afforded a 75% yield of **7**. As was envisioned in advance, the photolytic redox reaction of **5** had apparently given rise to **6**, which in a 2 + 4 cycloaddition (presumably a "dark" step)[14] yielded the fused oxazine **7**. The effects of incorporating aromatic substituents of relevance to the synthesis of **1** were explored. Reaction of methyl 4-formyl-3-methoxybenzoate[15] with the butadienyl anion afforded a 56% yield of **8**. Photolysis of **8**, as above, afforded a 60% yield of **9**, the structure of which was proven by crystallographic means.

We next studied the possibility of incorporating "pre-mitomycin" functionality on the aromatic ring. Accordingly, the addition of the butadienyl anion to 4-methyl-6-nitro-2,3,5-trimethoxybenzaldehyde[15] was carried out. The product, **10**, obtained in 80% yield, was photolyzed as above. In this case there was directly obtained a 45% yield of the pyrroloindoxyl derivative **12**. That the expected **11** is at least a permissible intermediate in this amazing transformation was shown by its isolation in low yield from the same reaction and its conversion to **12** by subsequent photolysis under the same conditions. The structure of **12** was fully corroborated by a crystallographic determination of its derived acetate **13**.[16]

We were intrigued by the difference in photochemical behavior in the two series. Thus, **7** and **9**, each produced from photolysis reactions, are apparently photostable under the conditions of their formation. In contrast, **11** suffers photochemically induced conversion to **12**. It seemed possible that the confluence of highly electron donating substituents in the aromatic nucleus of **11** favors its photoconversion to **12**. While maintaining the aromatic substitution pattern of the pre-FR-900482 series, we examined the consequences of removing the electron-withdrawing "keto" group[17] of **9**. The hope was that the resultant product would be more electronically similar to **11**. In the event, compound **9** was smoothly (80%) converted to **14** through the agency of $TMSCH_2MgCl$.[18] Interestingly, photolysis of **14** produced an 80% yield of **15** (Scheme II).

Our experiments have not thus far been directed to providing new insights as to the precise nature of the transformation of **11** and **14** to **12** and **15**, respectively. Certainly, the sequence of photocleavage of an NO bond, C → N hydrogen migration, and cyclization is not without precedent.[19] In summary, a highly concise entry to intermediates closely related to the mitomycins[20] and FR-900482 has been developed.

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Supplementary Material Available: Complete experimental details, NMR, IR, and mass spectral data for all reactions reported, UV spectral data for compounds **5**, **8**, **9**, **11**, and **14**, and experimental details, ORTEP drawings, and tables containing fractional coordinates, temperature factors, bond distances, torsional angles, and anisotropic temperature factors for the X-ray crystallographic analyses of compounds **9** and **13** (26 pages). Ordering information is given on any current masthead page.

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(14) The intermediacy of **6** is assumed on the basis of the generally accepted photoreactions of *O*-nitrobenzyl derivatives (ref 12). The conversion of the intermediate **6** to the fused oxazine **7** could in principle proceed by a photochemical or thermal pathway.

(15) The preparation of the aromatic aldehydes is described in the supplementary material.

(16) While the stereochemistry of the acetate **13** is known, we have not rigorously shown that the alcohol and acetate have the same configurations.

(17) Since the conversion of oxazine **11** to the hemiaminal **12** is reasoned to begin with homolysis of the N–O bond (ref 19), the transformation is in part a function of the N–O bond strength. In the absence of competing electron donation, the presence of a carbonyl group in conjugation with the nitrogen seems to impart stability to the N–O bond, possibly by stabilizing the aminyl radical.

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Synthesis of Bis(buckminsterfullerene)nickel Cation, $Ni(C_{60})_2^+$, in the Gas Phase

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The advent of a simple synthesis for generating macroscopic amounts of the fullerenes,[1] C_{60} and C_{70}, has spawned an intensive effort to study the physical and chemical properties of this new state of carbon.[2] One of the most intriguing aspects of the fullerenes is their topography, which, as exemplified by the "soccer ball" structure of buckminsterfullerene (C_{60}), has an internal volume and an external surface.[3] Incorporation of elements,[4a] particularly transition metals,[4b,c] and perhaps even small compounds, inside the carbon cage may lead to useful new materials with unique properties. Alternatively, the fullerenes may prove to be highly versatile ligands for the generation of unusual organometallic complexes. The aromatic nature of the fullerenes, together with their five- and six-membered-ring makeup and low reduction potentials, suggests that they may function like cyclopentadienyl or benzene ligands. Exemplifying the feasibility of this approach is the recent report of a cyclopentadienyl–ruthenium–C_{60} compound.[5]

Expanding the potential utility of the fullerenes as ligands, we felt that a bis-C_{60} metal ion complex should be formed in the gas phase in analogy to the bis-benzene or metallocene complexes. This idea was realized with the formation of the bis complex $Ni(C_{60})_2^+$, which was observed in a Fourier transform mass spectrometer to arise at longer trapping times in the presence of a background of C_{60} as a result of direct attachment of C_{60} to NiC_{60}^+.[6] Figure 1 shows selected mass spectra from the multistep (in situ) synthesis[7] of the bis complex, which entailed (1) laser desorption of Ni^+,[8] (2) isolation of the $^{58}Ni^+$ isotope by double

