1A). The catalase Mn site is dramatically altered on reduction, with longer Mn-(O,N) distances and no 2.7-Å Mn-Mn interaction (Figure 1C). The outer-shell peaks ($R + \alpha \approx 3.0$ and 3.8 Å) are typical of, but smaller than, those observed for Mn-imidazole complexes.

Curve fitting results are summarized in Table I (and in Table S1 in the supplementary material). The data for the superoxidized enzyme cannot be fit without including two shells of nearest-neighbor scatterers and an Mn-Mn interaction at 2.7 Å. The 1.82-Å Mn-O distance is typical of Mn-bridging oxo distances. Both the Fourier transform and the curve fitting suggest additional low-Z scatterers, consistent with second and third shell N/C atoms in coordinated imidazoles.[18] The apparent coordination numbers suggest an average of 1-2 imidazoles per Mn. However, this number is not well defined due to the limited k range of the data and interference from the strong Mn-Mn scattering.

As suggested by the Fourier transform, the EXAFS for reduced catalase is dominated by a single shell of low-Z scatterers at 2.19 Å. There is no evidence for a shell of scatterers at ca. 1.8 Å (i.e., a bridging oxo ligand); however, the fit quality is improved significantly if additional shells of C and N/C scatterers are included at ca. 3.2 and 4.4 Å. The apparent coordination numbers suggest an average of 2-4 imidazoles per Mn, although once again this number is not well defined. There is a *small* improvement in the fit if a shell of Mn is added at 3.55 Å. However, equivalent improvements are observed if instead the Mn is added at 3.99 Å or if a shell of C is added at 3.64 Å. In no case is the improvement sufficient to support the conclusion that the reduced catalase contains an EXAFS detectable Mn-Mn interaction. All of the Mn-scatterer distances in reduced catalase are slightly but significantly shorter than those in Mn(II)(imidazole)$_6$. This may be due to a coordination number less than six for one or both of the Mn atoms, the presence of oxygen ligands (e.g., from carboxylate bridges), or a combination of these effects. Overall, the Mn ligation appears very similar to that of Fe in deoxy hemerythrin.[20]

On the basis of ESEEM spectra, Dikanov et al. suggested[21] that one or more imidazoles are coordinated to the Mn in superoxidized catalase. The EXAFS data confirm this ligation for *both* superoxidized and reduced catalase. Although not well defined, the apparent coordination numbers suggest that imidazole ligands are lost on forming the superoxidized enzyme. This could occur if one or more imidazoles are replaced by bridging oxo groups.

The short Mn-Mn distance demonstrates that there are two oxo bridges in superoxidized catalase.[12] Although there are few examples, it appears that unsupported (μ-O)$_2$ bridges[22] have Mn-Mn distances of ≥2.70 Å, while additional bridging ligands lead to shorter Mn-Mn distances.[23] The 2.67-Å Mn-Mn distance thus suggests an additional bridge, e.g., (μ-O)$_2$(μ-carboxylato). A carboxylate bridge is consistent with the proposal[12b,24] that the oxidized Mn(III)/Mn(III) enzyme has a (μ-O)(μ-carboxylato)$_2$ bridged core.

The EXAFS data for the reduced enzyme do not permit unambiguous definition of an Mn-Mn distance. Similar difficulties in defining metal-metal distances in binuclear iron proteins[25] have been attributed to the loss of bridging ligands. In the present case, the absence of readily detectable Mn-Mn EXAFS allows us to rule out (μ-O)$_2$ or (μ-OH)$_2$ bridged structures. Bridging structures consistent with the data include (μ-carboxylato)$_n$ and (μ-OH)(μ-carboxylato)$_n$, where $n = 1-3$.

