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[18] Notes: 1) For the synthesis of nonsymmetrical linear sulfamides (Table 4), only 1.3 equiv of Burgess reagent is used to facilitate the reaction process. 2) HCl salts of the starting amines and amino alcohols do not provide good conversion into the desired product. The free base must be isolated prior to reaction with **1**–**3**. 3) Removal of protecting groups was carried out by using conventional protocols: CO_2Me: NaOH, MeOH:H_2O (2:1), 25°C, 2 h;[19] Cbz: 10% Pd/C, H_2, EtOH:EtOAc (4:1), 25°C, 5 h;[20] Alloc: $Pd(OAc)_2$ (10 mol%), 3,3′,3″-phosphinidynetris(benzenesulfonic acid) trisodium salt (20 mol%), $HNEt_2$ (40 equiv), MeCN:H_2O (1:1), 25°C, 15 min;[21] Bn: 20% $Pd(OH)_2$/C, H_2 (60 psi), EtOH:EtOAc (4:1), 25°C, 24 h.[22] Subsequent alkylation was carried out by using a conventional protocol: sulfamide, NaH, DMF, 0°C to 25°C then alkyl halide, tetrabutylammonium iodide (cat), 25°C 4 h.[2d,5]

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$[\mathrm{Os^{III}(tpy)(Cl)(NCCH_3)(NSAr)}]$: Reversible Reduction of Acetonitrile by $\mathrm{Os^{III}}$–Sulfilimido Complexes**

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Earlier reports have revealed an extensive electron–proton, reversible redox chemistry based on the $\mathrm{Os^{V/IV}}$ couples $[\mathrm{Os^{V}(tpy)(Cl)_2\{NN(CH_2)_4O\}}]^+/[\mathrm{Os^{IV}(tpy)(Cl)_2\{N(H)\text{–}N(CH_2)_4O\}}]^+$ (tpy = 2,2′:6,2″-terpyridine, $N(CH_2)_4O$ is a morpholide),[1] $[\mathrm{Os^{V}(tpy)(Cl)_2\{NS(3,5\text{-}C_6H_3Me_2)\}}]^+/[\mathrm{Os^{IV}(tpy)(Cl)_2\{NS(H)(3,5\text{-}C_6H_3Me_2)\}}]^+$,[2] and $[\mathrm{Os^{V}(Tp)(Cl)_2(NPEt_2)}]/[\mathrm{Os^{IV}(Tp)(Cl)_2\{NP(H)Et_2\}}]$ (Tp = tris(pyrazolyl)borate).[3] These couples are reminiscent of oxo/hydroxo/aqua couples such as *cis*-$[\mathrm{Ru^{IV}(bpy)_2(py)(O)}]^{2+}$/*cis*-$[\mathrm{Ru^{III}(bpy)_2(py)(OH)}]^{2+}$ and *cis*-$[\mathrm{Ru^{III}(bpy)_2(py)(OH)}]^{2+}$/*cis*-$[\mathrm{Ru^{II}(bpy)_2(py)(H_2O)}]^{2+}$ (bpy = 2,2′-bipyridyl, py = pyridyl), where the change in proton content between oxidation states is a consequence of differences in proton acidity of several orders of magnitude.[4]

We report here the existence of a related electron–proton chemistry, but based on the reversible two-electron reduction of a nitrile ligand and the couples $[\mathrm{Os^{III}(tpy)(Cl)(N{\equiv}CCH_3)(NSAr)}]$ / $[\mathrm{Os^{III}(tpy)(Cl)(NH{=}CHCH_3)(NSAr)}]$ (Ar = C_6H_5, 4-MeC_6H_4, 3,5-$Me_2C_6H_3$). At more negative potentials, the $\mathrm{Os^{III}}$–imino complexes undergo further reduction and solvolysis to give $[\mathrm{Os^{III}(tpy)(Cl)(NCCH_3)(NSAr)}]$ and $CH_3CH_2NH_2$.

