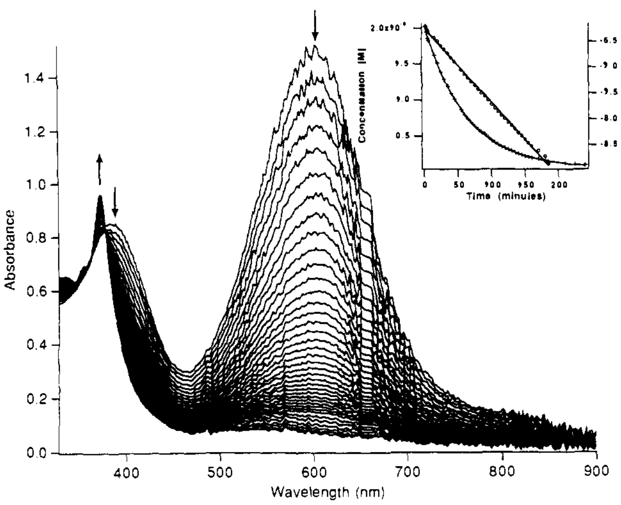

Figure 2. Electronic absorption spectra of a 2.0 mM solution of [Ni(TIM)SPh]PF_6 in acetone at 30 °C taken over 4 h showing isosbestic points at 380 and 362 nm. The inset shows kinetic data for the decrease in the absorption at 603 nm from which first-order rate constants and molar extinction coefficients were extracted. Solid lines represent a fit to a single exponential (left scale) and a least-squares fit to the linear ln A_{603} vs time plot (right scale).

thiolate ligand. The Ni–S distance of 2.452 (4) Å is the longest that has been characterized in a low-spin Ni thiolate complex. The geometry of an analogous Cu(II) complex, [Cu(Pre-H)S-p-C_6H_4Cl],[11] is quite similar, but with a larger metal displacement from the basal plane (0.430 Å), smaller trans-basal angles [153.2 (1)°, 156.4 (1)°], and a shorter M–S bond [Cu–S = 2.424 (1) Å].

Solutions of the thiolate complexes are characterized by deep blue colors due to an intense absorption near 600 nm[8] (Figure 2), which is presumably a thiolate → Ni charge-transfer transition. In solution, this color is bleached in a few hours to the orange color of **2**. Red-orange crystals of the product (**2**) were obtained from the reaction of [Ni(TIM)S-p-C_6H_4Cl]PF_6 (200 mg, 0.37 mmol) in CH_2Cl_2 followed by the vapor-phase diffusion of Et_2O at ambient temperature under N_2 [isolated yield = 87 mg, 0.22 mmol (60%)].[12,13] The Ni geometry in the cation (Figure 1B) is essentially planar. The four N atoms are coplanar to within ±0.019 (4) Å, and the Ni is required by symmetry to lie in that plane. The six-membered β-diiminate chelate ring is also essentially planar (±0.023 (5) Å, with Ni and C8 required by symmetry to lie in the plane). The Ni–N distances in this delocalized ring are shorter than those involving isolated imines.

The reactions of the Ni(TIM)S-p-$C_6H_4R^+$ complexes may be followed spectrophotometrically using UV/vis spectroscopy (Figure 2). The final spectra are not dependent in any significant way on the nature of the thiol or the solvent and are the same as those obtained from isolated samples of **2**. ^1H NMR spectra of reaction product mixtures reveal the peaks assigned to free thiol. The kinetics of the reactions have been studied by monitoring the decrease in absorbance near 600 nm at 30 °C. The reaction is first order in Ni(TIM)S-p-$C_6H_4R^+$ (Figure 2).[14] The rates of reaction are sensitive to the basicity of the thiolate[15] and increase with increasing basicity [k (R) × 10^{-2} min^{-1} = 0.15 (NO_2), 1.3 (Cl), 1.6 (H)]. The reaction rates are also sensitive to the nature of the solvent and show an inverse dependence with solvent polarity as expressed by dielectric constants[16] or Z values[17] [k (R = Ph) × 10^{-2} min^{-1} = 0.35 (MeOH), 1.6 (acetone), 2.2 (CH_2Cl_2)].

The solvent dependence of the reaction appears to rule out a dissociative mechanism, since the reaction rate is slower in solvents that would tend to dissociate the complex. A nondissociative mechanism is also supported by the lack of evidence for stable intermediates (e.g., no $Ni(TIM)^{2+}$ is formed) and by the fact that the proton lost is not an acidic proton in $Ni(TIM)^{2+}$. Reaction of $Ni(TIM)^{2+}$ in D_2O in the presence of NaOD leads to deuteration of only the iminyl methyl groups.[18] The first-order kinetics eliminates a bimolecular process and is consistent with a unimolecular, nondissociative mechanism.

