Coordination Chemistry

Cationic Bismuth Aminotroponiminates: Charge Controls Redox Properties

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Dedicated to Professor Wolfgang Kaim on the occasion of his 70th birthday

Abstract: The behavior of the redox-active aminotroponiminate (ATI) ligand in the coordination sphere of bismuth has been investigated in neutral and cationic compounds, [Bi(ATI)] and [Bi(ATI)n[A] (L = neutral ligand; n = 0, 1; A = counteranion). Their coordination chemistry in solution and in the solid state has been analyzed through (variable-temperature) NMR spectroscopy, line-shape analysis, and single-crystal X-ray diffraction analyses, and their Lewis acidity has been evaluated by using the Gutmann–Beckett method (and modifications thereof). Cyclic voltammetry, in combination with DFT calculations, indicates that switching between ligand- and metal-centered redox events is possible by altering the charge of the compounds from 0 in neutral species to +1 in cationic compounds. This adds important facets to the rich redox chemistry of ATIs and to the redox chemistry of bismuth compounds, which is, so far, largely unexplored.

Introduction

In recent years, redox-active ligands have been established as a versatile and valuable tool to diversify and control the properties and reactivity of coordination entities.[1] In compounds of first-row transition metals, for instance, redox-active ligands have been used to stabilize unusual oxidation states of the central atom[2] or to foster reactions that involve two-electron processes rather than single-electron transfer.[3] In compounds of p-block elements, redox-active ligands have been used to enable facile and reversible electron transfer and to open up reaction pathways for controlled radical reactions.[4][5][6]

It has been demonstrated that redox-active ligands may also be directly involved in selective bond-forming events, such as the dimerization of radical species, which result from a high spin density at specific sites of the redox-active entity.[7] However, strategies to control such reactivity remain rare. Aluminum complex A has been reported to undergo dimerization through C–C bond formation to give A2 (Scheme 1a, left), whereas the closely related species B is isolable in the monomeric form (Scheme 1a, right).[4a] This has been ascribed to intramolecular ferromagnetic coupling between the radical ligands in B, which leads to a reduced effective spin density in these compounds. We have demonstrated that rhodium complexes of aminotroponiminates (ATIs) are susceptible to reversible (ligand-centered) electron transfer (Scheme 1b (left), C → D), whereas the corresponding alkali-metal complexes readily undergo reductively induced dimerization (Scheme 1 b (right), C → 0.5 E).[8] Thus, modifying the metal bond to a redox-active ligand can have a dramatic influence on ligand-centered redox events and reactivity.

Although the chemistry of redox-active ligands is well developed for central atoms across large parts of the periodic table,[1] the redox chemistry of heavier Group 15 elements, and the heaviest congener bismuth, in particular, has been focused on metal(oid)-centered radical species and redox-shuttling.[5][7] Remarkable advances in the field include the incorporation of Bi[4]/Bi[4] and proposed Bi[6]/Bi[6] reox couples in catalytic cycles.[9] The first examples of persistent and isolable bismuth radical complexes,[9] the generation of an organometallic biradical,[10] unusual reactivity patterns (e.g., towards P2 and S2),[11] and catalytic applications in cycloisomerization and dehydrocoupling reactions,[12] olefin polymerization,[13] and photochemistry.[12c] These findings were largely based on strategies in which the radical center (if present) was stabilized through bulky ligands or through reversible radical recombination reactions. In contrast, the use of (potentially) redox-active ligands in the field of bismuth chemistry is only little explored. Examples include bismuth(I) and bismuth(III) complexes with ferrocenyl groups in the ligand backbone (F, G),[14] as well as bismuth(III) pyridine dipyrrolid complexes H (Scheme 2).}[15]
Herein, we report on the synthesis, isolation, characterization, and redox properties of the first series of cationic bismuth ATI complexes.

**Results and Discussion**

**Synthesis and structure**

Starting from a reported sodium ATI compound [Na(ATI<sup>Pr<sub>i</sub>Pr')(thf)], with its unsymmetric Ph/iPr substitution pattern, neutral and cationic bismuth ATIs 1 and 2-X were synthesized in straightforward salt elimination protocols (Scheme 3; X = OTf, SbF<sub>6</sub>; OTf = O<sub>3</sub>SCF<sub>3</sub>; B Ar<sub>F</sub> = B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>). Following the same synthetic approach, cationic bismuth ATIs 3-X and 4-X based on ATI<sup>Pr<sub>i</sub>Pr</sup>', which has been reported in the literature, and the new ATI<sup>Pr<sub>i</sub>Pr</sup>Me<sub>i</sub>Pr ligand were obtained (Scheme 3; for details on the synthesis and characterization of [Na(ATI<sup>Pr<sub>i</sub>Pr</sup>')(thf)] and related species, see the Experimental Section and the Supporting Information). The products were isolated as red to orange solids.

