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Photoinduced ring expansion of cyclobutyliron .sigma.-complexes: an example of rearrangement of an aryl group from saturated carbon to a transition metal to give a carbene complex

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clear carbonyl clusters in reactions such as the hydrogenation and hydroformylation of olefins and the transalkylation of amines.[13-15] We examined the activity of these bis(imido) clusters and found that under 3 atm of H_2 at 98 °C catalytic olefin hydrogenation occurred, but the solutions rapidly turned from red to orange. From these solutions a new hydrido cluster was isolated that contained only terminal carbonyl absorptions in the infrared spectrum and an unusually low-field (−8.7 ppm) chemical shift for a hydride.[16] A low-temperature (−95 °C), single-crystal X-ray crystallographic analysis[17] of $H_2Ru_3(NC_6H_4Cl)_2(CO)_8$ revealed a structure (Figure 1) that is very similar to the starting nonacarbonyl.[18] The systematic asymmetry of the bridging hydrogen atoms (average Ru1–H12(13) = 1.69 (5) Å; average Ru2(3)–H12(13) = 1.90 (5) Å) may be the cause of the unusual chemical shift. The dihydrides could be prepared in the absence of olefin, and the reverse reaction occurred quantitatively under CO (3 atm) at 110 °C. It appears as if the equilibrium constant for reaction 3 is not far from unity and, therefore, similar to that found from studies of related ruthenium[19] and iron[20] systems containing bridging alkylidyne ligands.

$$Ru_3(NC_6H_4X)_2(CO)_9 + H_2 \rightleftharpoons CO + H_2Ru_3(NC_6H_4X)_2(CO)_8 \quad (3)$$

When the catalysis was conducted by using the dihydrides, the reactions remained visually homogeneous, and the rate was typically 0.5 turnover/min at 98 °C and 3 atm of H_2.[21] Two crossover experiments, monitored by HPLC, indicated that no scrambling of the arylimido ligands occurred during the reaction. Catalysis by an equimolar mixture of $H_2Ru_3(NPh)_2(CO)_8$ and $H_2Ru_3(NC_6H_4OMe)_2(CO)_8$ failed to yield any of the crossover product $H_2Ru_3(NPh)(NC_6H_4OMe)(CO)_8$. Further, a sample of this unsymmetric cluster catalyzed the hydrogenation without forming either of the two symmetric clusters. The catalytic rates of these three clusters were the same within our current experimental error. It must be stressed that these experiments alone do not prove that the cluster remains intact throughout the reaction. Further studies that are necessary to establish the details of the mechanism are underway.

Acknowledgment. This work was supported by a grant (CHE-8410999) from the National Science Foundation.

Supplementary Material Available: Tables of crystallographic data, bond distances, bond angles, general temperature factor expressions, and positional and thermal parameters (9 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(14) Mani, D.; Vahrenkamp, H. *J. Mol. Catal.* **1985**, *29*, 305–317.

(15) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1986**, *107*, 6107–6109.

(16) Anal. Calcd for $H_2Ru_3(NC_6H_4Cl)_2(CO)_8$: C, 30.78; H, 1.29; N, 3.59. Found: C, 30.48; H, 1.28; N, 3.48. IR (cm^{-1}, hexane): 2108 w, 2092 s, 2033 vs, 2013 w, 1977 s. ^1H NMR (CD_2Cl_2, ppm): 7.04, 7.01, 6.66, 6.63 (phenyl region), −8.76 (hydride region). Mass spectrum (m/e, ^{102}Ru, ^{37}Cl): 786 (parent ion).

(17) X-ray diffraction data for $C_{20}H_{10}Cl_2N_2O_8Ru_3$: M_r 782.3; d(calcd) = 2.092 g/cm^3; crystal system = monoclinic; space group = $P2_1/n$; T = −94 (2) °C; a = 10.969 (5) Å, b = 12.991 (7) Å, c = 17.642 (5) Å; β = 99.78 (2)°; V = 2478 (3) Å^3; Z = 4; μ = 20.37 cm^{-1} (empirical correction applied); radiation = Mo Kα; scan range = 0–50°; reflections collected = 5815 unique, 4307 with $F_o > 1.0\ \sigma(F_o)$; R = 0.0257; R_w = 0.0296.

