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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: CO₂Me: NaOH, MeOH:H₂O (2:1), 25°C, 2 h;^[19] Cbz: 10% Pd/C, H₂, 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 %), HNEt₃ (40 equiv), MeCN:H₂O (1:1), 25°C, 15 min;^[21] Bn: 20% Pd(OH)₂/C, H₂ (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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[Os^{III}(tpy)(Cl)(NCCH₃)(NSAr)]: Reversible Reduction of Acetonitrile by Os^{III}–Sulfilimido Complexes**

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Thomas J. Meyer*

Earlier reports have revealed an extensive electron–proton, reversible redox chemistry based on the Os^{V/IV} couples [Os^V(tpy)(Cl)₂{NN(CH₂)₄O}]⁺/[Os^{IV}(tpy)(Cl)₂{N(H)–N(CH₂)₄O}]⁺ (tpy = 2,2':6,2''-terpyridine, N(CH₂)₄O is a morpholide),^[1] [Os^V(tpy)(Cl)₂{NS(3,5-C₆H₃Me₂)}]⁺/[Os^{IV}(tpy)(Cl)₂{NS(H)(3,5-C₆H₃Me₂)}]⁺,^[2] and [Os^V(Tp)(Cl)₂(NPEt₂)]/[Os^{IV}(Tp)(Cl)₂{NP(H)Et₂}] (Tp = tris(pyrazolyl)borate).^[3] These couples are reminiscent of oxo/hydroxo/aqua couples such as *cis*-[Ru^{IV}(bpy)₂(py)(O)]²⁺/*cis*-[Ru^{III}(bpy)₂(py)(OH)]²⁺ and *cis*-[Ru^{III}(bpy)₂(py)(OH)]²⁺/*cis*-[Ru^{II}(bpy)₂(py)(H₂O)]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 [Os^{III}(tpy)(Cl)(N≡CCH₃)(NSAr)] / [Os^{III}(tpy)(Cl)(NH=CHCH₃)(NSAr)] (Ar = C₆H₅, 4-MeC₆H₄, 3,5-Me₂C₆H₃). At more negative potentials, the Os^{III}–imino complexes undergo further reduction and solvolysis to give [Os^{III}(tpy)(Cl)(NCCH₃)(NSAr)] and CH₃CH₂NH₂.

A rapid reaction occurs when *cis*-[Os^{VI}(tpy)(Cl)₂(N)]⁺ ([**1**]⁺) and aromatic thiols (C₆H₅SH, 4-MeC₆H₄SH, or 3,5-Me₂C₆H₃SH) are mixed in CH₃CN under N₂ at room temperature [Eq. (1)]. The products are *cis*-

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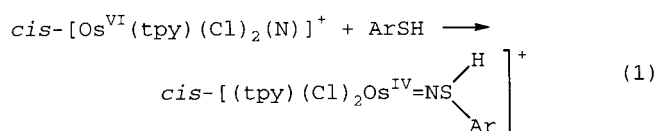
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$[Os^{IV}(tpy)(Cl)_2[NS(H)Ar]]^+$ (Ar = C₆H₅ ([**2A**]⁺), 4-MeC₆H₄ ([**2B**]⁺), 3,5-Me₂C₆H₃ ([**2C**]⁺)).^[5]

Addition of a small amount of water to [**2**]⁺ in CH₃CN causes solvolysis and deprotonation to give the monosolvento complexes $[Os^{IV}(tpy)(Cl)(NCCH_3)(NSAr)]^+$ (Ar = C₆H₅ ([**3A**]⁺), 4-MeC₆H₄ ([**3B**]⁺), 3,5-Me₂C₆H₃ ([**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 PF₆[−] salts and characterized by elemental analysis and cyclic voltammetry as well as ¹H NMR, infrared, and UV/Vis spectroscopies.^[5]

Crystals of [**3B**]PF₆ were grown by slow diffusion of Et₂O into a solution in CH₃CN.^[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(CH₃CN) 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 sp³ 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 d⁴ 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 [**3C**]⁺ in dry CH₃CN (5.0 × 10^{−3} M) containing 0.1 M NBu₄PF₆ 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)-C₆H₃Me₂]]⁺ 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 CH₃CN. The corresponding couples for *cis*-[Os^{IV}(tpy)(NCCH₃)₂(NSC₆H₃Me₂)]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]