![Scheme 3. Synthesis of neutral and cationic bismuth ATI complexes.](image-url)
NMR spectroscopic analysis in solution revealed the expected signal patterns for bismuth complexes with one set of magnetically equivalent ATI ligands in all cases. In the case of neutral 1, a second set of resonances with minor intensities of 6% was detected. This was ascribed to fac/mer isomerism in this M[AIr]$_2$-type compound, the main isomer is the fac species, according to DFT calculations ($\Delta G$ (fac$\rightleftharpoons$mer$\rightleftharpoons$1) = + 1.9 kcal mol$^{-1}$) and structural analysis of 1 in the solid state (see below). In all compounds with the [ATI$^{\text{Ph,Pr}}$] ligand, the resonances for all protons of the phenyl groups were significantly broadened at room temperature. Variable-temperature (VT) H NMR spectroscopy revealed coalescence temperatures of 40 °C for neutral 1 and 15–25 °C for cationic 2-X and five well-resolved signals for the phenyl groups in the low-temperature scenario. This indicates a hindered rotation of the phenyl groups around the N$^\text{aryl}-C^\text{Ph}$ bond. Line-shape and Eyring plots revealed activation parameters of $\Delta G^\circ$ (298 K) = 14.9 kcal mol$^{-1}$ for neutral 1 and $\Delta G^\circ$ (298 K) = 13.6–13.9 kcal mol$^{-1}$ for cationic 2-X (for details, see the Supporting Information). Thus, the ATI ligands in neutral and cationic complexes experience similar steric clash in the coordination sphere of bismuth, although a significantly less crowded coordination environment and a more easily accessible metal center is found for the cationic species (see below). This was ascribed to the coordination geometry of the cationic species being dictated by orbital interactions rather than Coulomb interactions.

Compounds 1, 2-X, 3-X, and 4-BAr$^f$ were characterized by single-crystal X-ray diffraction analyses. Compound 1 crystallized in the monoclinic space group $P2_1/n$ with $Z = 4$ and showed a fac configuration (Figure 1a). The central atom is found in a distorted octahedral coordination geometry: angles of ligands in cis orientation range from 65 to 118°. Strong deviations from ideal symmetry are due to the small bite angle of the ATI ligand (chelating: N-Bi-N, 65–67°). In addition, the HOMO-3 shows significant contributions from an s-type bismuth atomic orbital, which is polarized towards the empty site created by deviations from an octahedral symmetry, as determined by DFT calculations (Figure 1b; for details, see the Supporting Information). This may be associated with a stereochemically active lone pair at bismuth. Due to its fac configuration, compound 1 bears three pairs of trans-oriented NPh and NPr groups. Delocalization of electron density in the ATI ligands prohibits the unequivocal assignment of amido and imino groups. Nevertheless, it is apparent that the C–NPr bonds (1.31–1.33 Å) are, on average, slightly shorter than the C–NPh bonds (1.34–1.35 Å). In agreement with this observation, the Bi–NPr bonds (2.53–2.58 Å) are significantly longer than the Bi–NPh bonds (2.35–2.38 Å). This is further supported by the Wiberg bond indices (WBI), which are considerably smaller for the Bi–NPr bonds (WBI = 0.22–0.23) than for the Bi–NPh bonds (WBI = 0.32–0.33). This is in contrast to the only other homoatomic bismuth ATI complex [Bi[ATI$^{\text{Ph,Pr}}$]]$_2$, which crystallizes in a mer configuration, leading to an even more pronounced variation in Bi–N bond lengths (2.33–2.61 Å).  

