereas those in 3 are 5.266–5.314 Å; overall, therefore, the Y1As3 core of 3 is more compact than that of 2. Relative to 2, a broader range of Y–C bond lengths, that is, 2.59(2)–2.73(2) Å, and a greater average Y–C bond length of 2.67 Å, are found in 3. The distortion of the Y1As3 chair conformation in 3 is reflected in the As–Y–As and Y–As–Y bond angles of 91.59(2)–94.87(2)° and 133.59(2)–136.49(2)°, respectively. The lithium cation in 3 is ligated by three arsine ligands and resides 0.889(8) Å above the mean plane of the arsenic atoms. The Li–As bond lengths are 2.539(8), 2.563(7) and 2.615(8) Å, and the As–Li–As angles are 107.2(3), 108.2(3) and 110.0(3)°. An ortho methyl group on one mesityl substituent is oriented towards Li1, and the relatively short Li1···C54 distance of 2.777(8) Å may indicate an agostic interaction similar to that observed in other lithium complexes containing CH3 groups.

The \(^1\)H NMR spectrum of [Li(thf)]3·thf, recorded 30 min after sample preparation in [D6]thf at 298 K (Supporting Information, Figure S6), features two resonances at \( \delta^e(\text{H}) = 6.71 \) and 6.80 ppm, both of which integrate to six protons. Distinct singlets for the ortho, para, and meta environments were observed in the region \( \delta^e(\text{H}) = 1.54–2.62 \) ppm. The appearance of the \(^1\)H NMR spectrum of [Li(thf)]3·thf is therefore consistent with the arsine complex possessing a C4 symmetry axis coincident with Li1 and approximately perpendicular to the Y1 plane. The \(^1\)Li NMR spectrum of [Li(thf)]3·thf features two resonances, with a sharp peak at \( \delta^e(\text{Li}) = -0.59 \) ppm corresponding to the [Li(thf)]\(^+\) cations and a broader peak at \( \delta^e(\text{Li}) = 4.41 \) ppm corresponding to the [Li(thf)]\(^-\) environment in [Li(thf)]3·thf (Supporting Information, Figure S8). An additional feature of the \(^1\)H NMR spectrum of [Li(thf)]3·thf is that, over time, additional resonances which were observed as minor components after 30 min grow in intensity (Supporting Information, Figure S7). After a period of only two hours, the additional resonances account for a significant component of the NMR spectrum. It was not possible to identify the decomposition products; however, this unexpected feature suggests that the arsine ligands in [Li(thf)]3·thf react with the thf solvent.

To the best of our knowledge, complex 3 is the first rare-earth metal complex of an arsine ligand, which is surprising given that arsine ligands are well-known in transition-metal chemistry.\(^{[30]}\) Several alkali metal complexes of arsine ligands have also been structurally characterized.\(^{[21]}\) Complex 3 is related to the rare-earth metal phosphinidine complexes, particularly the heterobimetallic lithium-scandium complex \([\text{PNP} \text{Se}(\mu_2-\text{dmp})(\mu-\text{Br})\text{Li}])\) (PNP = N(2-Pr,PC6H4,4-Me)2, 2.6-Mes2C6H3, dme = dimethoxyethane).\(^{[30]}\) Notably, the arsine ligands in 3 adopt a \( \mu_2 \)-bridging coordination mode, which is an obvious parallel with rare-earth metal phosphinidine complexes.

The variation in the character of the yttrium–arsenic bonding in complexes 1, 2, and 3 was investigated using density functional theory: the calculations were simplified by replacing the para and Cp’ methyl groups with hydrogen atoms. Geometry optimizations employing two exchange correlation functionals were carried out in the gas-phase and using a continuum dielectric, and the results of the calculations with the hybrid PBE0 functional, including dielectric effects, are described.