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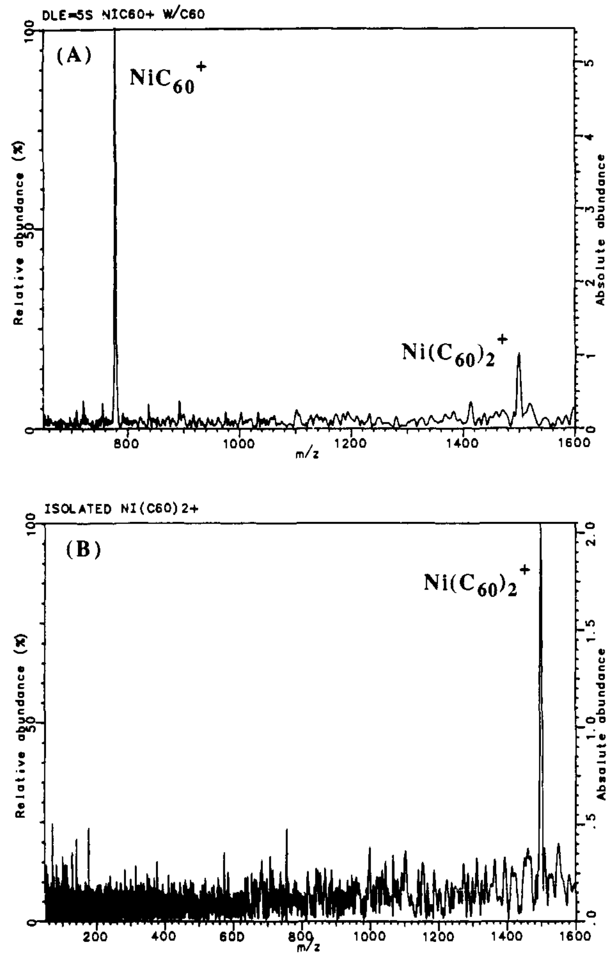

Figure 1. (A) Reaction of isolated NiC_{60}^+ with C_{60} background. (B) Isolated $Ni(C_{60})_2^+$. Absolute abundance is an arbitrary measure of FTMS signal intensity.

resonance ejection[9] of the less abundant isotopes, (3) subsequent sequential reactions of $^{58}Ni^+$ by direct attachment with preformed C_{60} heated off a solids probe at 350 °C to generate $^{58}NiC_{60}^+$ (*m/z* 778) and, following its isolation, then $Ni(C_{60})_2^+$ (*m/z* 1498) (Figure 1A), and (4) isolation of the $^{58}Ni(C_{60})_2^+$ by double resonance ejection (Figure 1B). Unfortunately, under these conditions the remaining signal intensity was not sufficient to obtain unambiguous collision-induced dissociation data.[10]

The results reported here suggest the possibility of a stable family of bis-fullerene "dumbbell" complexes in analogy to the bis-benzene and metallocene compounds. While only the bis-C_{60} nickel complex has been observed to date, variation of the experimental conditions will undoubtedly yield additional members of the bis-fullerene family (other metals and other fullerenes). Furthermore, we are also currently attempting to synthesize macroscopic amounts of these interesting and potentially useful complexes in our laboratory.[11]

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Crystal Structure of Lithium Diisopropylamide (LDA): An Infinite Helical Arrangement Composed of Near-Linear N-Li-N Units with Four Units per Turn of Helix

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Although the number of crystal structure reports of organic lithium derivatives has mushroomed over the past decade or so,[1] a report of the most important lithium reagent, indeed, one of the most utilized reagents throughout organic synthesis, lithium diisopropylamide (LDA), has been conspicuously absent. A combination of low nucleophilicity and high kinetic basicity makes this hindered amide invaluable in proton abstraction applications.[2] Collum and Galiano-Roth recently discussed[3] the scarce structural information that is available on LDA systems in their account of the (LDA·tetrahydrofuran)$_2$[4] solution dimer established by ^{6}Li and ^{15}N NMR spectroscopic studies. The problem is that although LDA does have some solubility in hydrocarbon solvents, it tends to readily precipitate when prepared in them. Dissolution can be effected by addition of the donor tetrahydrofuran although its concentration and the solution temperature must be carefully controlled to minimize solvent degradation.[5] Described herein is a simple procedure involving the donor TMEDA (tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$),[6] which yields a *crystalline* form of LDA showing no complexation. Once isolated from solution, the crystals retain their integrity under a protective inert atmosphere, and their quality is such that we have successfully determined the crystal structure by an X-ray diffraction study. This confirms that uncomplexed LDA is a polymer,[7] but the nature of the infinite association is unprecedented with near-linear N-Li-N units in a helical assembly.

The crystalline composition can be prepared in the following way. Commercial samples (10-mmol scale) of *n*-butyllithium (or *tert*-butyllithium) and diisopropylamine mixed together in hexane at 295 K under an argon blanket afford the conventional LDA precipitate, to which is added TMEDA (20 mmol). Complete dissolution is achieved by gently warming the stirred mixture. Gradual cooling to ambient temperature deposits from the solution

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