The molecular structures of the cationic bismuth ATIs 2-X, 3-X, and 4-BAr$^f$ are shown in Figure 2. Selected crystallographic and structural information are summarized in Table 1. The coordination geometries of the cationic species are disphenoidal (2-BAr$^f$, 3-OTT, 4-BAr$^f$) or square pyramidal (2-OTT, 2-SbF$_6$, 3-SbF$_6$; $\tau_2 = 0.18–0.28$), if only the AI and thf ligands are considered. If additional weak bonding interactions with counteranions or the thioether group in 4-BAr$^f$ are also taken into account, the coordination geometries are best described as square pyramidal (2-BAr$^f$; $\tau_2 = 0.22$), distorted octahedral (3-OTT, 3-SbF$_6$), and irregular (2-OTT, 2-SbF$_6$, 4-BAr$^f$). The Bi–N bond lengths of the cationic species (2.21–2.38 Å) are, on average, significantly shorter than those in neutral 1 (2.35–2.58 Å), although the same or even higher coordination numbers are reached in the cationic species. This is due to the interactions between the bismuth atoms of the cationic species and their counteranions or neutral donor groups (thf or thioether) being weak compared with the Bi–N$^\text{aryl}$ interactions in neutral 1. In all cationic species, the Bi–N bonds that face another Bi–N bond in the trans position (2.31–2.38 Å) are significantly longer than those that have a Bi–X bond or a free coordination site in the trans position (2.21–2.25 Å; $X = \text{O}^\text{THF}, \text{O}^\text{OTT}, S^\text{thioether}, F^\text{SbF}_6$), that is, there is a considerable thermodynamic trans effect in these compounds. Notably, this is also observed in compounds 3-X, in which the substituents at nitrogen are identical and any

Figure 1. a) Molecular structure of [Bi(ATI$^{\text{Ph,Pr}}$)]$_2$ (1) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Carbon atoms of Ph and Pr groups are shown in the wireframe model and hydrogen atoms are omitted for clarity. B1–N1 2.532(4), B1–N2 2.384(4), B1–N3 2.247(4), B1–N4 2.354(4), B1–N5 2.581(4), B1–N6 2.368(4), N1–C13 1.316(3), N2–C2 1.349(6), N3–C17 1.326(6), N4–C18 1.354(6), N5–C33 1.319(7), N6–C34 1.342(6); A1–B1–N1 155.87(14), B1–N1–N6 158.65(13), N1–B1–N5 117.64(13). b) HOMO-3 of compound 1 (isosurface = 0.05), as determined by DFT calculations. This molecular orbital (MO) shows contributions by an s-type bismuth atomic orbital that is polarized toward the hemispheric in which the NPr groups are localized and may be associated with a stereochemically active lone pair (for details, see the Supporting Information).
impact of the substitution pattern on Bi–N bond lengths is thus ruled out. The Bi–O\textsuperscript{THF} bond lengths in the cationic bismuth ATIs (2.81–2.94 Å) are within the broad range of Bi–O\textsuperscript{THF} bond lengths reported for other cationic bismuth amides (e.g., 2.57–3.19 Å in [Bi(NiPr\textsubscript{3})\textsubscript{3}(thf)]\textsubscript{2}[BAr\textsubscript{4}]).\textsuperscript{101} As a trend, a stronger electron-donating ability of the ATI ligand ([ATI\textsubscript{PhPr}]+) in 3-SbF\textsubscript{5} versus [ATI\textsuperscript{PhPr}]\textsuperscript{+} in 2-SbF\textsubscript{5}\textsuperscript{115} and the counteranion (OTF\textsuperscript{−} in 2-OTF vs. [SbF\textsubscript{6}]\textsuperscript{−} in 2-SbF\textsubscript{5} increase the Bi–O\textsuperscript{THF} bond lengths (Table 1). The Bi–S\textsubscript{thioether} interactions in 4-BAr\textsubscript{F} are very weak (if they exist) based on distance criteria (Bi···S 3.87 Å; identical to the sum of the van der Waals radii), which is ascribed to geometrical constraints in the ligand framework. While bonding in-
teractions between the bismuth atom and the counteranion are significant in the case of the triflate species (\(\text{Bi}–\text{OTf}^–\)) 2.87–3.22 Å; 10–20% below the sum of the van der Waals radii, they are less pronounced for the hexafluoroantimonates (\(\text{Bi}–\text{F}^–\)) 3.08–3.14 Å; 11–13% below the sum of the van der Waals radii), and only minor in the \(\text{BAR}^–\) species (\(\text{Bi}–\text{F}^–\)) 3.29–3.47 Å; 2–7% below the sum of the van der Waals radii). The cationic species generally form typical mononuclear complexes in the solid state. As an exception to this, compound 3-OTf crystallizes as a coordination polymer due to a bridging coordination mode of the triflate anion (for details, see the Supporting Information). Surprisingly, the cationic species 2-BAR\(^2\), which forms only very weak interactions with the borate counteranion, crystallizes from solutions of difluorobenzene without any thf ligands bound to the bismuth atom. This shows that the thf adduct (as obtained from the isolation of analytically pure bulk material) may release its neutral ligand in solutions of moderately polar and weakly donating solvents.

