

## Coupling of Acyl and Iminoacyl Groups on Zirconium and $\sigma^2, \pi$ -Coordination of the Resulting Enamidolate Ligand

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The transition-metal-acyl group is a critical function in organometallic chemistry as its structure and reactivity determine the pathway that catalytic and stoichiometric cycles based on the migratory insertion of carbon monoxide into metal alkyl bonds can take.<sup>1</sup> For early d-block and actinide elements the reactivity of these functions is best accommodated into a bonding description in which an oxycarbene resonance makes a significant contribution.<sup>2,3</sup> A similar picture also exists for the less well-studied isoelectronic iminoacyl group. We wish to communicate here our initial findings on the products of migratory insertion of carbon monoxide and alkyl isocyanides into a series of zirconium-benzyl compounds containing the bulky ligand 2,6-di-*tert*-butylphenoxide (OAr'). This work demonstrates some novel reactivity and furthermore indicates a possibly general ground-state structural feature of simple heteroatom-substituted metalloclopentenes.

The complex  $\text{Zr}(\text{OAr}')_2(\text{CH}_2\text{Ph})_2$ <sup>4</sup> reacts readily with 2 equiv of alkyl isocyanide RNC (R = *t*-Bu; 2,6-dimethylphenyl) in hydrocarbon solvents to give almost quantitative yields of the bisinsertion products (2) (Scheme I).<sup>5</sup> Intermediate, monoinsertion complexes were detected spectroscopically and in the case of the insertion of the more sterically demanding 2,6-xylyl ligand, the intermediate compound was also isolated (1b).<sup>6</sup> All of the insertion products contain bands in their infrared spectra around 1560  $\text{cm}^{-1}$  assignable to  $\bar{\nu}(\text{CN})$  of a  $\eta^2$  imino-acyl function,<sup>5,6</sup> while the iminoacyl carbon atom is observed to resonate between  $\delta$  235–250 in the <sup>13</sup>C NMR spectra. A single-crystal X-ray diffraction study of the bis(iminoacyl) complex 2a was carried out and confirmed the  $\eta^2$  bonding of the two groups.<sup>7</sup> Figure 1 shows an ORTEP view of the molecule emphasizing the central coordination sphere. Although formally six-coordinate, the complex is best described as pseudotetrahedral about the zirconium atom with each of the  $\eta^2$ -iminoacyl groups occupying a single coordination site. The two iminoacyl groups are oriented parallel with each other in a head to tail fashion and also parallel with the O–Zr–O plane.<sup>8</sup> The Zr–C and Zr–N distances are essentially identical

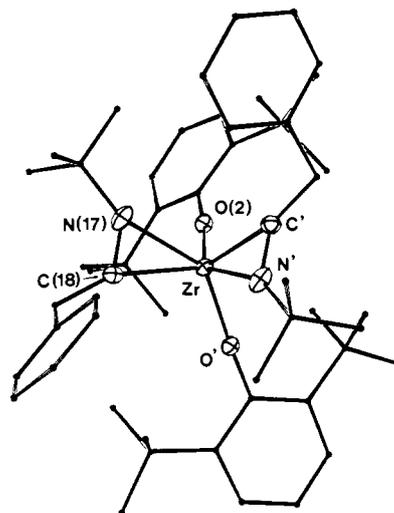
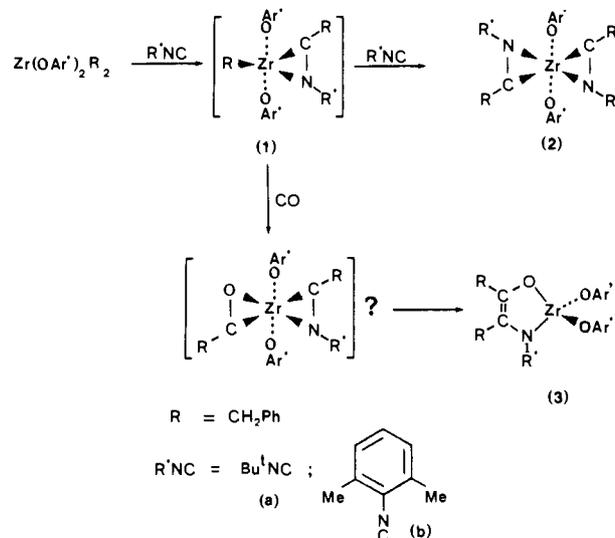


Figure 1. ORTEP view of  $\text{Zr}(\text{OAr}')_2(t\text{-BuNCCH}_2\text{Ph})_2$  (2a). Important bond distances (Å) and angles (deg): Zr(1)–O(2) = 2.027 (2); Zr(1)–N(17) = 2.221 (3); Zr(1)–C(18) = 2.228 (3); N(17)–C(18) = 1.286 (4); O(2)–Zr–O(2)' = 97.3 (1); N(17)–Zr–C(18) = 114.8 (1); N(17)–Zr–N(17)' = 102.3 (1); C(18)–Zr–C(18)' = 108.3 (2); Zr–N(17)–C(18) = 73.5 (2); Zr–C(18)–N(17) = 72.9 (2).