(18) Clegg, W.; Sheldrick, G. M.; Stalke, D.; Bhaduri, S.; Gopalkrishnan, K. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*(6), 927.

(19) Bravaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977–4981.

(20) Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491–493.

(21) A typical reaction involves 0.007 mmol of cluster and 0.35 mmol of 3,3-dimethylbutene in 10.0 mL of heptane. Hexane was used as the internal GC standard. Since some of the volatile olefin and alkane escaped during the monitoring process, the rate was based on the actual amount of alkane detected by gas chromatography. All of the olefin was consumed during the reaction. While detailed kinetic studies are underway, preliminary studies indicated the reaction is sensitive to the pressure of hydrogen and was inhibited by the addition of CO. HPLC monitoring of the reaction indicated that the dihydrido cluster was present throughout the catalysis. At the end of the reaction only a small amount (3%) of the dihydrido cluster was lost by the cleavage of one of the arylimido ligands to form aniline (or the substituted derivative) and the known cluster $H_2Ru_3(NAr)(CO)_9$.[10] Pure samples of this species also catalyzed the reaction, but the rate was no faster than that for the bis(imido) clusters.

Photoinduced Ring Expansion of Cyclobutyliron σ-Complexes: An Example of Rearrangement of an Aryl Group from Saturated Carbon to a Transition Metal To Give a Carbene Complex

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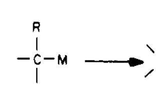
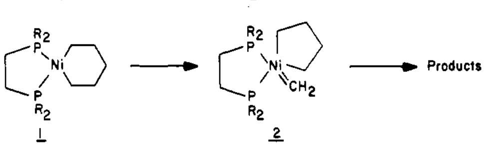
Summary: Photolysis of dicarbonyl(η^5-cyclopentadienyl)(1-methoxybenzocyclobutenyl)iron (**10**) gives a mixture of two rearranged carbene complexes (**11** and **12**) in a ratio of 73/27. These products are suggested to arise respectively from rearrangement of phenyl and benzyl from C-1 to coordinatively unsaturated iron. From the product ratio, it is concluded that aryl rearranges a bit faster than benzyl. The rearrangement is irreversible up to 77 °C. Photolysis of dicarbonyl(η^5-cyclopentadienyl)(1-p-thiocresylbenzocyclobutenyl)iron (**13**) also leads to a new product that is tentatively assigned structure **14**. If correct, this is the first example of a thiocresyl-induced rearrangement of this type. An X-ray crystal structure of **11** is reported.

Rearrangement of alkyl groups from saturated carbon to electron-deficient transition metals (eq 1) has recently

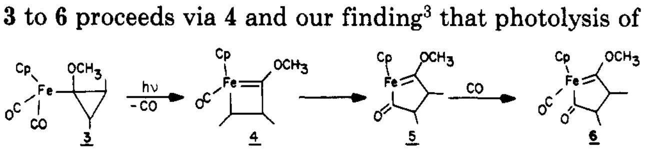


$$-\overset{R}{\overset{|}{\underset{|}{C}}}-M \longrightarrow \overset{R}{\overset{|}{>C=M}} \qquad (1)$$

been extended from Grubbs' original report[1] that deuterium-labeling studies on the decomposition of 1 were most consistent with intermediacy of the carbene complex 2 to our suggestion[2] that the photoinduced conversion of



3 to 6 proceeds via 4 and our finding[3] that photolysis of



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(1) Miyashita, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

(2) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944.

(3) Stenstrøm, Y.; Jones, W. M. *Organometallics* **1986**, *5*, 178.