### Lewis acidity

The Lewis acidity of molecular cationic bismuth compounds can be a crucial factor for the realization of unusual phenomena and reactivity patterns in coordination chemistry,\(^{[21]}\) group-transfer reactions,\(^{[18]}\) CH activation,\(^{[22]}\) small-molecule activation,\(^{[23]}\) and catalytic applications.\(^{[13b, 24]}\) It has recently been quantified by using the Gutmann–Beckett (GB) method, that is, through adduct formation of the bismuth species with \(\text{OPEt}_3\).\(^{[25]}\) We have recently reported that the use of \(\text{EPMe}_3\) \((E = S, Se)\) instead of \(\text{OPEt}_3\) can be exploited for the assessment of the soft character of a Lewis acid, which is demonstrated to be especially pronounced for bismuth cations.\(^{[26]}\) Because the Lewis acidity of cationic bismuth compounds based on chelating N,N-donor ligands has not been quantified, to date, selected bismuth ATI complexes were investigated with the original and modified GB methods (Table 2).

By using one equivalent of \(\text{OPEt}_3\) as a donor in dichloromethane, all bismuth ATIs showed relatively low acceptor numbers of AN(\(\text{OPEt}_3\)) = 21–29. As a trend, bismuth ATI cations without significant bonding interactions to the counteranion showed slightly larger ANs of 25–29 than those with Bi–OTf interactions or neutral 1\(^{[27]}\) (AN(\(\text{OPEt}_3\)) = 21–22).

These ANs are larger than that of \(\text{B(NMe}_3)_4\) (AN(\(\text{OPEt}_3\)) = 9) and similar to that of \(\text{B(OMe}_3)_4\) (AN(\(\text{OPEt}_3\)) = 23).\(^{[28]}\) Compound 4-BAR\(^2\) was additionally investigated with the modified GB method, but also showed low ANs if the soft donors EPMe\(_3\) were applied (AN(\(\text{SPMe}_3\)) = 11; AN(\(\text{SePMe}_3\)) = 6). Thus, the ATI ligand (an example of a bidentate monoanionic N,N-donor ligand) quenches large parts of the Lewis acidity of the bismuth center towards external Lewis bases, even in cationic species. This raises the question of whether the reduction of cationic bismuth ATIs would predominantly be a ligand- or a metal-centered event (or an intermediate scenario; see below).

### Redox properties

The redox-active nature of ATI ligands has recently been established. Specifically, it has been demonstrated that alkali-metal ATI complexes undergo reductively induced dimerization reactions, whereas rhodium ATI species are susceptible to reversible, ligand-centered electron transfer (Scheme 1b).\(^{[26]}\) To shed some light on the redox properties of the bismuth complexes presented herein, they were analyzed by cyclic voltammetry (all potentials referenced vs. ferrocene/ferrocenium; for details, see the Experimental Section and the Supporting Information). An irreversible redox event in the range of 0.27–0.39 V was observed for all compounds (see the Supporting Information). Under reducing conditions, neutral bismuth ATI complex 1 showed a reduction wave at \(-2.26\) V, with the corresponding oxidation wave appearing at \(-1.20\) V (Figure 3a and Table 3, entry 1). This indicates that a chemical reaction takes place after electron transfer. The ratio, \(i_{\text{pc}}/i_{\text{pa}}\) of these redox waves is close to one and the shape of the cyclic voltammogram does not change significantly upon increasing the number of cycles, which indicates the reversibility of the ECEC sequence. This be-

![Figure 3](image-url)

**Table 2.** \(^{13}\)P NMR chemical shifts and acceptor numbers (ANs), according to the original GB method (\(\text{OPEt}_3\) as a Lewis base) and modifications thereof (\(\text{SPMe}_3\), \(\text{SePMe}_3\) as Lewis bases).\(^{[26]}\)

| Compound | OPEt\(_3\) AN \(^{13}\)P [ppm] | APMe\(_3\) AN \(^{13}\)P [ppm] | SePMe\(_3\) AN \(^{13}\)P [ppm] | AN |
|----------|-----------------|-----------------|-----------------|-----|
| 1        | 50.3            | 21              |                 |     |
| 2-OTF    | 50.4            | 21              |                 |     |
| 2-\(\text{BAR}^–\) | 53.4 | 27              |                 |     |
| 3-\(\text{BAR}^2\) | 52.4 | 25              |                 |     |
| 4-\(\text{BAR}^2\) | 51.1 | 22              |                 |     |
| 1        | 54.0            | 29              | 30.9            | 11  |
| 2-OTF    | 54.0            | 29              | 30.9            | 11  |
| 2-\(\text{BAR}^–\) | 52.4 | 25              | 19              | 8.9 |
| 3-\(\text{BAR}^2\) | 51.1 | 22              | 21              | 6   |