A rapid reaction occurs when *cis*-$[\mathrm{Os^{VI}(tpy)(Cl)_2(N)}]^+$ ([**1**]$^+$) and aromatic thiols (C_6H_5SH, 4-MeC_6H_4SH, or 3,5-$Me_2C_6H_3SH$) are mixed in CH_3CN under N_2 at room temperature [Eq. (1)]. The products are *cis*-

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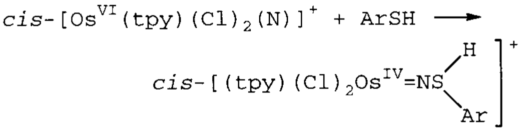


$$cis\text{-}[Os^{VI}(tpy)(Cl)_2(N)]^+ + ArSH \longrightarrow cis\text{-}[(tpy)(Cl)_2Os^{IV}{=}NS(H)(Ar)]^+ \qquad (1)$$

$[Os^{IV}(tpy)(Cl)_2\{NS(H)Ar\}]^+$ ($Ar = C_6H_5$ ($[\mathbf{2A}]^+$), 4-MeC_6H_4 ($[\mathbf{2B}]^+$), 3,5-$Me_2C_6H_3$ ($[\mathbf{2C}]^+$)).[5]

Addition of a small amount of water to $[\mathbf{2}]^+$ in CH_3CN causes solvolysis and deprotonation to give the monosolvento complexes $[Os^{IV}(tpy)(Cl)(NCCH_3)(NSAr)]^+$ ($Ar = C_6H_5$ ($[\mathbf{3A}]^+$), 4-MeC_6H_4 ($[\mathbf{3B}]^+$), 3,5-$Me_2C_6H_3$ ($[\mathbf{3C}]^+$)) on a time scale of minutes and the corresponding disolvento complexes *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NSAr)]^{2+}$ on a time scale of hours.[6] The mononitrile complexes were isolated as their PF_6^- salts and characterized by elemental analysis and cyclic voltammetry as well as ^1H NMR, infrared, and UV/Vis spectroscopies.[5]

Crystals of $[\mathbf{3B}]PF_6$ were grown by slow diffusion of Et_2O into a solution in CH_3CN.[7] The structure shows that the distorted octahedral arrangement of ligands at Os in the *cis* parent nitrido complex is retained (Figure 1).[7] The Os–N(tpy) bond lengths range from 1.948(6) to 2.078(7) Å with the shortest one *trans* to the Os–N(CH_3CN) bond. The Os–N(sulfilimido) and N4–S1 bond lengths of 1.899(8) and 1.535(9) Å, respectively, are consistent with multiple bonding.[8–10] The angle N4-S1-C16 is 107.9(6)° and thus indicates pseudo sp^3 hybridization at the S atom of the sulfilimido ligand. The Os–N(sulfilimido) bond length, the bent angle Os1-N4-S1 of 129.3(5)°, and the diamagnetism of the complexes (as shown by ^1H NMR spectroscopy) are all consistent with d^4 spin-paired Os^{IV}. There are structural similarities with related complexes such as $[Os^{IV}(tpy)(Cl)(NCCH_3)\{NN(CH_2)_4O\}]^+$,[11] *cis*-$[Os^{IV}(tpy)(NCCH_3)_2\{NN(CH_2)_4O\}]^{2+}$,[12] and *trans*-$[Os^{IV}(tpy)(NCCH_3)_2(NSC_6H_4Me)]^{2+}$.[7]

Cyclic voltammograms of $[\mathbf{3C}]^+$ in dry CH_3CN (5.0×10^{-3} M) containing 0.1 M NBu_4PF_6 show the following couples: $Os^{V/IV}$ at +1.56 V, $Os^{IV/III}$ at +0.65 V, and $Os^{III/II}$ at −0.79 V (versus SSCE). These couples are shifted to more positive potentials compared to those for *cis*-$[Os^{IV}(tpy)(Cl)_2\{NS(H)C_6H_3Me_2\}]^+$ with +1.21 V for $Os^{V/IV}$, −0.09 V for $Os^{IV/III}$, and −1.24 V for $Os^{III/II}$. The more negative potentials result from the exchange of the electron-donating Cl^- ligand for CH_3CN. The corresponding couples for *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NSC_6H_3Me_2)]^{2+}$ appear at +1.94 V for $Os^{V/IV}$, +0.98 V for $Os^{IV/III}$, and +0.09 V for $Os^{III/II}$.[6]