### Scheme I



and similar to those found for the only previously reported zirconium-iminoacyl complex.<sup>9</sup> Although diastereotopic benzyl  $\text{CH}_2\text{Ph}$  protons would be expected for this static structure, the <sup>1</sup>H NMR spectrum of compounds 2a,b show only singlets for this group, indicating that rapid rotation of the coordinated iminoacyl is occurring. At –65 °C (toluene, 90 MHz) broadening of this signal occurs, indicating the freezing out of this motion (possibly  $\eta^2$ - $\eta^1$ - $\eta^2$ ).

The complex  $\text{Zr}(\text{OAr}')_2(\text{CH}_2\text{Ph})_2$  reacts with carbon monoxide only at high pressures to yield a number of, as yet, unidentified products. However, in the presence of pyridine (py) a sparingly soluble complex of stoichiometry  $[\text{Zr}(\text{OAr}')_2(\text{COCH}_2\text{Ph})_2(\text{py})]$  is obtained in good yield.<sup>10</sup> On the basis of spectroscopic data

(1) Ford, P. C., Ed.; American Chemical Society: Washington, DC, 1981; "Catalytic Activation of Carbon Monoxide"; ACS Symp. Ser. No. 152.

(2) (a) Bercaw, J. E.; Wolczanski, P. T. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103 and references therein.

(3) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989.

(4) Latesky, S.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Organometallics*, in press.

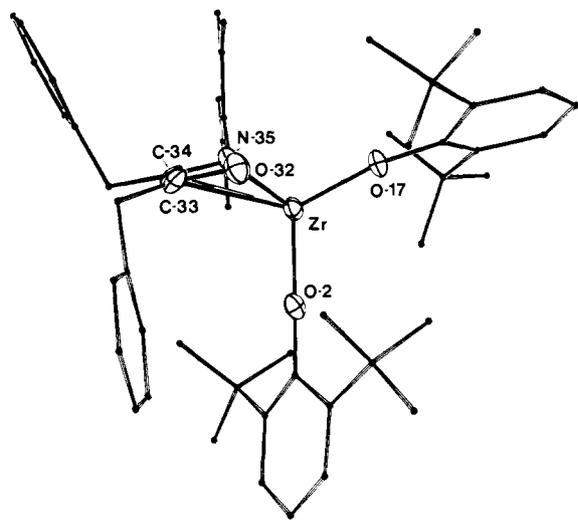
(5) All compounds gave satisfactory analytical data. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) (2a)  $\delta$  4.30 (s, CH<sub>2</sub>Ph), 0.96 (s, N-*t*-Bu), 1.50 (OC<sub>6</sub>H<sub>3</sub>-*t*-Bu), 6.8–7.3 (m, Ar), (2b) 4.18 (s, CH<sub>2</sub>Ph), 1.80 (s, NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>), 1.40 (s, OC<sub>6</sub>H<sub>3</sub>-*t*-Bu), 6.7–7.3 (m, Ar); <sup>13</sup>C NMR (50.3 MHz, C<sub>6</sub>D<sub>6</sub>) (2a)  $\delta$  244.3 (*t*-BuNCCH<sub>2</sub>Ph), (2b) 239.0 (C<sub>6</sub>H<sub>3</sub>NCCH<sub>2</sub>Ph); IR (Nujol mull)  $\bar{\nu}(\text{CN})$  (2a) 1570, (2b) 1560  $\text{cm}^{-1}$ .

(6) 1b: <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  3.19 (s, ZrCH<sub>2</sub>Ph), 3.97 (s, *t*-BuNCCHPh), 1.69 (s, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>NCCH<sub>2</sub>Ph), 1.43 (s, OC<sub>6</sub>H<sub>3</sub>-*t*-Bu), 6.8–7.3 (m, aromatics); <sup>13</sup>C NMR (50.3 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  246.3 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>NCCH<sub>2</sub>Ph); IR (Nujol mull)  $\bar{\nu}(\text{CN})$  1530  $\text{cm}^{-1}$ .