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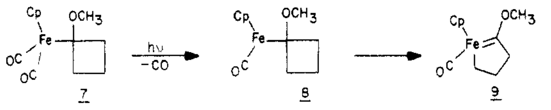
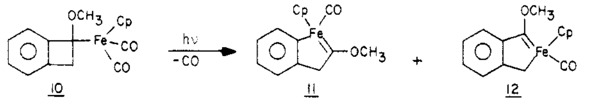
7 gives 9. We considered the last observation particularly

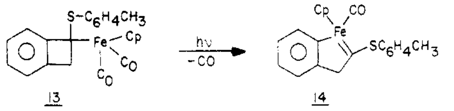


significant not only because it was the first case where the primary rearrangement product was isolated and characterized but also because it clearly demonstrates that the special bonding that is present in the cyclopropane in 3 is not required for the rearrangement to take place.

At this time we report our finding that photolysis of **10** gives a mixture of **11** and **12** in a ratio of about 73/27.



From this observation we conclude that both aryl and benzyl can migrate in this kind of rearrangement and that aryl appears to migrate a bit faster than benzyl. We also report an X-ray crystal structure for **11** and our tentative finding that photolysis of **13** gives **14**, the first example of a thiocresyl-induced rearrangement of this type.



Syntheses of the known sigma complex **10**[4] and the new complex **13**[5] are outlined in Scheme I. Samples were photolyzed in C_6D_6 by using a 450-W Hanovia medium-pressure mercury lamp. From NMR studies, photolysis of **10** gave a mixture of **11** and **12** in a ratio of 73/27 in an overall yield of 90%. Careful flash chromatography of the mixture over silica gel (230–400 mesh; ethyl acetate/hexane (30/70, v/v)) gave **11**[6] as blood red prisms (from ethyl acetate/hexane (30/70, v/v) at −20 °C), followed by **12**[7] as dark green prisms (from hexane at −20 °C).[8]

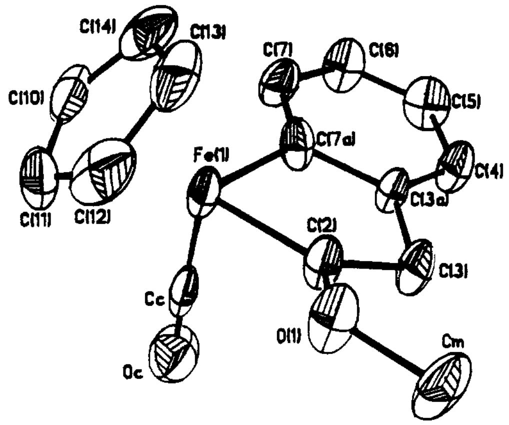
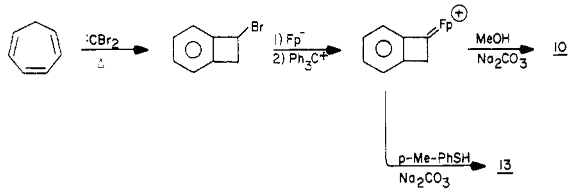


Figure 1. ORTEP drawing of 11.

Scheme I



Gross structural assignments to the two isomers rest primarily on their ^1H and ^{13}C NMR spectra. Especially significant are their very low-field ^{13}C resonances (347.27 and 311.99 ppm for **11** and **12**, respectively) that are typical of carbene carbons. The very similar mass spectra are also indicative of **11** and **12** as structural isomers. Isomeric assignments initially rested primarily on the high-field ^{13}C resonance in **12** (CH_2 bonded to Fe at 15.69 ppm) and slows spontaneous deuterium exchange with acetone-d_6 by **11** (attempts to induce exchange with base led to decomposition) which is consistent with highly acidic hydrogens α to a carbene carbon. This assignment was confirmed by an X-ray structure determination on the red isomer **11**. X-ray quality crystals were grown from a CH_2Cl_2/hexane (9/1, v/v) solution by slow evaporation of the solvent at ca. −20 °C. A small crystal (0.23 × 0.12 × 0.12 mm) mounted on a glass fiber was used for the X-ray measurements. The crystal was monoclinic with $a = 7.408$ (1) Å, $b = 10.223$ (3) Å, $c = 16.855$ (4) Å, and $\beta = 98.98$ (2)°. The space group is $P2_{1c}$, and, with four molecules per cell, the calculated density is 1.48 g/cm³. A total of 1861 reflections was measured by using graphite-monochromatized Mo Kα radiation. The structure was solved and refined by using the Nicolet SHELXTL package. The final R and R_w were 0.60 and 0.054, respectively, for the 1502 reflections with $F > 3\sigma(F)$ used in the analysis. The weights were $1/\sigma(F)^2$.