The cyclic voltammetric characteristics of [**3C**]⁺ in H₂O/CH₃CN (1/1, v/v; I = 1.0 M in NH₄PF₆) are strikingly different from those in CH₃CN (Figure 2).^[13] Besides the electrochemi-

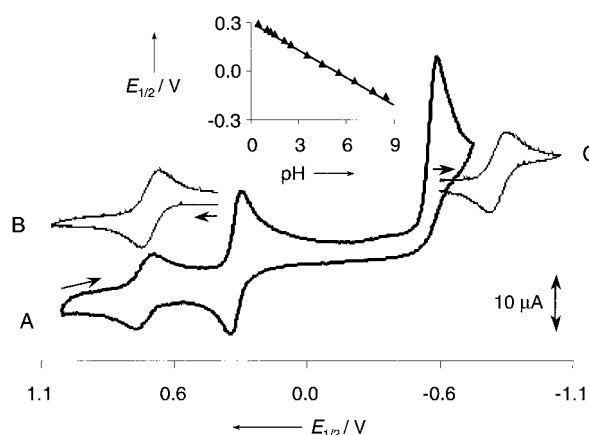
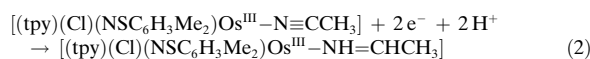


Figure 2. A) Cyclic voltammogram of [**3C**]⁺ in CH₃CN/H₂O (1/1, v/v) at pH 0.48 and I = 1.0 M in NH₄PF₆ (V versus SSCE). B) The Os^{IV/III} couple in 0.2 M CH₃CN/NBu₄PF₆. C) The Os^{III/II} couple under the same conditions as in (B). Inset: The pH dependence of $E_{1/2}$ for the Os^{IV/III} couple of [**3C**]⁺ in CH₃CN/H₂O from pH 0.48 to 8.50. A line of slope 57 mV/pH unit is shown drawn through the data.

cally 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.

Measurements of $E_{1/2}$ as a function of pH value show that in the case of [**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



been obtained for [**3A**]⁺ and [**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 CH₃CN/H₂O (1/1, v/v; pH 2.5, I = 0.5 M NH₄PF₆) at E_{app} = −0.35 V with *n* = 2. Once formed, [Os^{III}(tpy)(Cl)-(NH=CHCH₃)(NSC₆H₃Me₂)] undergoes air oxidation

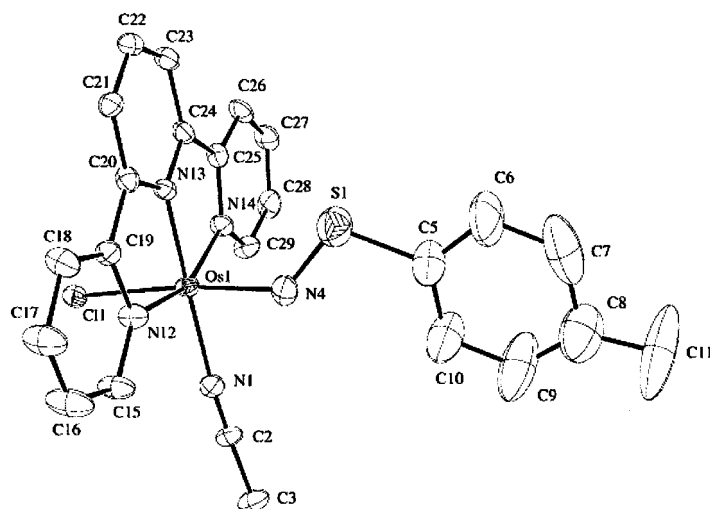
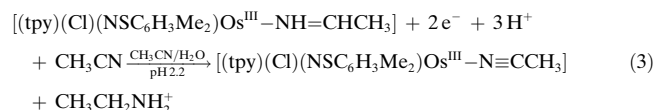


Figure 1. ORTEP diagram (30% ellipsoids) for [**3B**]PF₆.

to $[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})(\text{NH}=\text{CHCH}_3)(\text{NSC}_6\text{H}_3\text{Me}_2)]^+$ within minutes and then to $[\mathbf{3C}]^+$ 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 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1/1, v/v). The E_{pc} values for this wave decrease by 55 mV/pH unit from $E_{\text{pc}} = -0.57$ V at pH 0.48 to $E_{\text{pc}} = -0.69$ 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 $[\mathbf{3C}]^+$ at $E_{\text{app}} = -0.85$ V in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at pH 2.2 at $n = 4$ 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 $2e^-/2\text{H}^+$ reduction followed by rapid solvolysis as shown in Equation (3). Reduction of the



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.

