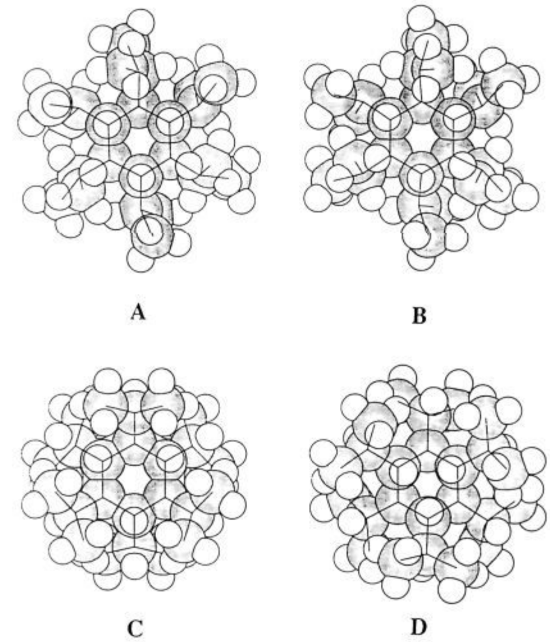

Figure 2. Space-filling models of the calculated equatorial conformations of **1**. Atom balls are drawn with 33% of the atomic radius. All conformations are viewed along the normal to the mean cyclohexane plane. The carbon skeleton is overlayed on the space-filling models for clarity.

groups (B), and syn-periplanar (C) and anti-periplanar (D) arrangements of the two $CHCHMe_2$ methine hydrogens. The minimized conformations had S_6, D_3, D_{3d}, and S_6 symmetries and were calculated to lie 13.9, 17.1, 51.2, and 58.1 kcal mol^{-1} above the axial conformation. The calculations indicate that the all-axial conformation of S_6 symmetry indeed corresponds to the minimum energy conformation. In general, there is excellent agreement between calculated and experimental structural parameters of **1** (Table I). The calculated energy difference between the gear meshed (A) and gear clashed (B) equatorial conformations of **1** (3.2 kcal mol^{-1}) is appreciably lower than for hexaisopropylbenzene (31.9 kcal mol^{-1}).[12]

What is the reason for the relative destabilization of the equatorial conformation? It seems likely that the unavoidable torsional and/or steric strain present at any equatorial disposition of the isopropyl group is responsible of the equatorial → axial stability reversal. Even in the low-energy equatorial conformation A, one of the methyls of each isopropyl group is nearly eclipsed ($\phi = 20.2°$) with the axial cyclohexane methine proton. Work is under way to see whether the axial $\rightleftharpoons$ equatorial conformational reversal could be present in other cyclohexane systems.

Acknowledgment. We thank Dr. James H. Geiger for helpful discussions and Dr Shmuel Cohen for the crystal structure determination. This research was supported by a grant from the United States–Israel Binational Science Foundation (BSF), to whom we are grateful. The Fritz Haber Research Center at the Hebrew University is supported by the Minerva Gesellschaft für die Forschung, mbH, Munich, Federal Republic of Germany.

Registry No. 1, 124358-20-9; **2**, 88919-68-0.

Supplementary Material Available: Crystallographic data for **1** and tables of final positional parameters, bond lengths, bond angles, and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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Generation and Trapping of the Diphenylhydrazido(2−) Complex $Cp_2Zr(N_2Ph_2)$. Insertion of Internal Alkynes into a Metal–Nitrogen Bond, Leading to 2,3-Diazametallacyclopentenes

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Despite the large number of early-metal complexes containing metal–nitrogen or metal–oxygen bonds, insertion of olefins or alkynes into these bonds is rare.[1,2] In fact, this process is not well documented for transition-metal amide complexes in general. Insertion of nonpolar carbon–carbon bonds into early-metal nitrogen bonds represents an especially challenging problem because of their high (81–95 kcal/mol)[3] bond energy.