An ORTEP representation of the molecule is shown in Figure 1. The Fe–C(2) distance of 1.827 (6) Å is one of the shortest Fe–C(non CO group) distances reported to date. A possibly shorter distance of 1.82 (2) Å was found in a similar "Fischer-type" carbene complex;[9] however, the large estimated standard deviation should be noted. In the only other CpFe(CO) complex, σ-bonded to a phenyl group and carbene moiety, the Fe–C distance was 1.916 (2) Å.[10] The π-donation of the oxygen to the carbene can be seen by the short C(2)–O(1) distance of 1.336 (7) Å which is intermediate between a single and double bond.[11]

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(4) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430.

(5) Dicarbonyl(η^5-cyclopentadienyl)(1-*p*-thiocresylbenzocyclobutenyl)iron (**13**): IR (C_6D_6) 2005, 1965 cm⁻¹; ^1H NMR (60 MHz, C_6D_6) δ 1.86 (s, 3 H, CH_3), 3.23 (d, $J = 14$ Hz, 1 H), 3.50 (d, $J = 14$ Hz, 1 H), 4.76 (s, 5 H, Cp), 6.5–7.3 (m, 8 H); ^{13}C NMR (25 MHz, C_6D_6) δ 21.08 (CH_3), 46.42 (C), 51.39 (CH_2), 86.58 (Cp), 120.01, 123.22, 127.51, 133.85, 134.82, 137.45, 137.94, 161.92, (aromatic carbons), 215.62 (CO), 216.69 (CO); mass spectrum, *m/e* 374 ($M^+ - CO$), 346 ($M^+ - 2CO$), 280 ($M^+ - C_7H_6S$), 224 ($M^+ -$ FpH), 186 ($FeCp_2^+$), 121 ($FeCp^+$). Anal. Calcd for $C_{22}H_{18}FeO_2S$: C, 65.68; H, 4.51. Found: C, 65.77; H, 4.57.

(6) 1-Carbonyl-1-(η^5-cyclopentadienyl)-2-methoxy-1-ferraindene (**11**): mp 135–136 °C (ethyl acetate/hexane (30/70, v/v), −20 °C); IR ($CDCl_3$) 1950 cm⁻¹; ^1H NMR (100 MHz, CD_2Cl_2) δ 3.76 (d, $J = 22$ Hz, 1 H), 3.86 (d, $J = 22$ Hz, 1 H), 4.53 (s, 3 H, OCH_3), 4.80 (s, 5 H, Cp), 6.8–7.1 (m, 3 H), 7.4–7.6 (m, 1 H); ^{13}C NMR (25 MHz, CD_2Cl_2) δ 66.18 (CH_3O), 66.37 (CH_2), 85.67 (Cp), 121.34 (CH), 122.32 (CH), 125.34 (CH), 142.69 (CH), 148.73 (C), 163.94 (C), 219.88 (CO), 347.27 (carbene C); mass spectrum, *m/e* 282 (M^+), 254 ($M^+ - CO$), 239 ($M^+ - C_2H_3O$), 186 ($FeCp_2^+$), 167, 153, 133, 89. Anal. Calcd for $C_{15}H_{14}FeO_2$: C, 63.86; H, 5.00. Found: C, 63.91; H, 5.01.