Recently we have shown that the superoxidized catalase is inactive, due to its inability to oxidize H_2O_2.[9] The present results suggest an explanation for this observation. If the oxidized enzyme has an [Mn(III)(μ-O)(μ-carboxylato)$_2$Mn(III)] core,[12,24] conversion to the superoxidized derivative involves addition of an oxo bridge. This is expected to stabilize Mn with respect to reduction, thus converting the Mn(III)/Mn(III) derivative, which is a good oxidant, into a species that, although formally more oxidized, is in fact a poor oxidant.[9] The similarity between the EXAFS for superoxidized catalase and for the OEC suggests that they contain similar, probably di-μ-oxo-bridged, Mn structures. The relatively poor oxidizing power of this unit may play an important role in stabilizing the OEC against premature oxidation of water. With the findings that the *L. plantarum* Mn catalase possesses structural, as well as chemical and spectroscopic, similarities to the OEC, Mn catalase takes on added significance as a well-characterized example of a high oxidation state biological Mn dimer.

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Supplementary Material Available: Table S1 and Figures S1 and S2 showing the quality of fit for different models and the EXAFS spectra (3 pages). Ordering information is given on any current masthead page.

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(18) Predicted distances are ca. 3.14 and 4.29 Å, based on the geometry of Mn(II)(imidazole)$_6$ and the 2.14-Å Mn-(N,O) distance.

(19) Garrett, T. P. J.; Guss, J. M.; Freeman, H. C. *Acta Crystallogr.* **1983**, *39*, 1027.

(20) Sanders-Loehn, J. In *Iron Carriers and Iron Proteins*; VCH: New York, 1989; pp 373-466.

(21) Dikanov, S. A.; Tsvetkov, Y. D.; Khangulov, S. V.; Goldfeld, M. G. *Dokl. Akad. Nauk SSSR* **1988**, *302*, 1255-1257.

(22) (a) Stebler, M.; Ludi, A.; Bürgi, H.-B. *Inorg. Chem.* **1986**, *25*, 4743-4750. (b) Plaksin, P. M.; Stoufer, R. C.; Mathew, M.; Palemik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121.

(23) (a) Bashkin, J. S.; Schake, A. R.; Vincent, J. B.; Chang, H. R.; Li, Q.; Huffmann, J. C.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1988**, 700-702. (b) Wieghardt, K.; Bossek, U.; Zsolnai, L.; Hattner, G.; Blandin, G.; Girerd, J.-J.; Babonneau, F. *J. Chem. Soc., Chem. Commun.* **1987**, 651-653. (c) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 967-969.

(24) (a) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435-1444. (b) Vincent, J. B.; Christou, G. *Adv. Inorg. Chem.* **1989**, *33*, 197-257.

(25) (a) Kauzlarich, S. M.; Teo, B. K.; Zirino, T.; Barman, S.; Davis, J. C.; Averill, B. A. *Inorg. Chem.* **1986**, *25*, 2781-2785. (b) DeWitt, J. G.; Bentsen, J. G.; Rosenzweig, A. C.; Hedman, B.; Green, J.; Pilkington, S.; Papaefthymiou, G. C.; Dalton, H.; Hodgson, K. O.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 9219-9235.

Nature of the Frontier Orbitals of Tungsten Benzylidyne Complexes

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Transition-metal alkylidyne (or carbyne) complexes[1,2] differ electronically from metal-oxo and nitrido complexes,[2] their first-row, triply bonded relatives, in that they tolerate a much broader spectrum of ancillary ligands, ranging from strong π-acceptors, for which Fischer's group VI M($\equiv$CR)(CO)$_4$X complexes are the archetypes,[3] to strong π-donors, as exemplified by

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(1) (a) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227-324. (b) Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH Publishers: New York, 1988. (c) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51-111.

(2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(3) (a) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59-81. (b) Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857-870.

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Table I. Average Bond Distances and Bond Angles for **1** and **1**[PF_6]

	distances (Å)			angles (deg)			
compd	W≡C	W−Br	W−P	C−W−P	P−W−P[a]	C−W−Br	W−C−C
1	1.796 (11)	2.744 (2)	2.441 (4)	93.4 (4)	80.6 (1)	177.5 (4)	177.0 (9)
1[PF_6]	1.772 (16)	2.702 (2)	2.494 (5)	93.4 (4)	80.7 (1)	179.1 (5)	178.5 (13)

[a] Angle within the dmpe ligand.