A detailed understanding of the mechanism hinges on ascertaining whether the tautomerization drives the deprotonation or vice versa. Tautomerization of the imines to form a β-diimine would generate a ligand with an acidic proton, similar to acetylacetone.[19] This acidic proton could then be removed by the thiolate ligand that is in van der Waals contact[20] with this proton (H–S = 3.12 Å) to form the β-diiminate chelate ring. Alternatively, C–H bond activation involving the axial thiolate could lead to the formation of a carbanion that is stabilized by tautomerization of the imines. The resolution of which alternative best describes the reaction of **1** awaits the completion of activation parameter studies and kinetics studies utilizing isotopically labeled materials that are currently in progress.

Acknowledgment. This work was supported by NIH Grant GM-38829. We thank Prof. Norman J. Rose for helpful discussions and for allowing the quotation of unpublished results. Technical assistance from Drs. Csaba Bagyinka and Gerard J. Colpas is gratefully acknowledged.

Supplementary Material Available: Additional details of the X-ray studies, atomic coordinates, bond lengths and angles, and hydrogen atom parameters for both **1**·PF_6 and **2**·PF_6 (15 pages). Ordering information is given on any current masthead page.

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[11] Anderson, O. P.; Perkins, C. M.; Brito, K. K. *Inorg. Chem.* **1983**, *22*, 1267.

[12] Anal. Calcd for $C_{24}H_{23}N_4PF_6Ni$: C, 37.28; H, 5.14; N, 12.42. Found: Cm 36.99; H, 4.96; N, 12.23. UV–vis (1.1 mM/CH_2Cl_2): λ_{max} (nm) (ϵ in cm^{-1} M^{-1}) 372 (11 000), 354 (8000), 339 (sh), 296 (12 000), 267 (15 000). ^1H NMR (300 MHz, CD_2Cl_2): δ = 6.78 (d, 2 H, J, = 6.0 Hz), δ = 4.23 (q, 1 H, J = 6.0 Hz), δ = 3.19 (t, 4 H, poorly resolved), δ = 2.02 (s, 6 H), δ = 1.87 (m, 2 H), δ = 1.49 (br, 2 H), δ = 1.37 (d, 6 H, J = 7.1 Hz). IR (Nujol) (cm^{-1}): 3095 w (ν_{CH}), 1640 s ($\nu_{C=C}$ or $\nu_{C=N}$), 1598 s ($\nu_{C=C}$ or $\nu_{C=N}$), 1506 s ($\nu_{C=C}$ or $\nu_{C=N}$), 1354 s, 1338 m, 1320 s, 1272 s, 1224 m, 1200 w, 1100 s, 850 vs (br, PF_6^-), 558 s (PF_6^-).

[13] Crystal data for **2**·PF_6: monoclinic space group $C_{2/c}$, a = 10.682 (1) Å, b = 20.969 (4) Å, c = 8.653 (1) Å, β = 107.35 (1)°, and Z = 4 (Ni and C8 on 2-fold axis; C1 disordered). Refinement as for **1**·PF_6, but with H atoms on C1 and C2 omitted due to disorder and $2\theta_{max}$ = 50°, gave R = 0.052 and R_w = 0.058 for 1474 observed reflections.

[14] The decrease in absorbance at 606 nm can be fit with a single exponential. Plots of ln (absorbance) vs time are linear over at least 3 half-lives, and the reaction shows no concentration dependence in the range 0.4–2 mM.

[15] Crampton, M. R. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; John Wiley and Sons: New York, 1974; p 406.

[16] *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC Press, Inc.: Boca Raton, FL, 1986; p E50.

[17] Drago, R. S. In *Physical Methods in Chemistry*; W. B. Saunders Co.: Philadelphia, 1977.

[18] Baldwin, D. A.; Rose, N. J., unpublished results.

[19] Elfring, W. H., Jr.; Rose, N. J. *Inorg. Chem.* **1975**, *14*, 2759 and references therein.