We have been seeking to prepare strained systems containing nitrogen bonded to zirconium, in the hope that they will exhibit enhanced Zr–N reactivity toward simple organic compounds and lead to reactions that involve the formation of new carbon–nitrogen bonds (the few known complexes with strained Zr–O and Zr–N bonds also contain Zr–C bonds, and insertion occurs into the latter preferentially[4]). We now report our first observation of M–N bond insertion, in the generation of the (η^2-1,2-diphenylhydrazido(2−))zirconocene complex $Cp_2Zr(N_2Ph_2)$ (**2**). This species has not been isolated, but can be trapped by coordination with various dative ligands. Significantly, the complex undergoes insertion of alkynes into one of the Zr–N bonds, leading to the formation of diazametallacyclopentenes.

The chemistry we have observed is summarized in Scheme I. The (η^2-hydrazido)methylzirconium complex **1** was prepared in 83% yield by treatment of $Cp_2Zr(Me)(Cl)$[5] with the monopotassium salt of 1,2-diphenylhydrazine in toluene. Our first evidence for the generation of **2** was obtained by thermolysis of this material in THF at 65 °C for 2.5 days, which provides $Cp_2Zr(N_2Ph_2)(THF)$ (**3**) in 80% yield. Complex **3** can be prepared independently (60–80% yield) by addition of 1-lithio-1,2-diphenylhydrazine to $[Cp_2Zr(H)(Cl)]_n$ in THF, but it is obtained most efficiently (90–95% yield) by the addition of Cp_2ZrCl_2 in THF to a slurry of the 1,2-dithio-1,2-diphenylhydrazide[6a] in ether at room temperature.[6b]

The coordinatively unsaturated intermediate **2** is most conveniently generated by dissociation of THF from adduct **3**. Thus, treatment of **3** with pyridine or trimethylphosphine led to complexes **4** and **5** in 72% and 83% isolated yields, respectively. Crystals of the pyridine complex **4** suitable for an X-ray diffraction study were grown from a 50/50 mixture of toluene and hexane

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[1] (a) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood Limited: West Sussex, England, 1980. For a comparison of the relative insertion reactivities of group 4 metal amide and alkyl complexes, see: (b) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928. For reviews on late transition-metal amido complexes, see: (c) Bryndza, H.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (d) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1.

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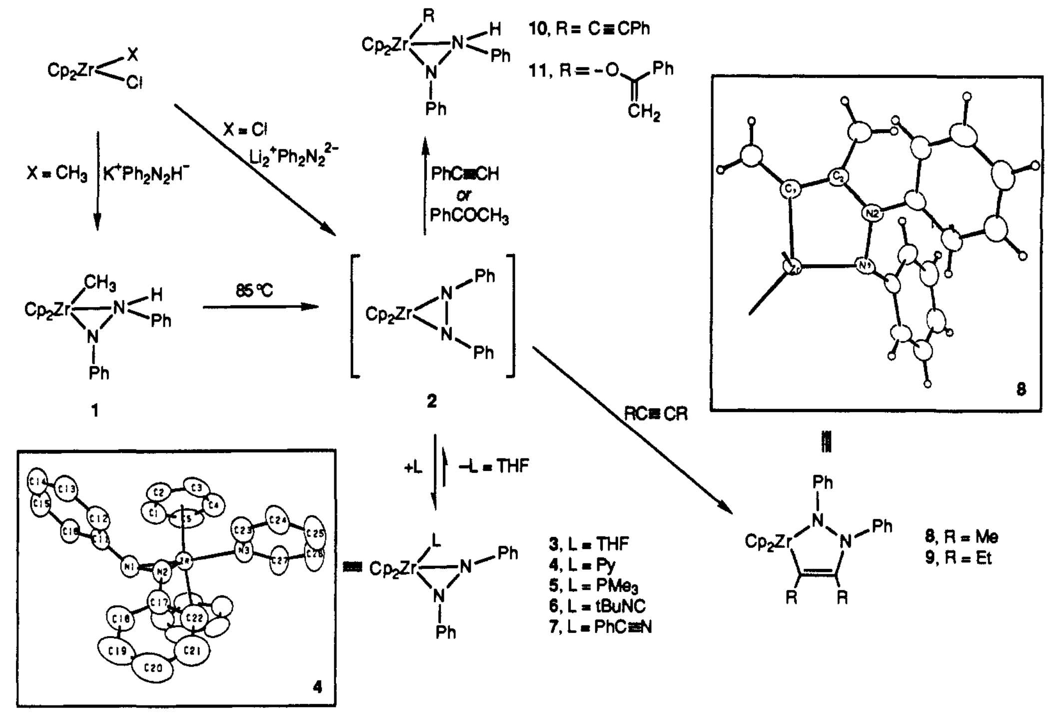
[5] (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *34*, 155. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

[6] (a) Wittig, G. *Angew. Chem.* **1940**, *53*, 241. (b) For a review of 1,2-hydrazido complexes, see: Bruce, M. I.; Goodall, B. L. In *Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: NY, 1975; Chapter 9.