Schrock's W(≡CR)(OR'$_3$) compounds,[4] and are known for metals as far to the right in the transition series as iridium.[5] The reactivity of alkylidyne complexes is correspondingly distinct, being highlighted by their catalysis of alkyne metathesis and activation of related substrates;[4] it also includes a rich cluster-building,[6] C–C-bond-forming,[1,7] and excited-state chemistry.[8-10] In view of these differences, it is curious that, unlike oxo and nitrido complexes, the electronic structures of alkylidyne compounds have not been subjected to extensive experimental scrutiny.[9-12] Herein we report the first studies of the molecular structures of metal–alkylidyne redox congeners and of their electronic-absorption spectra at high resolution, the results of which provide direct assignments of the HOMO and LUMO for an important class of alkylidyne complexes.

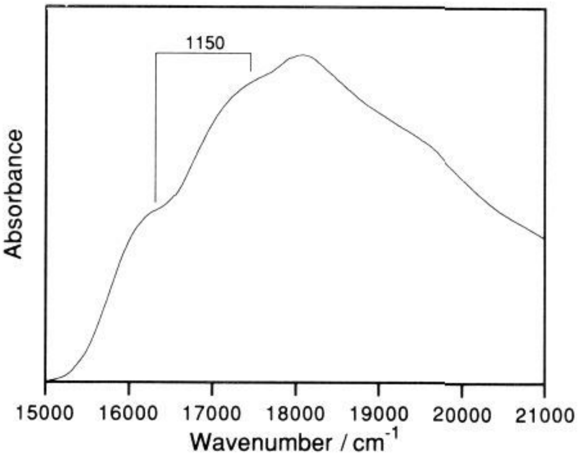
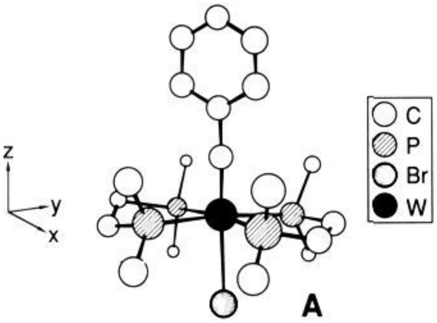


Figure 1. Electronic-absorption spectrum of **2** in 2-methylpentane at 77 K. The vibronic spacing (cm^{-1}) due to ν(W≡CPh) is indicated.

The benzylidyne complexes W(CPh)(dmpe)$_2$Br[13] (**1**; dmpe = 1,2-bis(dimethylphosphino)ethane) and W(CPh)(PMe$_3$)$_4$Br[14] (**2**) are representative of a large class of compounds that are electronically intermediate between low-valent Fischer carbyne and high-valent Schrock alkylidyne complexes, by virtue of the fact that the ancillary ligands are neither strong π-donors nor π-acceptors. The molecular structure of **1** was determined by a single-crystal X-ray diffraction study (Table I).[15a,b] As has been observed for all other M(CR)L$_4$X compounds,[1,2] the coordination of the metal in **1** is pseudooctahedral, with the benzylidyne and bromide ligands arranged trans to each other in an essentially linear C–C–W–Br linkage. The benzylidyne ligand is oriented such that the plane containing it bisects the ethylene backbone of the dmpe ligands; the resulting idealized symmetry is C_{2v} (structure A). The signature structural parameters of **1**, i.e., the short W≡C (1.796 (11) Å) and long W–Br (2.744 (2) Å)[16] bond distances, lie within the expected ranges for W(CR)L$_4$Br compounds (1.76–1.84 Å and 2.65–2.76 Å, respectively).[17] The short W≡C distance is consistent with the presence of a tungsten–carbon triple bond,[1,2] while the long W–Br distance is a manifestation of the strong trans influence of the alkylidyne ligand.[2]



A

Solutions of **1** react with [C_7H_7][PF_6] to cleanly provide [W(CPh)(dmpe)$_2$Br][PF_6] (**1**[PF_6]),[13b] which is only the second paramagnetic alkylidyne complex to be isolated.[11,18,19] Comparison of the core bond distances and angles of **1**[PF_6] (Table

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[4] (a) Chapter 5 in ref 1b. (b) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342–348. (c) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249–262.

[5] (a) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121–198. (b) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255–272.

