

1),^{15a,c} which adopts structure A, with those of **1** reveals that only the former are sensitive to molecular charge or metal oxidation state: the W≡C and W—Br bonds are 0.024 and 0.042 Å shorter in **1**[PF₆] than in **1**, while the W—P bonds are longer in the cation by 0.053 Å. Significantly, the W≡C and W—Br bond distances of **1**[PF₆] still lie within the ranges expected for W(CR)₄Br complexes,¹⁷ suggesting that its formal W≡C and W—Br bond orders are unchanged from those of **1**; presumably, electrostatic effects and/or the decrease in the covalent radius of tungsten with increasing oxidation state are responsible for the bond contractions of **1**[PF₆]. The lengthened W—P bond of **1**[PF₆] mirrors the general trend for redox-paired transition-metal phosphine complexes; such elongations have been attributed to a decrease in M→P π-bonding upon raising the oxidation state of the metal.²⁰ Taken together, the structural results for these redox congeners indicate that the HOMO of members of this class of compounds is the metal d_{xy} orbital, which is nonbonding (δ symmetry) with respect to the benzyldiyne and bromide ligands, and whose interactions with the dmpe ligands are of both σ and, to a greater extent, π symmetry. This orbital is doubly occupied for **1** and **2** and singly occupied for **1**[PF₆].

The determination of the HOMO for this class of compounds allows the nature of the LUMO to be directly probed by electronic-absorption spectroscopy. For compounds **1** and **2**, these spectra display weak ($\epsilon \cong 200 \text{ M}^{-1} \text{ cm}^{-1}$) bands at 18 980 and 18 350 cm⁻¹, respectively, as the lowest-energy feature. Replacing the phosphine ligands of **1** or **2** with 1,2-bis(diphenylphosphino)ethane, or the bromide ligand with chloride or iodide, has little effect on the transition energy—the transition energies for the set of compounds derived from all permutations of these ligands span only an 1100-cm⁻¹ range—but exchange of the alkylidyne phenyl group with a saturated group (H, *t*-Bu) causes the band to blue shift 6–9 × 10³ cm⁻¹.²¹ This indicates that the orbital character of the transition has a significant π(W≡CPh) component, a conclusion consistent with that of a similar qualitative spectroscopic analysis for carbonyl-containing carbyne complexes.⁹ Compelling evidence in support of this hypothesis is provided by the vibronic structure that is resolved on this band for **2** at low temperature (Figure 1).²² The red flank of the band consists of two distinct features that are separated by ca. 1150 cm⁻¹; since highly detailed vibrational-spectroscopic studies on the related compound W(CPh)(CO)₄Br have established the ground-state ν(W≡C) frequency to be ca. 1360 cm⁻¹,²³ we attribute the vibronic features of **2** to the excited-state ν(W≡C) mode, with the decrease in its frequency relative to that of the ground state suggesting that the W≡C bond is weakened in the lowest-lying excited state. Given that the orbital from which the electronic transition originates is W≡C nonbonding, we conclude that the LUMO is W≡C antibonding. Simple symmetry considerations indicate this orbital to be a π*(W≡CPh) orbital, derived from the out-of-phase combination d_{xz}(W)—p_x(C) or d_{yz}(W)—p_y(C); these π* orbitals are nondegenerate because of the 2-fold symmetry of the benzyldiyne ligand.

Although there are no theoretical studies on **1** and **2** to which these results can be compared,¹² our findings indicate that the frontier orbitals of these and related species conform to the symmetry-derived model of an approximately tetragonal, strongly axially compressed ligand field, similar to that for metal-oxo complexes.²⁴ An unresolved, but important,^{12,25} question is what

the quantitative tungsten and carbon parentages of the LUMO are. We are currently conducting photochemical and spectroscopic studies aimed at evaluating this.

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Supplementary Material Available: A listing of spectroscopic and analytical data for **1** and **1**[PF₆] (1 page). Ordering information is given on any current masthead page.

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Enantioselective Deprotonation: The Structure and Reactivity of an Unsymmetrically Complexed Isopropylolithium/Sparteine/Et₂O Dimer

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The structures of organolithium complexes used in synthetically useful reactions are of current interest.¹ In particular, reagents that effect highly enantioselective deprotonations to give dipole-stabilized carbanions have considerable potential for asymmetric synthesis.² Hoppe and co-workers first reported the use of a complex of *sec*-BuLi and the C₁ symmetric diamine sparteine (**1**) to lithiate a nonconjugated oxygen-substituted system,³ and we have recently reported a highly enantioselective deprotonation using *sec*-BuLi/sparteine for a nonconjugated nitrogen system.⁴ We have determined the solution structure of an isopropylolithium/sparteine complex⁵ by NMR techniques and find the structure of this complex to be a novel, unsymmetrically complexed dimer, different from most complexes of diamines with simple organolithium reagents.⁶

A 1:1 complex of *i*-PrLi/sparteine in either Et₂O or cyclopentane reacts with Boc-pyrrolidine at -78 °C to provide a configurationally stable α'-lithio carbamate,⁴ which reacts with TMSCl to give (*R*)-2-(trimethylsilyl)-Boc-pyrrolidine in 80% yield with 80 ± 5% ee in cyclopentane and in 65% yield with 95 ± 5% ee in ether. These results are similar to those found using *sec*-BuLi/sparteine.⁴ The yield of product and extent of asymmetric induction were found to be proportional to the amount of sparteine present.