\(\text{[a]}\) One equivalent of \(\text{OPEt}_3\), \(\text{SPMe}_3\), or \(\text{SePMe}_3\) was added to solutions of the respective bismuth compound in dichloromethane. For details, see the Experimental Section.
behavior (as determined from cyclic voltammetry) is strongly reminiscent of the situation found for the corresponding sodium compound, [Na(ATI$_{3}$)$_2$(thf)], which undergoes a highly selective, chemically reversible, reductively induced demerization with the formation of a C–C bond between two ATI moieties (cf. C–E in Scheme 1b).[18] In contrast, no indications for such redox behavior were obtained in the cyclic voltammetry analyses of the cationic bismuth ATI species 2-X, 3-X, and 4-BAr$^T$. While complexes with [OTf]$^-$ or [SbF$_6$]$^-$ counteranions show partially reversible redox events, compounds 2-BAr$^T$ and 4-BAr$^T$ show quasi-reversible redox events at strongly negative potentials of −2.61 and −2.57 V, respectively (shown for 2-BAr$^T$ in Figure 3b and Table 3, entries 2–7). While the redox potentials of cationic bismuth ATIs with [ATI$_{3}$]$^{3+}$ and [ATI$_{2}$SbF$_6$]$^{2+}$ ligands range from −2.57 to −2.64 V, those for complexes with the [ATI$_{2}$SbF$_6$]$^{2+}$ ligand were found from −2.71 to −2.80 V. This corresponds to a cathodic shift of up to 230 mV and reflects the more electron-donating nature of the [ATI$_{3}$]$^{3+}$ ligand, which has previously been discussed in the context of catalytic applications.[19]

Overall, these findings demonstrate that the redox properties of bismuth ATI compounds can be controlled by the choice of the charge of the complex. While the redox behavior of the neutral species resembles that of alkali-metal ATI complexes, the cationic species exhibit a redox behavior reminiscent of the corresponding rhodium compound. DFT calculations were performed to rationalize these differences (for details, see the Experimental Section and the Supporting Information). Frontier orbital analysis of 1 and 2-BAr$^T$ revealed that the LUMO is exclusively ligand-centered in the neutral complex, but has significant contributions from a bismuth p-type atomic orbital in the cationic species (Figure 4a,b). These findings are in agreement with an analysis of the spin-density distribution in the reduced species Na-1-rad and 2-rad. Compound Na-1-rad shows a negligible spin density of 0.6% at the bismuth atom, and an overwhelming spin density of 97% at one ATI ligand, which interacts with the sodium counterion (with spin densities of up to 27% at individual atoms of this ligand; Figure 4c). In contrast, compound 2-rad may be described as a bismuth-centered radical (72% spin density) supported by two redox-active ATI ligands, each of which has a spin density of 14% (with up to 3% spin density at individual atoms of these ligands; Figure 4d).[20]

**Conclusion**

We have prepared the first examples of cationic bismuth ATIs, [Bi(ATI)$_{2}$L$_n$]$/A$ (L = neutral ligand; $n$ = 0–1; $A$ = counteranion). Depending on the choice of the counteranion, contact ion pairs, solvent-separated ion pairs, or “naked” bismuth ATI cations with weak Bi–F interactions were obtained ([F]$^-$ = fluorine atom of BAr$^T$). According to VT-NMR spectroscopy studies and line-shape analyses, the ATI ligands in neutral and cationic species experience similar steric clash, which was assigned to a predominantly orbital-controlled coordination chemistry in the cationic compounds. The Lewis acidity of bismuth ATI cations towards hard and soft donors was relatively weak, according to the GB method (and its modifications), which was ascribed to the bidentate nature of the monoanionic ATI ligand. In turn, the empty p orbital of the bismuth atom in cationic species...
was accessible under reducing conditions and allowed for quasi-reversible electron transfer at bismuth (according to cyclic voltammetry and DFT calculations). In contrast, investigations into the redox chemistry of the neutral bismuth ATI complex [Bi(ATI)(H)3] indicated ligand-centered redox events. Thus, we demonstrated that the charge of the change in bismuth ATI complexes allowed switching from ligand-centered redox events (as previously reported for alkali-metal complexes) to metal-centered, quasi-reversible redox events. The latter was analogous to Rh ATI compounds in terms of reversibility, but are distinct in terms of the localization of spin density in the reduced species (metal-centered in [Bi(ATI)2]+, but ligand-centered in [Rh(ATI)(cod)+]). These findings open up perspectives for switchable redox-catalysis based on the heavy main-group element bismuth.