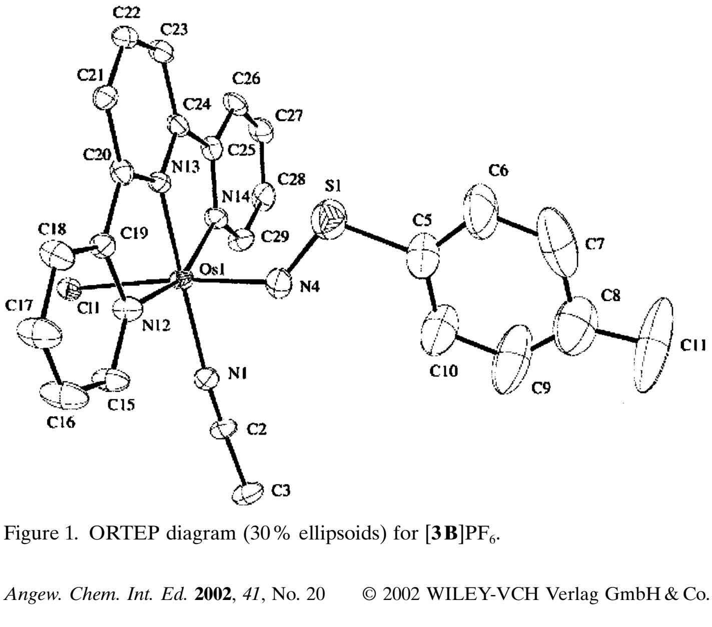


Figure 1. ORTEP diagram (30% ellipsoids) for $[\mathbf{3B}]PF_6$.

The cyclic voltammetric characteristics of $[\mathbf{3C}]^+$ in H_2O/CH_3CN (1/1, v/v; $I = 1.0$ M in NH_4PF_6) are strikingly different from those in CH_3CN (Figure 2).[13] Besides the electrochemically reversible $Os^{IV/III}$ wave at 0.67 V, a reversible, pH-dependent two-electron wave appears at $E_{1/2} = +0.29$ V at pH 0.48 and an irreversible, multiple-electron reduction wave is seen at $E_{pc} = -0.54$ V. The peak-to-peak separation for the two-electron, reversible wave is 37 mV, which is half that of the $Os^{IV/III}$ wave (73 mV) and consistent with a two-electron process. Comparison of relative peak currents confirms that the couple at $E_{1/2} = 0.29$ V is a two-electron couple.

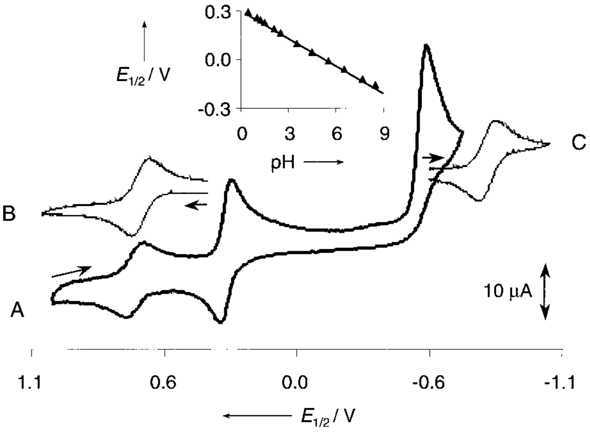


Figure 2. A) Cyclic voltammogram of $[\mathbf{3C}]^+$ in CH_3CN/H_2O (1/1, v/v) at pH 0.48 and $I = 1.0$ M in NH_4PF_6 (V versus SSCE). B) The $Os^{IV/III}$ couple in 0.2 M CH_3CN/NBu_4PF_6. C) The $Os^{III/II}$ couple under the same conditions as in (B). Inset: The pH dependence of $E_{1/2}$ for the $Os^{IV/III}$ couple of $[\mathbf{3C}]^+$ in CH_3CN/H_2O from pH 0.48 to 8.50. A line of slope 57 mV/pH unit is shown drawn through the data.