[20] Pauling, L. In *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

Generation, Dative Ligand Trapping, and N–N Bond Cleavage Reactions of the First Monomeric η^1-Hydrazido Zirconocene Complex, $Cp_2Zr{=}NNPh_2$. A Zirconium-Mediated Synthesis of Indoles

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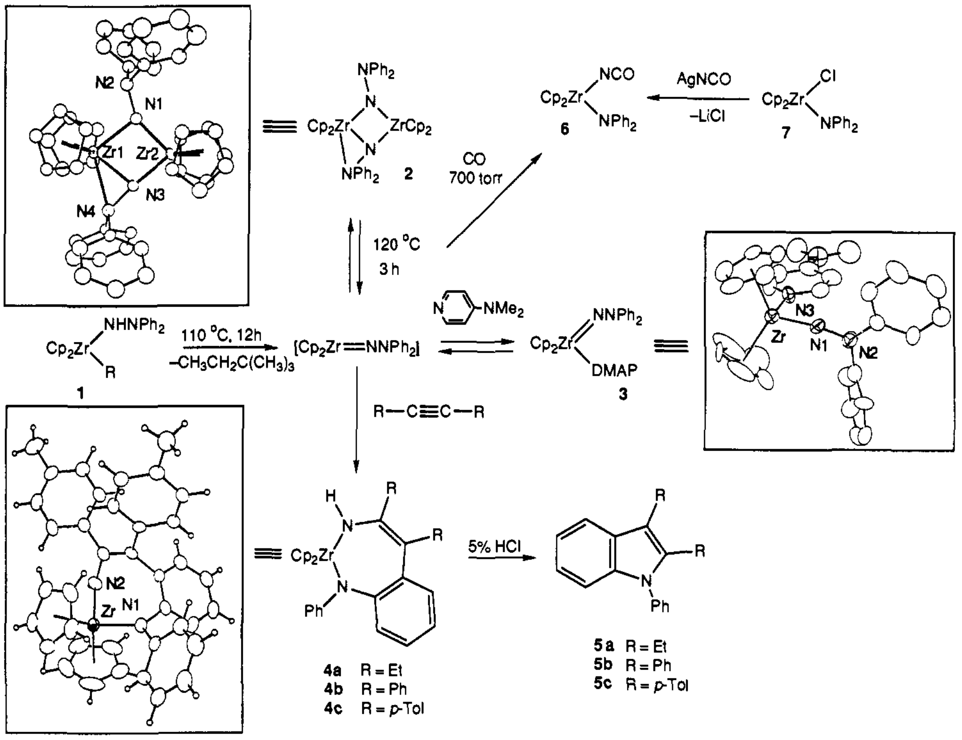
We report the generation and trapping of $Cp_2Zr{=}NNPh_2$, the first η^1-hydrazidozirconocene complex. This material exhibits reactivity markedly different from that of analogous monomeric

Scheme I



alkyl and aryl imido,[1] oxo,[2] and sulfido[2b] complexes.[3] The trapping of $Cp_2Zr{=}NNPh_2$ with alkynes or CO takes place with an unprecedented rearrangement that results in the cleavage of the N—N bond. We have also found that the alkyne addition product can be hydrolyzed to give a high-yield synthesis of certain indoles.

The chemistry we have observed is outlined in Scheme I. The alkyl hydrazido complex $Cp_2Zr(NHNPh_2)(CH_2CH_2CMe_3)$ (**1**) was prepared by reaction of the monolithium salt of 1,1-diphenylhydrazine with $Cp_2Zr(CH_2CH_2CMe_3)(Cl)$[4] in 72% yield after crystallization from ether at -30 °C. Thermolysis of **1** at 110 °C for 12 h causes loss of 2,2-dimethylbutane and generation of the transient intermediate $Cp_2Zr{=}NNPh_2$. In the absence of any trap, this species forms the bridging hydrazido dimer **2** (FAB-MS 18-crown-6/tetraglyme matrix, *m/e* 804, M^+) in 36% isolated yield (50% by ^1H NMR spectrometry[5]). Intrigued with the possibility of a dative interaction between the formally $16e^-$ metal centers and the β-nitrogens of the diphenylhydrazido ligands,[6] we grew orange crystals from a benzene solution of **2** by slow cooling to room temperature, and the structure was solved by Patterson methods. An ORTEP drawing is shown in Scheme I.[7] The solid-state structure of **2** is indeed dimeric with the β-nitrogens (N2 and N4) of *both* hydrazido ligands canted toward Zr1. The Zr1–N4 distance of 2.446 (6) Å suggests a dative interaction while the Zr1–N2 bond distance of 3.051 (7) Å is out of bonding range. The effect of coordination of N4 to Zr1 is reflected in the lengthening of the Zr1–N1 and Zr1–N3 bond distances (2.212 (7) and 2.130 (7) Å, respectively) with respect to the Zr2–N1 and Zr2–N3 bond distances (2.042 (6) and 1.996 (7) Å, respectively). Variable-temperature ^1H and $^{13}C\{^1H\}$ NMR spectrometry of the dimer **2** in CD_2Cl_2 gave results consistent with a symmetrical or averaged bridging structure down to -80 °C (with no sign or broadening of any of the resonances).