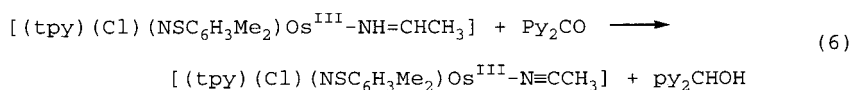
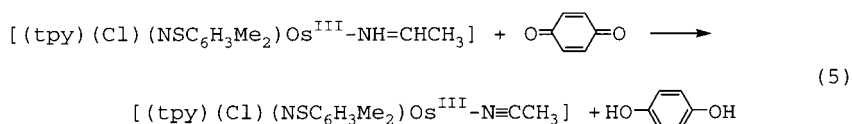
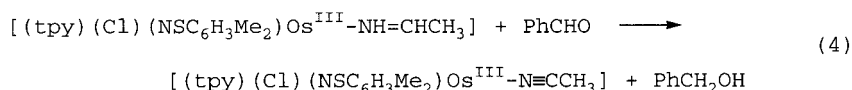
There is literature precedence for the reduction of coordinated acetonitrile ($-\text{N}\equiv\text{C}\beta-\text{CH}_3$) to acetimidoyl ($\eta^2-\text{N}(\text{H})=\text{C}-\text{CH}_3$; bonded through N_α and C_β), ethylenimido ($\eta^2-\text{N}=\text{CH}-\text{CH}_3$; bonded to M through N_α and to M' through the double bond),^[15] azavinylidenyl ($-\text{N}=\text{CH}-\text{CH}_3$),^[16] imino ($-\text{NH}=\text{CH}-\text{CH}_3$),^[16–17] ethylimido ($\equiv\text{N}-\text{CH}_2-\text{CH}_3$),^[18] ethylamido ($-\text{NH}-\text{CH}_2-\text{CH}_3$),^[16] and aza-allylic ($\eta^3-\text{CH}_2-\text{CH}-\text{NH}_2$)^[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 $\text{HBF}_4\cdot\text{Et}_2\text{O}$. 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 $2e^-/2\text{H}^+$ 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 $\text{Ru}^{\text{IV}}=\text{O}^{2+}/\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$ couples but with proton and electron acceptor sites on the two-atom nitrile ligand ($\text{Os}^{\text{III}}-\text{N}\equiv\text{CCH}_3/\text{Os}^{\text{III}}-\text{NH}=\text{CHCH}_3$).

Initial experiments show that $[\text{Os}^{\text{III}}(\text{tpy})(\text{Cl})(\text{NH}=\text{CHCH}_3)(\text{NSC}_6\text{H}_3\text{Me}_2)]$ undergoes hydrogen transfer with reduction of an organic carbonyl compound. The imino

complex acts as an electron–proton donor in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (3/1, v/v; pH 1.8, $I = 0.5$ M in NH_4PF_6) toward 1) benzaldehyde with reduction to benzyl alcohol [$k_{\text{PhCHO}}(25.0 \pm 0.1^\circ\text{C}) = (1.03 \pm 0.01) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, Eq. (4)], 2) benzoquinone with



reduction to hydroquinone [$k_{\text{O}}(25.0 \pm 0.1^\circ\text{C}) = (3.63 \pm 0.01) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, Eq. (5)], and 3) dipyriddy ketone with reduction to the corresponding alcohol [$k_{\text{Py}_2\text{CO}}(25.0 \pm 0.1^\circ\text{C}) = (1.07 \pm 0.01) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, Eq. (6)]. The reduced products in the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ reaction mixtures were quantitatively determined by GC-MS.^[25]