### Experimental Section

#### General

All air- and moisture-sensitive manipulations were carried out by using standard vacuum-line Schlenk or glove box techniques in an atmosphere of purified argon. Solvents were degassed and purified, according to standard laboratory procedures. NMR spectra were recorded on Bruker instruments operating at 200, 400, or 500 MHz with respect to H. 19F and 31P NMR spectra were recorded with proton decoupling. All chemical shifts (δ) are reported in ppm. 1H and 13C NMR chemical shifts are reported relative to SiMe4 by using the residual 1H and 13C chemical shifts of the solvent as a secondary standard. 19F and 31P NMR chemical shifts are reported relative to CFCl3 and 85% aqueous H3PO4, respectively, as external standards. Unless stated otherwise, NMR spectra were recorded at 23 °C. Elemental analyses were performed on a Lecou或Carlo Erba instrument. For MS analyses, an Exactive plus instrument was used. Cyclic voltammograms were recorded using a Gamry Instruments Reference 600 potentiostat at 23 °C in THF containing 0.1 M [N(NBu)4][PF6], unless otherwise noted. A standard three-electrode cell configuration was employed by using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire separated by a Teflon tip as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocinium (Fc/Fc+) electrode, and as silver wire separated by a Teflon tip as the reference electrode. Standard three-electrode cell configuration was employed by using a Lecou or Carlo Erba instrument. For MS analyses, an Exactive plus instrument was used.

#### Computational details

DFT calculations were performed with the Gaussian program by using the 6-31G(d,p) (H, B, C, N, O, F)30 6-311G(d,p) (Na)31 and LANL2DZ (B)32 basis sets and the (U)B3LYP functional.33 The D3 version of Grimme’s dispersion model with the original D3 damping function was applied.34 Frequency analyses of the reported structures showed no imaginary frequencies. Thermodynamic parameters were calculated at a temperature of 298.15 K and a pressure of 1.00 atm. Further details are given in the Supporting Information. Cartesian coordinates of optimized structures are provided in xyz format.

### General procedure for the original and modified GB methods

Equimolar amounts of the potential Lewis acid (usually 10 mg of the bismuth complex) and the Lewis base ([OEP] or [SPEP] or [SePMe2] were dissolved in CD3Cl2 (0.5 mL) and 1H and 31P NMR spectra were recorded.

#### Compound 1

Na[NiSiMe2]2 (42 mg, 0.23 mmol) and BiCl3 (24 mg, 76 µmol) were subsequently added to a solution of Ni-ph2-phenylammonium bromide (54 mg, 0.23 mmol) in THF (2 mL). All volatile compounds were removed from the red reaction mixture under reduced pressure. The residue was suspended in toluene (3 × 1.5 mL) and the resulting suspension was filtered. The residue was dried in vacuo. The red solid was redissolved in THF (2 mL) and was removed from the red reaction mixture under reduced pressure to give a deep-red solid, which was dried in vacuo (58 mg, 63 µmol, 83%). M.p. 198 °C (dec); 1H NMR (500 MHz, -40 °C, D2O/toluene): δ = 1.23 (d, J1/2H/3H = 5.5 Hz, 9H; Me); 1.32 (d, J1/2H/3H = 5.8 Hz, 9H; Me); 3.96–4.03 (brs, 3H; CH3); 4.80 (d, J1/2H = 8.2 Hz, 3H; o-H); 5.83 (d, J1/2H = 11.2 Hz, 3H; H), 6.00 (brd, J1/2H = 8.2, 8.9 Hz, 3H; 5-H); 6.43 (d, J1/2H = 11.8 Hz, 3H; 7-H); 6.44 (brd, J1/2H = 9.8, 11.2 Hz, 3H; 4-H); 6.77–6.80 (m, 3H; p-H); 6.87 (brd, J1/2H = 8.2, 11.8 Hz, 3H; 6-H); 6.97 (d, J1/2H = 8.2 Hz, 3H; o-P); 7.09–7.02 ppm (m, 6H; m-P); 13C NMR (126 MHz, -40 °C, D2O/toluene): δ = 23.3 (s, Me6), 24.1 (s, Me6), 49.9 (s, CHMe6), 116.8 (s, 7-C), 117.4 (s, 5-C), 117.4 (s, 3-C), 124.7 (s, p-P), 127.7 (s, p-P), 128.5 (s, m-PH/m-PH), 129.2 (s, m-PH/m-PH), 133.3 (s, 6-C), 133.6 (s, 4-C), 151.4 (s, ipso-P), 163.5 (s, 1-C), 168.0 ppm (s, 2-C); elemental analysis calculated (%) for C26H17Bi(N2): 61.43, 61.45, 61.39; found: C 62.60, H 5.58, N 9.13; C 62.69, H 5.41, N 9.09.