A 1:1 complex of *i*-Pr⁶Li/sparteine in Et₂O-*d*₁₀ was investigated using ⁶Li, ¹³C, and ¹H NMR.⁷ The ¹H NMR spectrum contains

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(22) Similar, though more diffuse, vibronic structure is observed on the corresponding absorption band of **1** at low temperature (Stoner, T. C.; Hopkins, M. D. Unpublished results).

(23) The ν(W≡C) mode of benzyldiyne compounds is strongly coupled both with ν(C—Ph) and with deformation modes of the phenyl group, as indicated both experimentally and by normal-coordinate analyses (Dao, N. Q.; Fischer, E. O.; Kappenstein, C. *Nouv. J. Chim.* **1980**, *4*, 85–94). We have not yet attempted such studies for **1**, **2**, or **1**[PF₆]. **Note Added in Proof:** A preliminary Raman spectrum of **1**[PF₆] displays a band at 1357 cm⁻¹ as the strongest feature. This band is presumably attributable to ν(W≡CPh), by analogy to W(CPh)(CO)₄Br.

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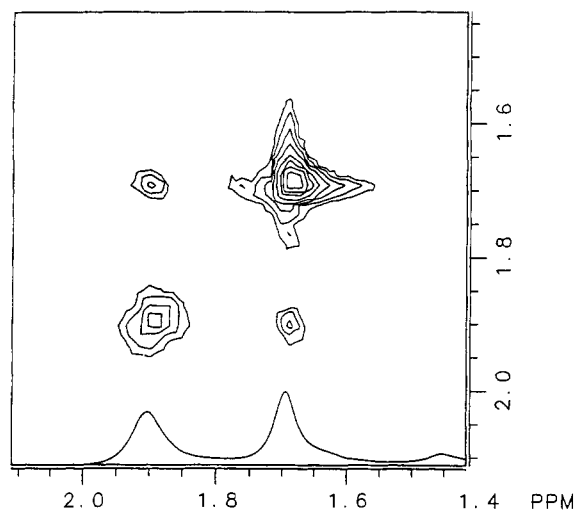


Figure 1. ${}^6\text{Li}$ - ${}^6\text{Li}$ COSY spectrum of *i*-Pr ${}^6\text{Li}$ /sparteine in Et $_2$ O at -80 °C (0.2 M).

two *i*-Pr ${}^6\text{Li}$ methine multiplets visible around -1.1 ppm, indicating the presence of two different types of methine protons. The ${}^{13}\text{C}$ spectrum contains two quintets ($J_{6\text{Li}-13\text{C}} = 8$ Hz) around 12 ppm, also indicating that two types of methine carbon atoms are present. The multiplicity of the signals indicates that each carbon is attached to two lithium atoms in a dimeric species.⁸ The ${}^6\text{Li}$ NMR spectrum also contains two major peaks, suggesting that there are two different *i*-PrLi units in solution that could result either from one, nonsymmetrical dimer or from two different dimeric species.

A ${}^6\text{Li}$ - ${}^6\text{Li}$ COSY experiment was carried out to determine if the two different types of ${}^6\text{Li}$ atoms indicated by the ${}^6\text{Li}$ NMR spectrum were present in the same aggregate.⁹ The presence of correlations between two ${}^6\text{Li}$ NMR resonances indicates that there are scalar spin-spin interactions between them and that they are in the same aggregate. Shown in Figure 1 is the ${}^6\text{Li}$ - ${}^6\text{Li}$ COSY spectrum of the solution of *i*-Pr ${}^6\text{Li}$ /sparteine in Et $_2$ O showing correlations between the two different ${}^6\text{Li}$ signals.¹⁰ This experiment suggests that there is one nonsymmetrical dimeric species present in solution. Additional insight into the structure of this aggregate was gained from the investigation of the *i*-Pr ${}^6\text{Li}$ /sparteine mixture in hydrocarbon solvents.