(7) Crystal data for  $\text{ZrC}_{22}\text{H}_{74}\text{O}_2\text{N}_2$  (2a) at –157 °C: space group C2/c,  $a = 23.612$  (8) Å,  $b = 11.198$  (4) Å,  $c = 21.243$  (8) Å,  $\beta = 123.52$  (2)°,  $Z = 4$ ,  $d_{\text{calc}} = 1.206$  g  $\text{cm}^{-3}$ . Of the 3066 unique reflections collected by using Mo K $\alpha$  radiation,  $6^\circ \leq 2\theta \leq 45^\circ$ , the 2665 with  $F > 3.00 \sigma(F)$  were used in the full-matrix refinement. Final residuals are  $R_F = 0.0345$  and  $R_{wF} = 0.0367$ .

(8) By far the most extensively studied acyl and imino acyl derivatives are those based on either Cp<sub>2</sub>M or Cp\*<sub>2</sub>M (M = Ti, Zr, Hf, Th) units. Here the acyl units lie in a plane perpendicular to the metallocene plane, see: (a) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112. (c) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206.

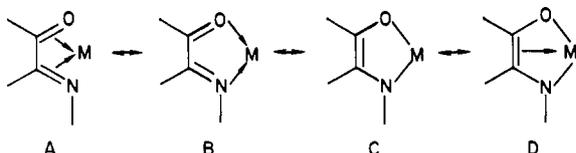
(9) Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *2*, 1763.



**Figure 2.** ORTEP view of  $(Ar'O)_2Zr[OC(CH_2Ph)C(CH_2Ph)N(C_6H_5)]$  (**3**) emphasizing the central coordination sphere. Important bond distances (Å) and angles (deg): Zr-O(2) = 1.967 (5); Zr-O(17) = 1.929 (5); Zr-O(32) = 2.004 (5); Zr-N(35) = 2.038 (6); Zr-C(33) = 2.549 (8); Zr-C(34) = 2.581 (8); O(32)-C(33) = 1.377 (9); C(33)-C(34) = 1.348 (11); C(34)-N(35) = 1.434 (10); O(2)-Zr-O(17) = 117.4 (2); Zr-O(32)-C(33) = 96.1 (4); O(32)-C(33)-C(34) = 118.8 (7); C(33)-C(34)-N(35) = 119.0 (7); Zr-N(35)-C(34) = 94.4 (5); O(32)-Zr-N(35) = 84.2 (2).

we believe this compound to contain an enediolate ligand formed by the coupling together of two  $\eta^2$ -acyl functions,<sup>10</sup> although the exact nature and molecularity of this compound is as yet unknown.

In contrast the monoalkyl complex  $Zr(OAr')_2(\eta^2$ -xyNCCH<sub>2</sub>Ph)(CH<sub>2</sub>Ph) (**1b**, xy = 2,6-dimethylphenyl) smoothly inserts CO at 200 psi and is quantitatively converted to complex **3** (Scheme I). Spectroscopic data for **3** are consistent with its formulation as containing an enamidolate ligand formed by a coupling reaction in a presumably intermediate mixed acyl, iminoacyl complex.<sup>11</sup> A single-crystal X-ray diffraction study of **3** confirmed this, but with an interesting structural feature (Figure 2).<sup>12</sup> It can be seen that although the  $Zr(OAr')_2$  coordination is unremarkable, the enamidolate ligand is distorted from a planar coordination that has typically been observed for chelating enediolates.<sup>13</sup> It is possible to write four resonance forms for the interaction of this group with zirconium. Resonances involving an  $\alpha$ -keto imine form (A, B) would involve a formal



oxidation state of +2 on zirconium and seem unreasonable. The

(10) A solution of  $Zr(OAr')_2(CH_2Ph)_2$  in benzene/pyridine reacts over a period of 24 h with 900 psi of CO to give a sparingly soluble product. Mass spectroscopic analysis shows a strong molecular ion at 818 (Zr-91). IR (Nujol mull)  $\bar{\nu}(C=C)$  1620  $cm^{-1}$ .

(11) **3**: <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  3.51 and 3.99 (s, CCH<sub>2</sub>Ph), 1.93 (s, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>N), 1.40 (s, OC<sub>6</sub>H<sub>3</sub>-*t*-Bu<sub>2</sub>), 6.8-7.3 (m, Ar); IR (Nujol mull)  $\bar{\nu}(C=C)$  1650  $cm^{-1}$ .