Measurements of $E_{1/2}$ as a function of pH value show that in the case of $[\mathbf{3C}]^+$ the $E_{1/2}$ value for the two-electron wave decreases by 57 mV/pH unit from pH 0.48 to 8.50 (Figure 2, inset). This is consistent with the chemically and electrochemically reversible $2e^-/2H^+$ couple shown in Equation (2). Similar results have

$$[(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}N{\equiv}CCH_3] + 2e^- + 2H^+ \rightarrow [(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}NH{=}CHCH_3] \qquad (2)$$

been obtained for $[\mathbf{3A}]^+$ and $[\mathbf{3B}]^+$ with the $2e^-/2H^+$ waves appearing at 0.31 V and 0.30 V, respectively, at pH 0.48.

The reduced Os^{III}–imino product shown in Equation (2) was electrochemically generated in CH_3CN/H_2O (1/1, v/v; pH 2.5, $I = 0.5$ M NH_4PF_6) at $E_{app} = -0.35$ V with $n = 2$. Once formed, $[Os^{III}(tpy)(Cl)(NH{=}CHCH_3)(NSC_6H_3Me_2)]$ undergoes air oxidation to $[Os^{IV}(tpy)(Cl)(NH{=}CHCH_3)(NSC_6H_3Me_2)]^+$ within minutes and then to **[3C]**$^+$ in about 1 h.[14] The imine complex was isolated as the PF_6^- salt and characterized by elemental analysis as well as UV/Vis, ^1H NMR, and infrared spectroscopies.[5] We have so far been unsuccessful at growing a suitable crystal for X-ray structure analysis.

The pH dependence of the irreversible, multiple-electron wave was also investigated in CH_3CN/H_2O (1/1, v/v). The E_{pc} values for this wave decrease by 55 mV/pH unit from $E_{pc} = -0.57$ V at pH 0.48 to $E_{pc} = -0.69$ V at pH 2.5.[5] Above pH 2.5, the peak current falls by a factor of 4, and E_{pc} becomes pH-independent. Electrolysis of **[3C]**$^+$ at $E_{app} = -0.85$ V in CH_3CN/H_2O at pH 2.2 at 5 °C to $n = 4$ followed by investigation with GC-MS reveals ethylamine as a product. The retention of the initial cyclic voltammogram at the end of the electrolysis and the appearance of ethylamine are consistent with $2e^-/2H^+$ reduction followed by rapid solvolysis as shown in Equation (3). Reduction of the

$$\begin{aligned}&[(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}NH{=}CHCH_3] + 2e^- + 3H^+\\&+ CH_3CN \xrightarrow[pH\,2.2]{CH_3CN/H_2O} [(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}N{\equiv}CCH_3]\\&+ CH_3CH_2NH_3^+\end{aligned} \tag{3}$$

nitrile complex is catalytic at −0.85 V, but changes occur in the complex upon electrolysis for extended periods of time, as shown by electrochemical measurements. The underlying chemistry remains to be investigated in detail.

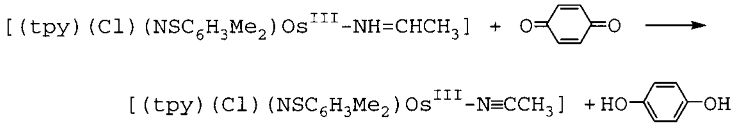
There is literature precedence for the reduction of coordinated acetonitrile ($-N_\alpha{\equiv}C_\beta{-}CH_3$) to acetimidoyl ($\eta^2$-N(H)=C−CH$_3$; bonded through N_α and C_β), ethylidenimido (η^2-N=CH−CH$_3$; bonded to M through N_α and to M′ through the double bond),[15] azavinylidenyl (−N=CH−CH$_3$),[16] imino (−NH=CH−CH$_3$),[16–17] ethylimido (≡N−CH$_2$−CH$_3$),[18] ethylamido (−NH−CH$_2$−CH$_3$),[16] and aza-allylic (η^3-CH$_2$−CH−NH$_2$)[19] ligands. In these reactions, hydrogen[20] and/or hydride (H^-,[21] $NaBH_4$,[22] $LiHBEt_3$,[16] and $LiAlH_4$[22]) are the reductants.