#### Compound 2-OTf

A solution of Na[Rh(30)30] (50 mg, 156 µmol) in THF (1 mL) was added dropwise to a suspension of sodium triflate (13.5 mg, 0.08 mmol) in THF (1 mL). The red suspension was filtered. All volatile compounds were removed from the red reaction mixture under reduced pressure. The residue was suspended in toluene (3 × 1.5 mL) and the resulting suspension was filtered. The residue was dried in vacuo. The red solid was redissolved in THF (1 mL) and was removed from the red reaction mixture under reduced pressure to give a deep-red solid, which was dried in vacuo (58 mg, 63 µmol, 83%). M.p. 198 °C (dec); 1H NMR (500 MHz, -40 °C, D2O/toluene): δ = 1.23 (d, J1/2H/3H = 5.5 Hz, 9H; Me); 1.32 (d, J1/2H/3H = 5.8 Hz, 9H; Me); 3.96–4.03 (brs, 3H; CH3); 4.80 (d, J1/2H = 8.2 Hz, 3H; o-H); 5.83 (d, J1/2H = 11.2 Hz, 3H; H), 6.00 (brd, J1/2H = 8.2, 8.9 Hz, 3H; 5-H); 6.43 (d, J1/2H = 11.8 Hz, 3H; 7-H); 6.44 (brd, J1/2H = 9.8, 11.2 Hz, 3H; 4-H); 6.77–6.80 (m, 3H; p-H); 6.87 (brd, J1/2H = 8.2, 11.8 Hz, 3H; 6-H); 6.97 (d, J1/2H = 8.2 Hz, 3H; o-P); 7.09–7.02 ppm (m, 6H; m-P); 13C NMR (126 MHz, -40 °C, D2O/toluene): δ = 23.3 (s, Me6), 24.1 (s, Me6), 49.9 (s, CHMe6), 116.8 (s, 7-C), 117.4 (s, 5-C), 117.4 (s, 3-C), 124.7 (s, p-P), 127.7 (s, p-P), 128.5 (s, m-PH/m-PH), 129.2 (s, m-PH/m-PH), 133.3 (s, 6-C), 133.6 (s, 4-C), 151.4 (s, ipso-P), 163.5 (s, 1-C), 168.0 ppm (s, 2-C); elemental analysis calculated (%) for C26H17Bi(N2): 61.43, 61.45, 61.39; found: C 62.60, H 5.58, N 9.13; C 62.69, H 5.41, N 9.09.

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Compound 3-OTF

A solution of Na(ATP)6

(200 mg, 808 μmol) in THF (1.5 mL) was added dropwise to a suspension of sodium triflate (70 mg, 404 μmol) and BiCl3 (127 mg, 404 μmol) under stirring. The red suspension was filtered and all volatile compounds of the filtrate were removed under reduced pressure to give an orange solid, which was washed with pentane (3 x 3 mL) and dried in vacuo. Crystals suitable for single-crystal X-ray analysis were obtained by layering a solution of 3-OTF (20 mg) in THF (0.5 mL) with pentane (0.1 mL). Yield: 162 mg, 210 μmol, 52%.

'H NMR (500 MHz, CD3OD): δ = 1.37 (d, J(2-H,3-H) = 6.7 Hz, 2H; CHMe), 4.73–4.81 (sept, J(2-H,3-H) = 6.7 Hz, 4H; CHMe3), 6.71 (t, J(2-H,3-H) = 9.1 Hz, 2H; 5-H), 6.92 (d, J(2-H,3-H) = 11.5 Hz, 4H; 3-H, 7-H), 7.48 ppm (dd, J(2-H,3-H) = 11.8, 9.1 Hz, 4H; 3-H, 7-H). 13C NMR (126 MHz, CD3OD): δ = 22.6 (s, CHMe), 52.3 (s, CHMe3), 120.8 (s, 3-C, 7-C), 120.7 (s, 3-C, 7-C), 123.5 (s, 5-C), 135.0 (s, 4-C, 6-C), 168.2 ppm (s, 1-C, 2-C); 'F NMR (740 MHz, CD3OD): δ = −76.16 ppm; elemental analysis calcd (%) for C42H32N6F12Bi4O24S6 (746.66 g mol−1): C 42.41, H 0.51, N 7.33, S 4.19; found: C 42.61, H 0.49, N 7.49, S 3.96.