[6] (a) Stone, F. G. A. *Adv. Organomet. Chem.* **1990**, *31*, 53–89. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89–172. (c) Buhro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311–369.

[7] Mayr, A. *Comments Inorg. Chem.* **1990**, *10*, 227–266.

[8] Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249–352.

[9] (a) Bocarsly, A. B.; Cameron, R. E.; Rubin, H.-D.; McDermott, G. A.; Wolff, C. R.; Mayr, A. *Inorg. Chem.* **1985**, *24*, 3976–3978. (b) Bocarsly, A. B.; Cameron, R. E.; Mayr, A.; McDermott, G. A. In *Photochemistry and Photophysics of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berlin, 1987; pp 213–216.

[10] Carter, J. D.; Kingsbury, K. B.; Wilde, A.; Schoch, T. K.; Leep, C. J.; Pham, E. K., McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 2947–2954.

[11] (a) Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jakobi, R.; Gütlich, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 334–337. (b) Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990**, *9*, 1434–1443.

[12] A review of theoretical studies of these species is provided in ref 1b.

[13] (a) Prepared by a route analogous to that reported for **2**. (b) Spectroscopic and analytical data are available as supplementary material.

[14] Mayr, A.; Asaro, M. F.; Kjelsberg, M. A.; Lee, K. S.; Van Engen, D. *Organometallics* **1987**, *6*, 432–434.

[15] (a) X-ray data were collected with a Siemens R3m/V diffractometer. An empirical absorption correction (XEMP) was applied to all data. The structure was solved by direct methods, which located the tungsten atom; all other non-hydrogen atoms were located from subsequent Fourier syntheses and refined anisotropically. Hydrogen-atom positions were calculated (d = 0.96 Å). (b) Crystal data for **1**: $P2_1/c$; a = 15.243 (3) Å, b = 11.793 (2) Å, c = 14.681 (3) Å, β = 99.14 (2)°, V = 2605.5 (7) Å^3, Z = 4, D_{calcd} = 1.665 g cm^{-3}, μ(Mo Kα) = 62.15 cm^{-1}. Of 4919 data collected (4° ≤ 2θ ≤ 46°), 2401 data with $F_o \geq 6\sigma(F_o)$ were used in the solution and refinement. **1** refined to R_F = 4.12% and R_{wF} = 3.95%; GOF = 1.20. (c) Crystal data for **1**[PF_6]: *Pnma*; a = 15.920 (2) Å, b = 12.748 (2) Å, c = 14.941 (2) Å, V = 3032.2 (7) Å^3, Z = 4, D_{calcd} = 1.759 g cm^{-3}, μ(Mo Kα) = 54.35 cm^{-1}. Of 2731 data collected (4° ≤ 2θ ≤ 48°), 1546 data with $F_o \geq 5\sigma(F_o)$ were used in the solution and refinement. **1**[PF_6] refined to R_F = 4.86% and R_{wF} = 5.78%; GOF = 1.24.

[16] Of the 62 crystal structures of tungsten–bromide compounds reported in the Cambridge Structural Database, only one (ref 17c) contains a terminal W–Br bond distance greater than 2.7 Å.

[17] (a) Neugebauer, D.; Fischer, E. O.; Dao, N. Q.; Schubert, U. *J. Organomet. Chem.* **1978**, *153*, C41–C44. (b) Cotton, F. A.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 387–390. (c) Filippou, A. C.; Völkl, C.; Grünleitner, W.; Kiprof, P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 207–209. (d) Carriedo, G. A.; Riera, V.; Gonzalez, J. M. R.; Sanchez, M. G. *Acta Crystallogr.* **1990**, *C46*, 581–584. (e) Manna, J.; Geib, S. J.; Hopkins, M. D. Unpublished results for W(CH)(dmpe)$_2$Br.

[18] The formation of **1**[PF_6] upon oxidation of **1** stands in contrast to the oxidation of W(CH)(PMe$_3$)$_4$Cl by C_2Cl_6 (in the presence of AlCl$_3$), which yields formally isoelectronic (but dimeric and diamagnetic) [W$_2$(CPMe$_3$)$_2$(PMe$_3$)$_4$Cl$_4$][AlCl$_4$]$_2$. Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476–484.