Scheme I



at room temperature; an ORTEP drawing of **4** is shown in Scheme I.[7] The structure consists of discrete molecules with no abnormally close intermolecular contacts. The N–N bond length of 1.434 (4) Å falls in the range of other known N–N single bonds. Interestingly, the C_{ipso}–N–N–C_{ipso} torsional angle is 91.32 (0.46)° and the nitrogens have a clearly pyramidal geometry. The zirconium–nitrogen bond lengths are 2.161 (3) Å, 2.105 (4) Å, and 2.431 (4) Å for Zr–N1, Zr–N2, and Zr–N3. The structure of **3** can be compared to the unligated titanium analogue $Cp_2Ti(N_2Ph_2)$,[8,9] where the N–N bond distance is significantly shorter (1.334 Å).

Nitriles have been observed to insert into group IV metal–nitrogen bonds to give amidino complexes.[10] In the case of **2**, however, neither nitriles nor isonitriles undergo insertion into the M–N bonds. Thus, addition of 2.0 equiv of *tert*-butyl isocyanide or benzonitrile to **2** in toluene leads to rapid formation of the complexes $Cp_2Zr(N_2Ph_2)(L)$ (**6**; L = CN-*t*-Bu; **7**, L = NCPh) in 78% and 69% yields, respectively. The IR spectra of these complexes exhibit absorptions at 2200 and 2256 cm^{-1}, consistent with their assignment as coordination complexes rather than insertion products.[10,11]

In contrast to early-metal amides,[1] internal alkynes react with THF complex **3** to give clean Zr–N insertion reactions. Thus, heating **3** at 45–65 °C for 2 days in toluene in the presence of 4 equiv of 2-butyne or 3-hexyne leads to 2,3-diazametallacyclopentenes **8** (78% yield) and **9** (91% yield). Compounds **8** and **9** are fluxional on the NMR time scale, due possibly to ring inversion of the metallacycle.[12]

Crystals of **8** were grown from a toluene/hexane solution at room temperature, and data were collected at −108 °C; an ORTEP drawing of the molecule is shown in Scheme I.[13] As suggested by the NMR observations, the 2,3-diazametallacyclopentene does exist in an envelope conformation, with a clearly localized (1.333 (7) Å) C–C double bond and a N1–N2 distance of 1.431 (6) Å. The nitrogen atom N1 has a pyramidal geometry while N2 is almost planar.

Group 4 metal amide complexes react with weakly acidic protons to liberate amine.[14] We have observed analogous reactivity with the hydrazido(2−) ligand. Phenylacetylene and acetophenone react with **3** to give new products **10** and **11**, both of which exhibit NH stretches in the IR spectrum at 3205 and 3220 cm^{-1}, respectively. Complex **10** was isolated in 64% yield and is formulated as the η^2-hydrazido(1−) acetylide complex. However, no absorption attributable to a CC triple bond was observed.[14,15] An X-ray structural study of **10** was undertaken, and preliminary results confirm the proposed connectivity. Complex **11**, isolated in 67% yield, is the O-bound η^2-hydrazido(1−) enolate which shows a strong absorption at 1591 cm^{-1} in the IR.[16]

In summary, the zirconium η^2-hydrazido(2−) complexes $Cp_2Zr(N_2Ph_2)(L)$ readily undergo M–N insertion of internal

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(7) The X-ray diffraction study was carried out at the University of California, Berkeley, X-ray diffraction center (CHEXRAY). Crystal data for the pyridine adduct **4**: *Pbca*, $V = 4561.9$ (18) Å, Mo Kα ($\lambda = 0.71073$ Å) $\mu = 4.9$ cm^{-1}, $d_{calcd} = 1.41$ g/cm^{-3}, $a = 14.420$ (2) Å, $b = 16.126$ (2) Å, $c = 19.618$ (2) Å, $T = 25$ °C, $Z = 8$; the final residuals for 280 variables refined against the 1643 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.78\%$, $wR = 3.04\%$, and GOF = 1.236. The *R* value for all 2978 data was 19.1%. Details of the structure determination are provided as supplementary material.