Compound 3-SbF6

A solution of Na(ATP)6

(25 mg, 101 μmol) in THF (1 mL) was added dropwise to a suspension of silver hexafluoroantimonate(V) (17 mg, 51 μmol) and BiCl3 (16 mg, 51 μmol) in a plastic vial under stirring. The red suspension was filtered and hexane was added (5 mL). The brown precipitate was isolated by filtration, washed with hexane (3 x 3 mL) and dried in vacuo. Drying for prolonged periods of time reproducibly led to the start of decomposition of the compound. Therefore, the amount of THF and residual hexane had to be checked individually for every batch. Typically, n equiv of THF and m equivalents of hexane were detected, with n = 0.07–1.0 and m = 0.0–0.5. Yield: 31 mg, 33 μmol (with n = 0.9 equiv of THF and 0.25 equiv of hexane), 65%. 'H NMR (400 MHz, CDCl3): δ = 1.48 (d, J(2-H,3-H) = 6.7 Hz, 2H; CHMe), 1.80–1.83 (m, n x 4-H; β-THF), 3.66–3.70 (m, n x 4-H; α-THF), 4.77–4.87 (sept, J(2-H,3-H) = 6.7 Hz, 4H; CHMe3), 6.74 (t, J(2-H,3-H) = 9.2 Hz, 2H; 5-H), 6.88 (d, J(2-H,3-H) = 11.5 Hz, 4H; 3-H, 7-H), 7.42 ppm (dd, J(2-H,3-H) = 11.8, 9.2 Hz, 4H; 3-H, 7-H). 13C NMR (101 MHz, CDCl3): δ = 23.0 (s, CHMe), 26.2 (s, β-THF), 52.4 (s, CHMe3), 68.3 (s, α-THF), 121.6 (s, 3-C, 7-C), 125.2 (s, 5-C), 135.1 (s, 4-C, 6-C), 167.4 ppm (s, 1-C, 2-C); elemental analysis calcd (%) for C42H32N6F12Sb4Bi4O24S6 (856.40 g mol−1): C 36.86, H 4.54, N 6.54; found: C 36.46, H 4.68, N 6.35. Fast decomposition of 3-SbF6 was observed in THF at ambient temperature, which was accompanied by the precipitation of a dark solid. According to 1H NMR spectroscopy, 23% of the free ligand were detected after about 30 min. After 5 d in solution, the complex was fully decomposed and only the free ligand was detected.

Compound 4-BAr6

Na(ATP)6

(hexa[100 mg, 259 μmol]) was added dropwise to a solution of BiCl3 (41 mg, 130 μmol) in THF (4 mL) and sodium tetrakis[5-bis(trifluoromethyl)phenyl]borate (115 mg, 130 μmol) was added under stirring. After 20 min, the red suspension was filtered and all volatile compounds were removed under reduced pressure. The crude product was washed with hexane (4 x 2 mL) and dried in vacuo (190 mg, 113 μmol with n = 0.5 equiv of THF, 87%). 'H NMR (500 MHz, −40°C, CD3OD): δ = 1.01 (d, J(2-H,3-H) = 6.0 Hz, 6H; CHMe), 1.33 (d, J(2-H,3-H) = 6.3 Hz, 6H; CHMe3), 2.44 (s, 6H; Me), 3.26–3.34 (brm, 2H; CHMe3), 5.33 (s, n x 4-H; CH2Cl), 6.17 (d, J(2-H,3-H) = 10.9 Hz, 2H; 3-H), 6.47 (d, J(2-H,3-H) = 11.9 Hz, 2H; 7-H), 6.50 (d, J(2-H,3-H) = 7.9 Hz, 2H; 6-H), 6.34 ppm (s, 1-C, 2-C); elemental analysis calcd (%) for C64H58N8F24Bi6Sb4(C6H5)18 (1618.95 g mol−1): C 50.45, H 3.36, N 3.46; found: C 50.73, H 3.20, N 3.48.
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Conflict of interest

The authors declare no conflict of interest.

Keywords: aminotroponiminates · bismuth · cationic species · redox chemistry · redox-active ligands

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Although compound 2-rad has two NPr groups in the apical positions of the bishenoidal coordination geometry, an isomer with one NPr and one NPh group in the apical positions (2-rad-isom) was found to be only slightly higher in energy ($\Delta H = +3.0$ kcal mol$^{-1}$; $\Delta G = +3.6$ kcal mol$^{-1}$) and showed a very similar spin density distribution (for details, see the Supporting Information).

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