Heating **1** in the presence of dative ligands such as 4-*tert*-butylpyridine and monitoring the reaction by ^1H NMR spectrometry gave a mixture of the dimer **2** (20%) and a new compound, which is believed to be the adduct $Cp_2Zr(NNPh_2)$(*tert*-butylpyridine) (63%). However, when the better σ-donor 4-(*N*,*N*-dimethylamino)pyridine (DMAP) was used, the only product observed by ^1H NMR spectrometry was the monomeric hydrazido(2^-) complex $Cp_2Zr(NNPh_2)(DMAP)$ (**3**), in 61–72% isolated yield (86% ^1H NMR yield). Complex **3** was also formed in 98% yield (^1H NMR) upon thermolysis of the dimer **2** for 3 h at 120 °C in the presence of 6.5 equiv of DMAP. Crystallization of **3** from benzene gave transparent yellow crystals that are extremely sensitive to solvent loss. A single crystal of **3** was mounted in viscous oil for an X-ray structure determination and data collected at -82 °C. The structue was solved by standard Patterson techniques; an ORTEP drawing is shown in Scheme I.[8] The asymmetric unit contains two in-

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[4] Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 5115.

[5] ^1H NMR yields were determined by integration against 1,4-dimethoxybenzene used as an internal standard.

[6] For a similar structure, see: Arvanitis, G. M.; Schwartz, J.; Van Engen, D. *Organometallics* **1986**, *5*, 2157.

[7] The X-ray diffraction studies were carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY). Crystal data for **2**: $P2_1$, $V = 1753.8$ (9) $Å^3$, Mo Kα ($\lambda = 0.71073$ Å), $\mu = 6.2\ cm^{-1}$, d_{calcd} 1.53 g cm^{-1}, $a = 10.6335$ (12) Å, $b = 15.3719$ (19) Å, $c = 11.7507$ (23) Å, $\beta = 114.064$ (12)°, $T = -85$ °C, $Z = 2$, the final residuals for 210 variables refined against the 2107 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.047$, $wR = 0.056$, and GOF = 2.31. The *R* value for all 2403 data was 5.8%. Details of the structure determination are provided as supplementary material.

[8] Crystal data for **3**·$[C_6H_6]_3$: $P2_1$, $V = 4050.9$ (28) Å, Mo Kα ($\lambda = 0.71073$ Å), $\mu = 3.01\ cm^{-1}$, d_{calcd} 1.25 g cm^{-1}, $a = 10.251$ (2) Å, $b = 34.145$ (7) Å, $c = 11.7503$ (16) Å, $\beta = 99.96$ (2)°, $T = -82$ °C, $Z = 4$, the final residuals for 734 variables refined against the 4325 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0536$, $wR = 0.0600$, and GOF = 2.125. The *R* value for all 5738 data was 7.67%. Details of the structure determination are provided as supplementary material.

dependent molecules of **3** and three benzene molecules of solvation per molecule **3**. The structure is similar to that of the monomeric imido complex $Cp_2Zr(=NCMe_3)(THF)$.[1b] The Zr═N bond distance is 1.873 (7) Å, the N1–N2 distance is 1.364 (10) Å (indicative of an N—N single bond),[9] and the Zr–N–N bond angle is 168.7 (6)°. This compares to a Zr–N distance of 1.826 (4) Å and Zr–N–C bond angle of 174.4 (3)° in $Cp_2Zr(NCMe_3)(THF)$.[1b]

Heating **1** at 110 °C for 15 h with diethyl-, diphenyl-, or di-*p*-tolylacetylene resulted in formation of new compounds **4a–c** in 72, 89, and 83% crystallized yields, respectively. In each of these complexes the N–N bond has been cleaved and both nitrogens are now bound to zirconium in a seven-membered metallacycle. These structures are supported by spectroscopic data and an X-ray diffraction study of **4c**. Crystals of the di-*p*-tolyl acetylene insertion product were grown by vapor diffusion of hexane into a THF solution of **4c** at room temperature, and the structure was solved by Patterson methods; an ORTEP diagram is shown in Scheme I.[10] The Zr–N1 and N2 bond lengths are 2.131 (3) and 2.120 (4) Å, respectively. Metallacycle **4a** was formed in 92% yield (^1H NMR spectrometry) when the monomeric hydrazido complex **3** and 3-hexyne were warmed to 42 °C for 48 h. No intermediates were observed by ^1H NMR spectrometry under these conditions. The reactivity of **3** contrasts sharply with that observed for the precursors of zirconium imido, oxo, and sulfido complexes $Cp_2Zr{=}NR$,[1b] $Cp^*_2Zr{=}O$,[2] and $Cp^*_2Zr{=}S$,[2b] which upon generation undergo 2 + 2 cycloadditions with alkynes to provide heterometallacyclobutenes in high yield.[11]

Finally, metallacycles **4a–c** contain enamido functionality, which can be used to furnish *N*-phenylindoles **5a–c**[12,13] as shown in Scheme I. These are obtained in 91, 96, and 81% isolated yields, respectively, by acid hydrolysis followed by simple extraction into toluene and filtration through a plug of silica (compound **5c** was further purified by sublimation). An intermediate in the indole formation is presumably a δ-keto amine, which eliminates H_2O after cyclization.