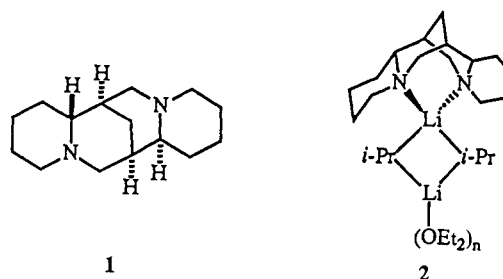
The NMR spectra of a 1:1 *i*-Pr ${}^6\text{Li}$ /sparteine complex in cyclopentane are quite different from those of the complex in Et $_2$ O. The ${}^6\text{Li}$ NMR spectrum contains only one broad peak at all temperatures. The ${}^{13}\text{C}$ NMR spectrum contains a very broad, unresolved peak for the methine carbon of *i*-PrLi at 14 ppm, which is in the chemical shift range normally observed for an *i*-PrLi dimer. However, addition of approximately 1 equiv or more of Et $_2$ O to this solution produces two peaks in the ${}^6\text{Li}$ NMR spectrum, reminiscent of the complex in Et $_2$ O.¹¹

A solution of *i*-Pr ${}^6\text{Li}$ - d_6 with 1 equiv of sparteine per Li and 2.5 equiv of Et $_2$ O per Li in methylcyclohexane- d_{14} was studied by ${}^{13}\text{C}$ NMR. The spectrum contains quintets at both 11 and 13 ppm with coupling constants of 7.4 Hz. This indicates that two different types of dimeric methine carbon atoms are present. The ${}^6\text{Li}$ NMR spectrum, which shows two different ${}^6\text{Li}$ resonances,

is very similar to the spectrum of the *i*-PrLi/sparteine complex in ether. A ${}^6\text{Li}$ - ${}^6\text{Li}$ COSY experiment established that the two different ${}^6\text{Li}$ atoms were present in the same aggregate.

The *i*-Pr ${}^6\text{Li}$ /sparteine complex in hydrocarbon solvents may exist as a mixture of fluxional dimeric species in which the sparteine ligands complex in both η_1 and η_2 fashions. This would provide the single, broad NMR signals observed and explain the lack of observable ${}^{13}\text{C}$ - ${}^6\text{Li}$ coupling. This fluxional behavior is apparently the result of the steric requirements of sparteine and *i*-PrLi, which do not allow both ligands to complex in an η_2 manner.

The changes in the NMR spectra upon addition of Et $_2$ O to the hydrocarbon solution of *i*-Pr ${}^6\text{Li}$ /sparteine and the similarities between these NMR spectra and the *i*-Pr ${}^6\text{Li}$ /sparteine complex in diethyl ether suggest that at least one molecule of Et $_2$ O is involved in a nonsymmetrical dimeric complex. We propose that the presence of Et $_2$ O allows formation of the *i*-Pr ${}^6\text{Li}$ dimer **2** in which one lithium atom is η_2 complexed by sparteine and the other lithium by diethyl ether.¹² Such a structure is in contrast to most dimeric organolithium/diamine complexes in which the diamine ligands chelate in an η_2 manner to both lithium atoms.^{6,13}



It is possible that the enantioselective deprotonation could occur through **2** by replacement of the Et $_2$ O by carbamate and subsequent lithiation. Although it is not known if the η_2 -complexed sparteine can "transmit" its asymmetry through the dimeric species, the steric effects of the sparteine on the opposite end of the dimer are evident from the results presented here. Reactions of organolithium reagents through dimers have been reported,¹⁴⁻¹⁶ but reaction through a monomeric species cannot be ruled out by the available data.

In summary, complex **2** is a novel unsymmetrically complexed *i*-Pr ${}^6\text{Li}$ dimer in which only one lithium atom is complexed by sparteine, while the other is complexed by Et $_2$ O. Efforts to determine the active lithiation species for the enantioselective deprotonation as well as the characterization of related complexes are underway.

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Supplementary Material Available: A series of ${}^6\text{Li}$ NMR spectra showing the effect of incremental addition of Et $_2$ O to the *i*-Pr ${}^6\text{Li}$ /sparteine cyclopentane solution and experimental procedures for the enantioselective deprotonations (5 pages). Ordering information is given on any current masthead page.

(7) All NMR spectra were obtained at -80 °C in order to be consistent with the synthetic work.^{3,4}

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(11) A series of ${}^6\text{Li}$ NMR spectra showing the effects of incremental addition of Et $_2$ O to the *i*-Pr ${}^6\text{Li}$ /sparteine cyclopentane solution is provided as supplementary material.

(12) The number of molecules of diethyl ether which are complexed to the lithium could not be definitively determined by the methods used for the incremental addition experiments.

(13) We are presently studying the solution structure of *i*-Pr ${}^6\text{Li}$ /TMEDA in Et $_2$ O. Preliminary results suggest that at low temperatures (-100 °C) a mixture of both η_1 and η_2 modes of complexation may exist.

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