(8) Fochi, G.; Floriani, C.; Bart, J. C. J.; Giunchi, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1515 and references therein.

(9) We were unable to prepare $Cp_2Zr(N_2Ph_2)$ by the same method used to make $Cp_2Ti(N_2Ph_2)$ in ref 8. Heating $Cp_2Zr(CO)_2$ to 70 °C in the presence of azobenzene resulted in formation of intractable products.

(10) Chandra, G.; George, T. A.; Lappert, M. F. *J. Chem. Soc. A* **1970**, 2550.

(11) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1. Free benzonitrile in Nujol absorbs at 2281 cm^{-1}.

(12) (a) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39. For examples of nonplanar heterometallacycles, see: Chamberlain, R. L.; Durfee, L. D.; fanwick, P. E.; Kobriger, L. M.; Latesky, S. I.; McMullin, A. K.; Steffey, B. D.; Rothwell, I. P. (b) Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068. (c) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668. Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712.

(13) Crystal data for the metallacycle **8**: *Pna*2$_1$, $V = 4259.1$ (25) Å, Mo Kα ($\lambda = 0.71073$ Å) $\mu = 5.2$ cm^{-1}, $d_{calcd} = 1.43$ g/cm^{-3}, $a = 17.6453$ (20) Å, $b = 8.2716$ (13) Å, $c = 29.181$ (10) Å, $T = -108$ °C, $Z = 8$; the final residuals for 522 variables refined against the 2497 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.18\%$, $wR = 2.55\%$, and GOF = 1.183. The *R* value for all 2837 data was 4.49%. Details of the structure determination are provided as supplementary material.

(14) (a) Chandra, G.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. A* **1968**, 1940. (b) Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc.* **1965**, 2157. (c) Collier, M. R.; Lappert, M. F.; McMeeking, J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 689.

(15) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911.

(16) (a) Gibson, C. P.; Gaddagh, G.; Bertz, S. H. *J. Chem. Soc., Chem. Commun.* **1988**, 603. (b) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855. (c) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664.

alkynes, unlike related unstrained amidometal complexes.[17] Further exploration of the reactions of these hydrazido complexes and their possible application to organic synthesis is under way.

Acknowledgment. We are grateful for financial support of this work from the National Institutes of Health (Grant No. GM25459) and for helpful discussions with Prof. Richard A. Andersen. We would also like to thank Michael J. Scott for his assistance in solving the crystal structure of compound **8**.

Supplementary Material Available: Spectroscopic and analytical data for complexes **1** and **3–11** and details of the structure determination for complexes **4** and **8**, including experimental description, ORTEP drawings showing full atomic numbering and packing in the crystal, and tables of crystal and data collection parameters, general temperature factor expressions (*B*'s), positional parameters and their estimated standard deviations, and intramolecular distances and angles (44 pages); tables of observed and calculated structure factors for **4** and **8** (35 pages). Ordering information is given on any current masthead page.

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[17] Three apparent exceptions: (a) See ref 9. (b) Casanuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738. (c) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108.

Intramolecular α-Amidoyl to Aryl 1,5-Hydrogen Atom Transfer Reactions. Heteroannulation and α-Nitrogen Functionalization by Radical Translocation

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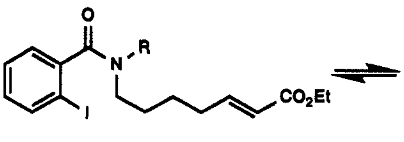
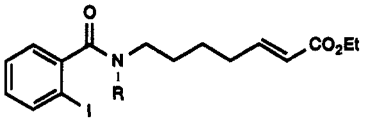
Received July 24, 1989
Revised Manuscript Received November 13, 1989

When the generation of oxygen-centered radicals at remote sites is followed by intramolecular hydrogen atom transfer, a powerful method to functionalize organic molecules results.[2] This strategy has recently been extended to the tin hydride method by generating carbon-centered radicals at remote sites (such as protecting groups) and translocating these radicals by 1,5-hydrogen atom transfer prior to cyclization.[3] In essence, this approach permits the indirect use of a C–H bond as a radical precursor in the tin hydride method. We now report that α-benzamidoyl radicals[4] generated from *o*-halobenzamides by a 1,5-hydrogen atom transfer undergo a variety of new radical addition and cyclization reactions. Our results indicate that the rotamer population of the starting *o*-halobenzamide often dictates the outcome of these reactions.