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- [6] In $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1/1, v/v), solvolysis of $[\mathbf{3}]^+$ occurs on a time scale of 4–5 h to give *cis*- $[\text{Os}^{\text{IV}}(\text{tpy})(\text{NCCH}_3)_2(\text{NSAr})]^{2+}$. Details will be reported elsewhere.
- [7] CCDC-184082 ($[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})(\text{NCCH}_3)(\text{NSC}_6\text{H}_3\text{Me}_2)]^+$), CCDC-184083 (*cis*- $[\text{Os}^{\text{VI}}(\text{tpy})(\text{Cl})_2(\text{N})]^{4+}$), and CCDC-184084 (*trans*- $[\text{Os}^{\text{IV}}(\text{tpy})(\text{NCCH}_3)_2(\text{NSC}_6\text{H}_3\text{Me}_2)]^{2+}$) 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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- reported are those measured in the mixed solvents and are the same to within experimental error of those measured in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$.
- [14] In the absence of air, $[\text{Os}^{\text{IV}}(\text{tpy})(\text{Cl})(\text{NH}=\text{CHCH}_3)(\text{NSC}_6\text{H}_3\text{Me}_2)]^+$ does not undergo ligand substitution to form $[\mathbf{3C}]^+$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1/1, v/v).
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The Ability of the α,α' -Diiminopyridine Ligand System to Accept Negative Charge: Isolation of Paramagnetic and Diamagnetic Trianions**

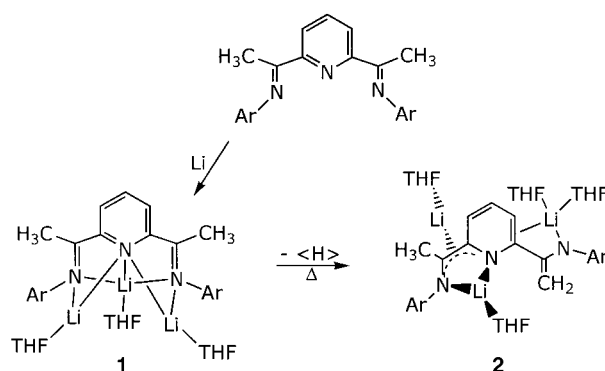
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Recent work, both in this research group and elsewhere, has shown that the α,α' -diiminopyridine ligand $[\alpha,\alpha'\text{-}\{2,6\text{-}(\text{iPr})_2\text{PhN}=\text{C}(\text{Me})_2\}_2(\text{C}_5\text{H}_3\text{N})]$, well known for its ability 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 $[\alpha,\alpha'\text{-}\{2,6\text{-}(\text{iPr})_2\text{PhN}=\text{C}(\text{Me})_2\}_2(\text{C}_5\text{H}_3\text{N})]$ with strong reductants such as Li and $[\text{Li}(\text{naphthalenide})]$, in the absence of transition metals. Herein we describe our findings.

The reactions were carried out by treating a solution of $[\alpha,\alpha'\text{-}\{2,6\text{-}(\text{iPr})_2\text{PhN}=\text{C}(\text{Me})_2\}_2(\text{C}_5\text{H}_3\text{N})]$ with either metallic Li under argon or $[\text{Li}(\text{naphthalenide})]$ under nitrogen in THF. Regardless of the stoichiometric ratio, the reduction with Li afforded a mixture of $[\alpha,\alpha'\text{-}\{2,6\text{-}(\text{iPr})_2\text{PhN}=\text{C}(\text{Me})_2\}_2(\text{C}_5\text{H}_3\text{N})][\text{Li}(\text{thf})_3]$ (**1**) and $[\alpha\text{-}\{2,6\text{-}(\text{iPr})_2\text{PhN}=\text{C}(\text{Me})\}\text{-}\{\alpha'\text{-}\{2,6\text{-}(\text{iPr})_2\text{PhN}=\text{C}(\text{CH}_2)\}_2\text{C}_5\text{H}_3\text{N}\}][\text{Li}(\text{thf})_2][\text{Li}(\text{thf})_2]$ (**2**) through a readily reproducible process. Both species contain a trianionic ligand (Scheme 1). Separation of the two ex-



Scheme 1.

tremely 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 $[\text{Li}(\text{naphthalenide})]$ afforded **2** as the only isolated compound (67%) and no evidence for the presence of **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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