There is also evidence for the protonation of neutral acetonitrile complexes, either diprotonation at C_β by HCl or monoprotonation at N_α and C_β by $HBF_4{\cdot}Et_2O$. At electron-rich metal centers, protonation is accompanied by oxidation of the metal center to form ethylimido[23] or imino complexes.[19] There are also examples of hydride formation at the metal.[24]

Our result is the first example of reversible $2e^-/2H^+$ reduction of the acetonitrile ligand to the corresponding imine. It may presage an extensive proton-coupled electron transfer or hydride transfer chemistry analogous to that of $Ru^{IV}{=}O^{2+}/Ru^{II}{-}OH_2^{2+}$ couples but with proton and electron acceptor sites on the two-atom nitrile ligand ($Os^{III}{-}N{\equiv}CCH_3/Os^{III}{-}NH{=}CHCH_3$).

Initial experiments show that $[Os^{III}(tpy)(Cl)(NH{=}CHCH_3)(NSC_6H_3Me_2)]$ undergoes hydrogen transfer with reduction of an organic carbonyl compound. The imino complex acts as an electron–proton donor in CH_3CN/H_2O (3/1, v/v; pH 1.8, $I = 0.5$ M in NH_4PF_6) toward 1) benzaldehyde with reduction to benzyl alcohol [$k_{PhCHO}(25.0 \pm 0.1\,°C) = (1.03 \pm 0.01) \times 10^{-2}\,M^{-1}s^{-1}$, Eq. (4)], 2) benzoquinone with reduction to hydroquinone [$k_Q(25.0 \pm 0.1\,°C) = (3.63 \pm 0.01) \times 10^{2}\,M^{-1}s^{-1}$, Eq. (5)], and 3) dipyridyl ketone with reduction to the corresponding alcohol [$k_{Py_2CO}(25.0 \pm 0.1\,°C) = (1.07 \pm 0.01) \times 10^{-2}\,M^{-1}s^{-1}$, Eq. (6)]. The reduced products in the CH_3CN/H_2O reaction mixtures were quantitatively determined by GC-MS.[25]

$$\begin{aligned}&[(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}NH{=}CHCH_3] + PhCHO \longrightarrow\\&[(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}N{\equiv}CCH_3] + PhCH_2OH\end{aligned} \tag{4}$$



(5)

$$\begin{aligned}&[(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}NH{=}CHCH_3] + Py_2CO \longrightarrow\\&[(tpy)(Cl)(NSC_6H_3Me_2)Os^{III}{-}N{\equiv}CCH_3] + py_2CHOH\end{aligned} \tag{6}$$

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[5] See the Supporting Information.

[6] In CH_3CN/H_2O (1/1, v/v), solvolysis of **[3]**$^+$ occurs on a time scale of 4–5 h to give *cis*-$[Os^{IV}(tpy)(NCCH_3)_2(NSAr)]^{2+}$. Details will be reported elsewhere.

[7] CCDC-184082 ($[Os^{IV}(tpy)(Cl)(NCCH_3)(NSC_6H_4Me)]^+$), CCDC-184083 (*cis*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$), and CCDC-184084 (*trans*-$[Os^{IV}(tpy)(NCCH_3)_2(NSC_6H_4Me)]^{2+}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[13] In these measurements, all buffer solutions from pH 0.0 to pH 14.0 have an ionic strength of 1.0 M in NH_4PF_6: HNO_3 for pH 0–2, KHP for pH 3–5, KH_2PO_4 and Na_2HPO_4 for pH 6–8, $Na_2B_4O_7{\cdot}10H_2O$ for pH 9–10, Na_2HPO_4 for pH 11, NaOH for pH 12–14. The pH values

reported are those measured in the mixed solvents and are the same to within experimental error of those measured in CH_3CN/H_2O.

[14] In the absence of air, $[Os^{IV}(tpy)(Cl)(NH{=}CHCH_3)(NSC_6H_3Me_2)]^+$ does not undergo ligand substitution to form $[\mathbf{3C}]^+$ in CH_3CN/H_2O (1/1, v/v).

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[25] The organic products from the reduction reactions were analyzed by GC-MS by using calibration curves and procedures similar to those found in ref. [12]. A typical product analysis is described in the Supporting Information.