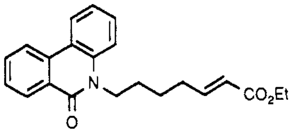
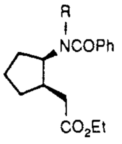
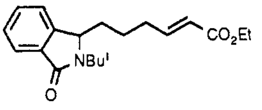
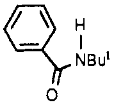
Table I. Tin Hydride Reduction of **6a–f**



6-anti



6-syn

R	anti/syn ratio	products from tin hydride reductn	
Ph (**6a**)	10/90		**7a**, 36%
C_6H_{11} (**6b**)	33/67		**7b**, 27%
C_4H_9 (**6c**)	50/50		**7c**, 43%
CH_2Ph (**6d**)	50/50		**7d**, 38%
$(CH_2)_4CH{=}CHCO_2Et$ (**6e**)[a]			**7e**, 82%
Bu^t (**6f**)	>98/2		**8**, 38%
			**9**, 41%

[a] Rotamers **6**-anti and **6**-syn are identical in this symmetrically substituted amide.

In 1968, a classic series of isotopic substitution experiments by Cohen et al.[5a] showed that 1,5-hydrogen transfer reactions of radicals **2** and **3**[5b] ($R^1 = R^2 = H/D$) were faster than rotation of amide C–N bonds (Scheme I). Modern knowledge of lifetimes of aryl radicals and rates of amide bond rotation supports the broader conclusion that the geometry of a typical amide C–N bond will be fixed during the entire lifetime of any aryl radical. Amide rotamers **1a** and **1b** interconvert in solution with typical lifetimes of 10^{-1}–10^{-2} s.[6] However, the maximum solution lifetime of radicals **2** and **3** probably cannot exceed 10^{-5} s,[7] precluding interconversion by C–N bond rotation. Assuming that rotamers **1a** and **1b** are equally reactive toward $Bu_3Sn^\bullet$, the relative amounts of **2** and **3** that are formed by halogen atom abstraction should be determined by the equilibrium concentrations of the starting

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[1] (a) University of Waterloo. (b) University of Pittsburgh. (c) NATO Postdoctoral Fellow, 1987–1989. (d) Dreyfus Teacher-Scholar, 1985–1989; recipient of a National Institutes of Health Career Development Award, 1987–1992.

[2] Intramolecular hydrogen atom transfer is a fundamental organic free radical process. Reviews: Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in the Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 161. Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol 1, p 333. Recent examples: Petter, R. C.; Powers, D. G. *Tetrahedron Lett.* **1989**, *30*, 659. Baldwin, J. E.; Adlington, R. M.; Robertson, J. *Tetrahedron* **1989**, *45*, 909.

[3] (a) Curran, D. P.; Kim, D.; Liu, H. T.; Shen, W. *J. Am. Chem. Soc.* **1988**, *110*, 5900. (b) Cuevas, J.-C.; Snieckus, V. Presented at the 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; Abstract ORGN 190.

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[5] (a) Cohen, T.; McMullen, C. H.; Smith, K. *J. Am. Chem. Soc.* **1968**, *90*, 6866. (b) For leading references to related 1,5-hydrogen atom transfer reactions, see: Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 593. Pines, S. H.; Purick, R. M.; Reamer, R. A.; Gal, G. *J. Org. Chem.* **1978**, *43*, 1337.

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[7] The maximum lifetime of these aryl radicals is limited by their rate of reaction with benzene. Phenyl radical adds to benzene with a second-order rate constant, $k = 4.5 \times 10^5$ M^{-1} s^{-1} (Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609). Therefore, 1,5-hydrogen transfer must be faster than the pseudo-first-order rate constant $k > 10^6$ s^{-1}.

0002-7863/90/1512-896$02.50/0