(12) Crystal data for  $Zr(OAr')_2[OC(CH_2Ph)C(CH_2Ph)N(C_6H_5)]$  (**3**) at -160 °C: space group P1,  $a = 20.445$  (9) Å,  $b = 11.750$  (4) Å,  $c = 10.059$  (3) Å,  $\alpha = 93.63$  (1)°,  $\beta = 88.56$  (1)°,  $\gamma = 88.73$  (1)°,  $\zeta = 2^\circ$ ,  $d_{calc} = 1.173$  g  $cm^{-3}$ . Of the 6318 unique intensities collected by using Mo K $\alpha$  radiation,  $6^\circ \leq 2\theta \leq 45^\circ$ , the 5100 having  $F > 3.00\sigma(F)$  were used in the full-matrix refinement. Final residuals are  $R_F = 0.0802$ ,  $R_wF = 0.0799$ .

(13) To date the solid-state structure of a simple, chelating enediolate coordinated to M(IV) (M = Ti, Zr, Hf, Th, U) has not been determined. However, that of a number of substituted derivatives formally containing the (M-OC=CO) chelating backbone have been reported. (a) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393. (c) Moley, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1983**, *105*, 5696.

solid-state structure is best accommodated into resonance form D involving  $\sigma$ -coordination of oxygen and nitrogen and then  $\pi$ -interaction to the olefinic function of the metallacycle. The distances to these ring carbons, 2.55-2.58 Å, although outside the range of typical Zr-C  $\sigma$ -bonds, is similar to that found between zirconium and the carbon atoms of Cp (C<sub>5</sub>H<sub>5</sub>) rings.<sup>14</sup> The coordination of the enamidolate fragment in **3** is strikingly similar to that characterized recently by Erker for a substituted butadiene coordinated to zirconium where the situation was also described as  $\sigma^2, \pi$ -coordination.<sup>15</sup>

We hence conclude that coupling of acyl and iminoacyl groups appears to be a facile reaction on zirconium-aryl oxide metal centers and, furthermore, that a ground state, nonplanar,  $\sigma^2, \pi$ -coordination of metallacycles  $Zr(XC(R)=C(R)Y)$  (X, Y = O, NR, CR<sub>2</sub>) is a general possibility.<sup>16</sup>

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**Supplementary Material Available:** Listings of atomic coordinates and temperature factors (8 pages). Ordering information is given on any current masthead page.

(14) Compare distances of 2.25 (2) Å found in  $Zr(OAr')_2(CH_2Ph)_2$  from ref 4 and "typical" Zr- $\eta^5$ -C<sub>5</sub>H<sub>5</sub> distances of 2.48-2.55 Å; see ref 13a and references therein

(15) Erker, G.; Engel, K.; Kruger, C.; Muller, G. *Organometallics*, **1984**, *3*, 128.

(16) It is possible that simple enediolates may adopt this ground state; those listed in ref 3 contain substituents on the chelate carbons that can interact with the olefinic  $\pi$ -cloud, favoring a planar geometry.

### Dynamic Isotope Dilution as a General Method for Ascertaining Partition of Photochemical Pathways Potentially Utilizing Nondiscernible Intermediates: Application to a New Reaction<sup>1,2</sup>

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In pursuing our objective of finding new photochemical reactions, we searched for a second example of the homo-di- $\pi$ -methane rearrangement; the case in which a three ring and an aryl group are bonded to the central (i.e. "methane") carbon was unknown and of particular interest.<sup>3</sup>

In this study we encountered a problem which has provided an obstacle in several of our investigations. Thus, in dealing with a new photochemical reaction one often finds that a starting material (e.g., A) may reasonably be formulated as proceeding directly to product (C) or, alternatively, proceeding totally or partially via an intermediate B. A particularly important case is where the intermediate proceeds onward photochemically.

Where the intermediate is isolable or readily discernible, one can simply extrapolate the B/C ratio to zero conversion to obtain the partition of the direct A  $\rightarrow$  C and indirect A  $\rightarrow$  B  $\rightarrow$  C routes. Where the reasonable intermediate B is either not detectable or is present in minute quantities, another approach is needed. The arylcyclopropylmethane reaction proved to be such a case, and the method of dynamic isotope dilution described below proved ideal in solving the dilemma.

(1) Mechanistic and Exploratory Organic Photochemical Series. 142.

(2) Part 141: Zimmerman, H. E.; Ramsden, W. D. *Can. J. Chem.* **1984**, *62*, 2592-2611.

(3) (a) Our only previous example consists of a vinylcyclopropyl-type system.<sup>3b</sup> (b) Zimmerman, H. E.; Samuel, C. J. *J. Am. Chem. Soc.* **1975**, *97*, 4025-4036.