The Ability of the α,α′-Diiminopyridine Ligand System to Accept Negative Charge: Isolation of Paramagnetic and Diamagnetic Trianions**

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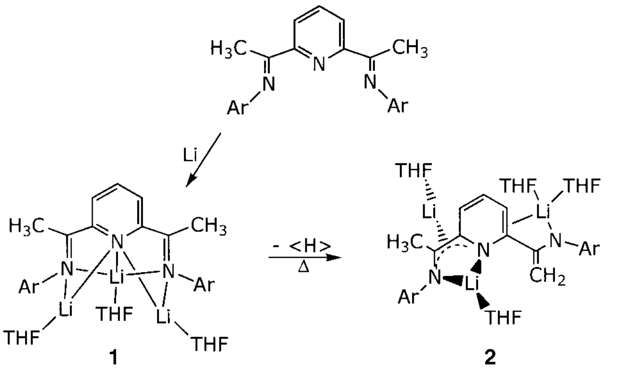
Recent work, both in this research group and elsewhere, has shown that the α,α′-diiminopyridine ligand $[\alpha,\alpha'\text{-}\{2,6\text{-}(i\mathrm{Pr})_2\mathrm{PhN{=}C(Me)}\}_2(\mathrm{C_5H_3N})]$, well known for its ability to form highly active polymerization catalysts,[1] can be involved in the organometallic transformations of metal centers. Alkylating agents may attack not only the imino function[2] but also all of the pyridine ring carbon atoms[3,4] and even the nitrogen atom.[5] In addition, dimerization may be achieved by imine reductive coupling[4] or by the cycloaddition of two pyridine rings to form a tricyclic system.[4] In parallel with all of these transformations, either one or both of the CH_3 groups attached to the imine functions may be partly deprotonated.[4,5] In this unusual variety of transformation, the metal center coordinated to the ligand may engage in redox reactions and may either lower or even increase its oxidation state.[3,6,7] This behavior illustrates the unique ability of this ligand system to a) accept negative charge with preferential spin-density localization on the imine groups and on the pyridine N and C_{para} atoms, and b) to engage in internal redox processes with the coordinated metal. The ability of the ligand to accept or to donate negative charge to the metal is paramount to the fine-tuning of the redox potential of the metal, and of its Lewis acidity which, in turn, determines the catalytic behavior of the metal complex.

Given the above scenario, we became interested in clarifying the ability of this remarkable ligand system to accept negative charge. For this purpose, we have carried out the reduction of $[\alpha,\alpha'\text{-}\{2,6\text{-}(i\mathrm{Pr})_2\mathrm{PhN{=}C(Me)}\}_2(\mathrm{C_5H_3N})]$ with strong reductants such as Li and [Li(naphthalenide)], in the absence of transition metals. Herein we describe our findings.

The reactions were carried out by treating a solution of $[\alpha,\alpha'\text{-}\{2,6\text{-}(i\mathrm{Pr})_2\mathrm{PhN{=}C(Me)}\}_2(\mathrm{C_5H_3N})]$ with either metallic Li under argon or [Li(naphthalenide)] under nitrogen in THF. Regardless of the stoichiometric ratio, the reduction with Li afforded a mixture of $[\alpha,\alpha'\text{-}\{2,6\text{-}(i\mathrm{Pr})_2\mathrm{PhN{=}C(Me)}\}_2(\mathrm{C_5H_3N})][\mathrm{Li(thf)}]_3$ (**1**) and $[\{\alpha\text{-}[2,6\text{-}(i\mathrm{Pr})_2\mathrm{PhN{=}C(Me)}]\}\{\alpha'\text{-}[2,6\text{-}(i\mathrm{Pr})_2\mathrm{PhN\text{-}C({=}CH_2)}]\}\mathrm{C_5H_3N}][\mathrm{Li(thf)}]_2[\mathrm{Li(thf)_2}]$ (**2**) through a readily reproducible process. Both species contain a trianionic ligand (Scheme 1). Separation of the two extremely air-sensitive species was possible because of their relative solubilities in hexane. However, we observed that reactions carried out at low temperature with 3 equiv of [Li(naphthalenide)] afforded **2** as the only isolated compound (67%) and no evidence for the presence of **1**.



Scheme 1.

The connectivity of **1** was elucidated by an X-ray crystal structure (Figure 1). The complex contains the intact ligand, which adopts the usual chelating tridentate conformation

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