Comparing the calculated and experimental Y–As bond lengths, we find good agreement for 1 (3.113 Å vs. 3.095 Å) but also that the calculations slightly overestimate the average distance for 2 (3.061 Å vs. 2.998 Å) and for 3 (2.912 Å vs. 2.872 Å). The discrepancies are most likely due to the inability of the simulations to fully account for solid-state intermolecular interactions, and also the effects of the counter cations on 3. Despite this, the overall trend in the decrease of the Y–As bond length is reproduced. The atomic charges were calculated by natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) analyses (Table 1).

|   | 1   | 2   | 3   |
|---|-----|-----|-----|
| Y–As [Å]\(^{[a]}\) | 3.0945(6) | 2.9981\(^{[b]}\) | 2.8722\(^{[c]}\) |
| Y–As [Å]\(^{[a]}\) | 3.113 | 3.061\(^{[b]}\) | 3.061\(^{[b]}\) |
| \( q_{\text{NMR}} \) (Y/As) | +1.09, +0.42 | +1.26, –0.10 | +1.13, –0.53 |
| \( q_{\text{QTAIM}} \) (Y/As) | +1.89, +0.86 | +1.85, +0.03 | +1.82, –0.81 |
| \( \lambda_{\text{QTAIM}} \) | 35.86, 30.36 | 35.89, 31.30 | 35.89, 32.20 |
| \( \rho \) | 0.024 | 0.030 | 0.038 |
| \( H \) | –0.00577 | –0.0338 | –0.0592 |
| \( \delta(\text{As}) \) | 0.200 | 0.302 | 0.438 |

[a] Experimental. [b] PBE0 + COSMO. [c] Average length.

Both types of analysis show an increasing negative charge on the arsenic donor atom on moving from 1 to 2 to 3. The QTAIM-derived localization index, \( \lambda \), which provides a measure of the number of electrons localized on a given atom, increases by 0.94 from 1 to 2, and again by 0.90 from 2 to 3. The analogous parameters for yttrium are essentially constant across the three complexes, which indicates that the observed decrease in Y–As bond lengths is due to stronger ionic interactions. However, the fact that the calculations produce \( \Delta \lambda \leq 1 \) implies a small-but-increasing non-ionic contribution as the negative charge on arsenic increases.

The Y–As bonding was investigated further by a topological analysis of the electron density. The parameter \( \rho \), which describes the electron density at the QTAIM-derived bond critical point (BCP), increases from 1 to 2 to 3, as expected based on the decreasing Y–As bond lengths, and which is consistent with the change in \( \lambda \). The \( \rho \) values indicate an enhancement in the non-ionic contribution to the Y–As bonding.
bonding in the arsinidene complex 3; however, the values are still markedly less than expected for a typical covalent bond \((p > 0.2)\). The values of the energy density \((H)\) at the BCP, and the values of the delocalization indices \((\delta)\), which provides a measure of the number of electrons shared between yttrium and arsenic, are indicative of considerable ionic bonding character in 1, 2, and 3. However, the general increase across the series also implies an increasing degree of non-ionic character in 3.

In summary, the synthesis and structure of yttrium complexes with arsine, arsenide, and arsineidene ligands have been described. The synthetic strategy involved initial assembly of an yttrium–arsenic bond, followed by stepwise deporation of the \([\text{YAsH}_2\text{R}]\) unit. The resulting yttrium–lithium complex \([\text{Cp}^*\text{Y}((\text{AsS})_2\text{Me})\text{Li}]\); (3) is the first rare-earth metal complex of an arsineidene ligand. As with closely related rare-earth metal phosphinidene complexes, the arsineidene ligands in 3 adopt a \(\mu\)-bridging coordination mode; stabilization of a terminally bonded \([\text{RAs}]^2\) ligand will require greater steric bulk than is provided by the substituents used in the current study. Our computational analysis of the Y–As bonding confirms the expected ionic character, but we also find a small and potentially significant change in non-ionic contributions across the arsine, arsenide, and arsineidene series. The 4f electronic structure of lanthanide(III) cations will be sensitive to such ligand field variations at low temperatures, and thus our study introduces new possibilities for the design of single-molecule magnets.\(^{[26]}\)

Keywords: arsenic · arsineidene ligands · lithium · rare-earth elements · yttrium

How to cite: Angew. Chem. Int. Ed. 2015, 54, 4255–4258

Angew. Chem. 2015, 127, 4329–4332

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Received: January 8, 2015
Published online: February 5, 2015