Reaction of the monomeric hydrazido complex **3** with CO (700 Torr) at room temperature also results in cleavage of the N–N bond to give $Cp_2Zr(NCO)(NPh_2)$ (**6**). The assignment of **6** as the N-bound cyanate amide complex was based on its IR stretch[14] at 2212 cm^{-1} and the $^{13}C\{^1H\}$ NMR shift of the cyanate carbon at δ 197 ppm. Further support for the proposed structure was gained through the independent synthesis of **6** from the amide chloride $Cp_2Zr(NPh_2)(Cl)$ (**7**) and silver cyanate.

In summary, complexes **4** are novel because of both the mode of their formation and their acid-induced conversion to indoles. The mechanism of the complicated **1**-to-**4** rearrangement is obscure at present; its elucidation will require extensive further investigation.

Acknowledgment. We are grateful for financial support of this work from the National Institutes of Health (Grant No. GM25457). M.J.C. gratefully acknowledges a postdoctoral (NRSA) fellowship from the NIH. We also thank Prof. Richard A. Andersen for helpful discussions and Dr. F. J. Hollander and Michael J. Scott for solving structures **2** and **4b**, respectively.

Supplementary Material Available: Spectroscopic and analytical data for complexes **1–3**, **4a–c**, **5a–c**, **6**, and **7** and details of the structure determination for complexes **2**, **3**, and **4c**, including experimental description, ORTEP drawings showing full atomic numbering, crystal and data collection parameters, positional parameters and their estimated standard deviations, and intramolecular distances and angles (31 pages). This information is provided in the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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[9] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, NY, 1972; p 107.

[10] Crystal data for **4c**: $P2_1/c$, $V = 2854$ (1) Å, Mo Kα (λ = 0.71073 Å), $\mu = 4.06$ cm^{-1}, d_{calcd} 1.396 g cm^{-1}, $a = 19.7337$ (23) Å, $b = 14.0328$ (16) Å, $c = 10.5916$ (9) Å, $\beta = 103.318$ (8)°, $T = -82$ °C, $Z = 4$, the final residuals for 370 variables refined against the 2588 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0356$, $wR = 0.0400$, and GOF = 1.469. The R value for all 3716 data was 7.92%. Details of the structure determination are provided as supplementary material.

[11] We cannot rule out the intermediacy of azametallacyclobutenes in formation of the metallacycles **4a–c**.

[12] For a general reference to indoles, see: Sundberg, R. J. *The Chemistry of Indoles*; Academic Press: New York, 1970.

[13] Indole **5b** has been previously prepared: Nair, V.; Kim, K. H. *J. Org. Chem.* **1975**, *40*, 3784.

[14] $Cp_2Zr(NCO)_2$ was shown to be N-bound by X-ray diffraction studies, and the IR (KBr) spectrum displays absorptions at 2217 and 2197 cm^{-1}; see: Andersen, S. J.; Brown, D. S.; Finney, K. J. *J. Chem. Soc., Dalton Trans.* **1979**, 152.

Additions and Corrections

The Complementary Redox Properties of Viologens and Pyromellitimides: A New Class of Organic Conductors [*J. Am. Chem. Soc.* **1991**, *113*, 376–377]. STEPHEN L. BUCHWALTER,* REVATHI IYENGAR, ALFRED VIEHBECK, and TERRENCE R. O'TOOLE

In connection with measurements of the sub-ambient electrical properties[1] of the viologen/pyromellitimide charge transfer salt, we have determined that the room temperature conductivity of the salt is significantly less than we reported. Although conductivity standards tested accurately on the four-point probe we employed, a reproducible error arose due to the inability of the instrument to properly measure substrates that are slightly thicker than the thin wafers for which it was designed. This problem caused our previously reported values to be more than four orders of magnitude higher than the correct value, which has now been verified at 10^{-1}–10^{-2} Ω^{-1} cm^{-1}.

[1] Ritter, M.; Buchwalter, S. L. To be published.