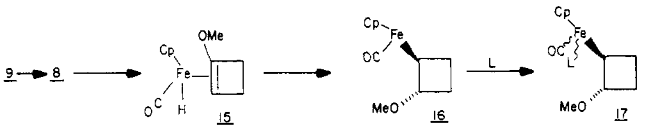
(7) 2-Carbonyl-2-(η^5-cyclopentadienyl)-1-methoxy-2-ferraindene (**12**): mp 115–116 °C (hexane, −20 °C); IR ($CDCl_3$) 1940 cm⁻¹; ^1H NMR (100 MHz, CD_2Cl_2): δ 2.66 (d, $J = 14$ Hz, 1 H), 2.78 (d, $J = 14$ Hz, 1 H), 4.59 (s, 3 H, OCH_3), 4.80 (s, 5 H, Cp), 6.8–7.9 (m, 4 H); ^{13}C NMR (25 MHz, CD_2Cl_2) δ 15.69 (CH_2), 66.37 (CH_3O), 85.28 (Cp), 116.67 (CH), 123.68 (CH), 126.70 (CH), 130.51 (CH), 153.22 (C), 168.03 (C), 222.51 (CO), 311.99 (carbene C); mass spectrum, *m/e* 282 (M^+), 254 ($M^+ - CO$), 239 ($M^+ - C_2H_3O$), 211 ($M^+ - C_3H_3O_2$), 186 ($FeCp_2^+$), 153, 133; high-resolution MS calcd for $C_{15}H_{14}FeO_2$ 282.0343, found 282.0341.

(8) It should be noted that **12** was always followed by a fluorescent, organic compound which was very hard to separate and which also made crystallization of **12** difficult. However, repeated flash chromatography over silica gel (230–400 mesh; ethyl acetate/hexane (10/90, v/v)) followed by recrystallization from hexane by very slow evaporation at −20 °C gave analytically pure **12**. Unfortunately, the crystals aggregated in a form unsuitable for X-ray analysis.

(9) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712.

(10) Adams, R. D.; Chodosh, D. F.; Golembeski, N. M.; Weissmann, E. C. *J. Organomet. Chem.* **1979**, *172*, 251.

Scheme II

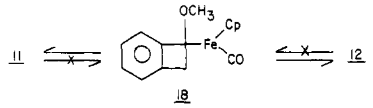


L = CO; Ph_3P[19]

The Fe–C(7a) distance of 1.958 (6) Å is not significantly different from the value of 1.968 (2) Å for a similar bond.[10] Both distances are significantly shorter than the values of 1.991 (8),[12] 2.037 (5),[13] and 2.120[14] reported for Fe–C-(phenyl) bonds in non-carbene-type complexes. The C-(5)–C(6) distance in the phenyl ring appears to be short but may be related to thermal motion in the ring. The dimensions of the Cp ring, the Fe–Cp ring distance, and the Fe–CO group dimensions are not unusual.

Where methoxy stabilizes a carbene complex enough to induce rearrangement in the cyclopropyl σ-complex **3**, we have found that the corresponding thiocresyl cyclopropyl σ-complex is photostable.[15] Assuming that this is due to the poorer electron-donating ability of sulfur as compared with oxygen, we thought it would be interesting to see if the presumed increase in strain relief resulting from expanding benzocyclobutene to a metallocyclopentadiene (as in **10** to **11**) would be enough to offset the loss of substituent stabilization. To this end **13**[5] was prepared in 66% yield as shown in Scheme I. Photolysis[16] in C_6D_6 at 5–10 °C gave a mixture in which the major product (75–80% of reacted material) showed spectroscopic properties[17] that are sufficiently similar to those of **11** (especially the ^{13}C resonance at 340.4 ppm) to lead us to tentatively assign it structure **14**. Unfortunately, all attempts to isolate this new material failed. For instance, although TLC (silica gel, EtOAc/hexane (10/90, v/v)) indicated a clean separation of the major product and flash chromatography on silica gave a sharp green band, evaporation of solvent invariably gave a gumlike, intractable material.[18]

Reaction of **9** with CO or Ph_3P at room temperature readily gives the rearranged σ-complex **17** which we have suggested[3] originates by the mechanism outlined in Scheme II. To test for a similar rearrangement of **12**, a sample was sealed under 6.5 atm of CO (ca. 100 molar equiv), and the solution was monitored at room temperature by ^1H NMR for 6 months. During this time virtually no reaction occurred. That the sluggishness of this reaction was due to slow contraction to **18** (rather than a slow later step) is clear since, if **18** were formed but could react no further, it should preferentially expand back to **11** rather than **12**.