[19] Transient 17-electron alkylidyne complexes have been proposed as reaction intermediates in ref 10 and in the following: Baker, P. K.; Barker, G. K.; Gill, D. S.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1321–1331.

I),[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 $W\equiv C$ and W—Br bonds are 0.024 and 0.042 Å shorter in **1**$[PF_6]$ than in **1**, while the W—P bonds are longer in the cation by 0.053 Å. Significantly, the $W\equiv C$ and W—Br bond distances of **1**$[PF_6]$ still lie within the ranges expected for $W(CR)L_4Br$ complexes,[17] suggesting that its formal $W\equiv C$ 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**$[PF_6]$. The lengthened W-P bond of **1**$[PF_6]$ mirrors the general trend for redox-paired transition-metal phosphine complexes; such elongations have been attributed to a decrease in $M\rightarrow P$ 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 benzylidyne 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**$[PF_6]$.

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 ($\epsilon \cong 200$ M^{-1} 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 × 10^3 cm^{-1}.[21] This indicates that the orbital character of the transition has a significant $\pi(W\equiv CPh)$ 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 $\nu(W\equiv C)$ frequency to be ca. 1360 cm^{-1},[23] we attribute the vibronic features of **2** to the excited-state $\nu(W\equiv C)$ mode, with the decrease in its frequency relative to that of the ground state suggesting that the $W\equiv C$ bond is weakened in the lowest-lying excited state. Given that the orbital from which the electronic transition originates is $W\equiv C$ nonbonding, we conclude that the LUMO is $W\equiv C$ antibonding. Simple symmetry considerations indicate this orbital to be a $\pi^*(W\equiv CPh)$ 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 benzylidyne 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**$[PF_6]$ (1 page). Ordering information is given on any current masthead page.

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(20) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206–1210 and references therein.

(21) Manna, J.; Gilbert, T. M.; Hopkins, M. D. Unpublished results.

(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 $\nu(W\equiv C)$ mode of benzylidyne 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**$[PF_6]$. **Note Added in Proof**: A preliminary Raman spectrum of **1**$[PF_6]$ displays a band at 1357 cm^{-1} as the strongest feature. This band is presumably attributable to $\nu(W\equiv CPh)$, by analogy to $W(CPh)(CO)_4Br$.

(24) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111–122.

(25) Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203–5208.

Enantioselective Deprotonation: The Structure and Reactivity of an Unsymmetrically Complexed Isopropyllithium/Sparteine/Et_2O 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 C_1 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 isopropyllithium/sparteine complex[5] 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 Et_2O 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*-Pr^6Li/sparteine in Et_2O-d_{10} was investigated using ^6Li, ^{13}C, and ^1H NMR.[7] The ^1H NMR spectrum contains

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(1) Williard, P. G.; Nichols, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 9671. Hall, P. L.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9575. Bühl, M.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R.; Fleischer, U.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1991**, *113*, 2459 and references therein.

(2) Dipole-stabilized carbanions. Beak, P.; Zajdel, W. J.; Reitz, D. B. *Chem. Rev.* **1984**, *84*, 471. Beak, P.; Lee, W. K. *Tetrahedron Lett.* **1989**, 1197.

(3) Hoppe, D.; Hintze, F.; Tebben, P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1422. For a crystal structure of a lithiated carbamate/sparteine complex, see: Marsch, M.; Harms, K.; Zschage, O.; Hoppe, D.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 321.

(4) Kerrick, S. T.; Beak, P. *J. Am. Chem. Soc.* **1991**, *113*, 9708.

(5) The use of isopropyllithium avoids formation of diastereomeric complexes which are observed with *sec*-BuLi. Fraenkel, G.; Henrichs, M.; Hewitt, M.; Su, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 255.

(6) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. For characterization of complexes of organomagnesiums with sparteine, see: Fraenkel, G.; Cottrell, C.; Ray, J.; Russell, J. *J. Chem. Soc., Chem. Commun.* **1971**, 273. Fraenkel, G.; Appleman, B.; Ray, J. G. *J. Am. Chem. Soc.* **1974**, *96*, 5113.

0002-7863/92/1514-5872$03.00/0