

dependent molecules of **3** and three benzene molecules of solvation per molecule **3**. The structure is similar to that of the monomeric imido complex $\text{Cp}_2\text{Zr}(=\text{NCMe}_3)(\text{THF})$.^{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 $\text{Cp}_2\text{Zr}(\text{NCMe}_3)(\text{THF})$.^{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 $\text{Cp}_2\text{Zr}=\text{NR}$,^{1b} $\text{Cp}^*\text{Zr}=\text{O}$,² and $\text{Cp}^*\text{Zr}=\text{S}$,^{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 H₂O 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 $\text{Cp}_2\text{Zr}(\text{NCO})(\text{NPh}_2)$ (**6**). The assignment of **6** as the N-bound cyanate amide complex was based on its IR stretch¹⁴ at 2212 cm⁻¹ and the ¹³C{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 $\text{Cp}_2\text{Zr}(\text{NPh}_2)(\text{Cl})$ (**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.

(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) Å³, Mo K α ($\lambda = 0.71073$ Å), $\mu = 4.06$ cm⁻¹, d_{calc} 1.396 g cm⁻³, $a = 19.7337$ (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) $\text{Cp}_2\text{Zr}(\text{NCO})_2$ 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 properties¹ 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.