For an estimation of a minimum barrier for contraction of **11** or **12** to **18**, samples were heated in C_6D_6 to 77 °C and monitored by ^1H NMR. In neither case (**11** heated for 18 h and **12** heated for 39 h) was any detectable isomerization observed. Assuming a first-order reaction and an NMR detection level of 5% leads to a minimum $\Delta G^\ddagger$ of about 30–31 kcal/mol. The difference between this and that observed for **9** ($\Delta G^\ddagger \le 21.6$ kcal/mol)[19] is presumably primarily due to the difference in strain energies of cyclobutane and benzocyclobutene.

Acknowledgment. This work was partially supported by the National Science Foundation to whom the authors are grateful. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The support from the Royal Norwegian Council for Scientific and Industrial Research (NTNF) to Y.S. is greatly appreciated. High-field NMR spectra were obtained on a Nicolet NT-300 spectrometer, operating at a field of 7 T; therefore, acknowledgment is made to the Instrument Program, Chemistry Division, National Science Foundation, for financial assistance in the purchase of the instrument.

Registry No. **10**, 49624-85-3; **11**, 104090-23-5; **12**, 104090-24-6; **13**, 104090-22-4; **14**, 104090-25-7; Fp^-, 12107-09-4; *p*-Me-PhSH, 106-45-6; 7-bromobicyclo[4.2.0]octa-1,3,5-triene, 21120-91-2.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, and bond angles (3 pages); a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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(11) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(12) Carre, F. H. *Cryst. Struct. Commun.* **1982**, *11*, 1009.

(13) Vierling, P.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1981**, *103*, 2466.

(14) Semion, V. A.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1969**, *10*, 88.

(15) Unpublished results of N. Conti, University of Florida.

(16) Photolysis was carried out under a N_2 atmosphere with a 450-W Hanovia medium-pressure lamp using a $CoSO_4$ filter. The reaction progress was monitored by NMR. The rearranged product is exceedingly sensitive, and it was found that if the temperature were allowed to rise, the $CoSO_4$ filter omitted or photolysis carried out beyond ca. 75% conversion, the reaction mixture became very complex, at least partly due to further reaction of the carbene complex.

(17) (a) 1-Carbonyl-1-(η^5-cyclopentadienyl)-2-*p*-thiocresyl-1-ferraindene (**14**): ^1H NMR (60 MHz, C_6D_6) δ 1.98 (s, 3 H, CH_3), 3.65 (s, 1 H),[17b] 3.75 (s, 1 H),[17b] 4.70 (s, 5 H, Cp), 6.5–7.5 (m, 8 H); ^{13}C NMR (25. MHz, C_6D_6) δ 21.08 (CH_3), 66.02 (CH_2), 89.31 (Cp), 119.91, 121.86, 122.93, 125.86, 130.44, 132.39, 134.82, 137.36, 142.42, 152.47, 160.85 (aromatic carbons), 221.47 (CO), 340.38 (carbene C). (b) As is the case for **11** and **12** these apparent singlets may well be doublets with very low intensity wings. However, as mentioned, this carbene complex could not be isolated in pure form, and it was therefore not possible to positively identify the wings. There is doubt about the major features of the spectrum.

(18) Interestingly, the photolysis showed a major and minor product in about 9/1 ratio (from the Cp resonances) which we suspect correspond to the thiocresyl analogues of **11** and **12**, but this is very tentative since we have no further evidence for the analogue of **12**.

(19) Unpublished results of Y. Stenstrøm.

Zirconium(IV) "Metalloazines" from Hydrazones: An "Umpolung" of a Carbonyl Group Derivative

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Received July 8, 1986

Summary: Zr(IV) "metalloazines" have been prepared from Zr(IV) salts and hydrazone derivatives (or from Zr(II) phosphine complexes and diazoalkanes). They are dimeric; X-ray analysis reveals an unsymmetrically bridged dizirconium center, and NMR analysis shows that the complexes are fluxional. They demonstrate susceptibility to electrophilic attack at carbon and thus represent an "umpolung" of the carbonyl group from which they were derived.

To activate an organic molecule toward an unusual transformation by coordination to a transition-metal center is a continuing theme in organometallic chemistry. Of