Organometallics 1990, 9, 1995-1997

This new, "surface-assisted" route compares favorably with the conventional homogeneous-phase syntheses. Reduction of $Os_3(CO)_{12}$ with sodium borohydride[5] leads to the formation of complex mixtures of hydrido carbonyls; after purification by preparative TLC and recrystallization, $HOs_3(CO)_{10}(OH)$ was obtained in low yield (27%). Deeming et al.[6] reported a new synthetic route via acid-induced displacement of acetaldehyde from a (μ-vinyloxy)triosmium cluster, yielding $HOs_3(CO)_{10}(OH)$ (36%) after chromatographic separation on silica. Our reported synthesis shows the effectiveness of the silica surface in providing a more efficient synthetic route to the preparation of organometallic complexes. This new field of "surface-mediated" reactions[7-9] should have promising applications in preparative organometallic chemistry.

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A Chemical Reaction Path from Crystal Structure Data: Isolation of Intermediates in the Reaction of a Bimetallic Chiral Enolate with Benzaldehyde

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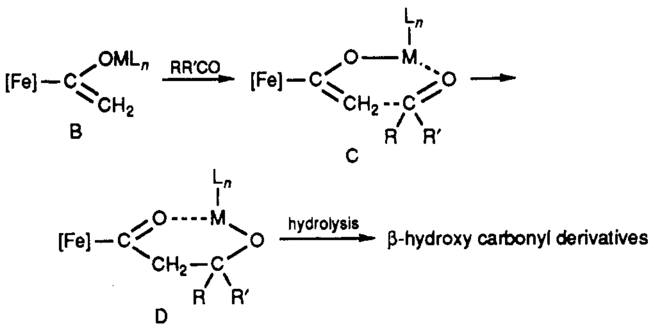
Summary: The isolation and the structural characterization of $[\mathrm{cp(CO)(PPh_3)Fe(COCH_2C(Ph)OTi(cp)_2Cl)}]$ (**2**), derived from the aldol reaction of $[\mathrm{cp(CO)(PPh_3)Fe(C(CH_2)OTi(cp)_2Cl)}]$ (**1**) with PhCHO, was achieved. When the Cl^- ligand was removed from **2** with use of BPh_4^-, the dimetallacycle $[\mathrm{cp(CO)(PPh_3)Fe(}\overline{\mathrm{COCH_2C(Ph)OTi}}\mathrm{(cp)_2)}]^+$ (**3**) was obtained. Its structure very closely mimics the structure of the cyclic transition state suggested for the aldol reaction.

The chiral auxiliary $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ (≡[Fe]) has been extensively developed by Liebeskind[2] and Davies[3] in the form $\{[Fe]\text{-}COCH_2^-\}$ (A) for the stereoselective delivery of the acyl fragment to organic electrophiles. Because of the important role played by the countercation M^+ in controlling reactivity and stereoselectivity,[2-4] our attention was focused on (i) the preparation of transition-metal derivatives of the anion A in either its keto or enolato form[5] and (ii) the elementary steps of the aldol reaction of A, in its dimetallic enolato form, first probed with PhCHO.

Scheme I



In a simplified scheme the aldol reaction is believed to proceed through some key steps: the cyclic transition state C and the adduct D, which has never been isolated but is hydrolyzed in the usual workup to the final β-hydroxy carbonylic derivative.[2,3,6]

In order to gain information on the intermediates sketched in Scheme I, we ran the reaction of benzaldehyde with the dimetallic version of the iron enolate A, as reported in Scheme II.

Complex 1[7] was synthesized by following the procedure

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(7) The procedure for 1 is the same as that reported for the zirconium analogue.[5] The yield is ca. 60%. The solid was recrystallized from THF–Et_2O to give a red-brown crystalline solid. ν(CO) (Nujol): 1918 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 3.91 (dd, 1 H, J_{H-P} = 3.70 Hz, J_{gem} = 1.90 Hz), 4.18 (pseudo t, 1 H, J_{H-P} = 1.50 Hz, J_{gem} = 1.90 Hz), 4.53 (d, 5 H, cp–Fe, J_{cp-P} = 1.00 Hz), 5.71 (s, 5 H), 6.20 (s, 5 H), 7.04–7.63 (m, 15 H). Anal. Calcd for $C_{36}H_{32}ClFeO_2PTi$: C, 64.84; H, 4.84; Cl, 5.32; P, 4.64. Found: C, 64.76; H, 4.82; Cl, 5.22; P, 4.54. The structure of 1 has been determined by an X-ray analysis.

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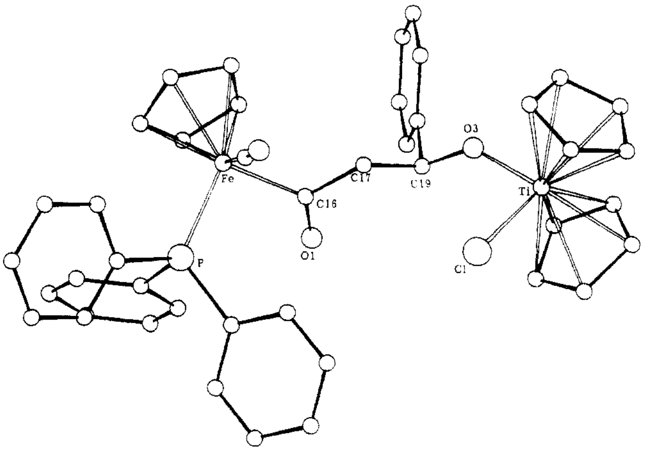
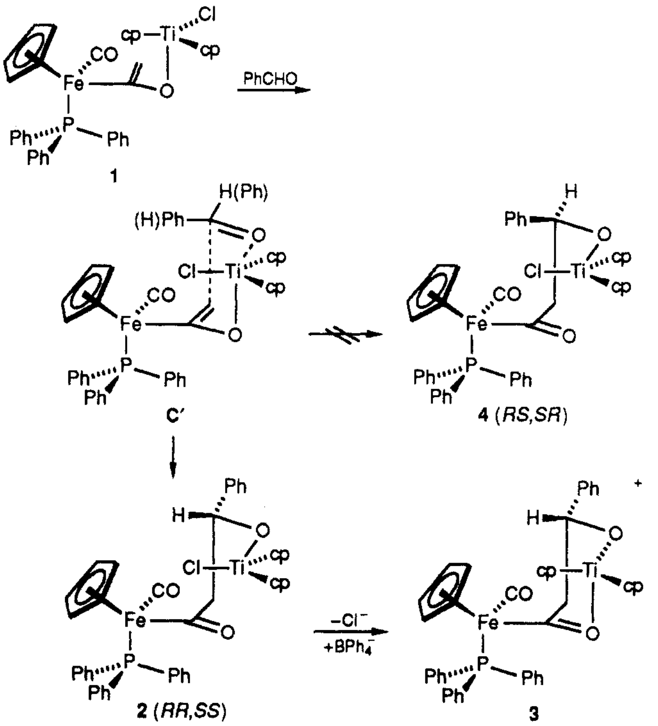


Figure 1. A view of complex 2. Bond distances (Å): Fe–P = 2.196 (3), Fe–cp = 1.745 (8), Fe–C16 = 1.961 (8), Fe–C18 = 1.711 (10), C16–O1 = 1.212 (12), C16–C17 = 1.538 (12), C17–C19 = 1.530 (12), C19–O3 = 1.412 (10), Ti–O3 = 1.846 (5), Ti–Cl = 2.399 (3), Ti–cp (mean) = 2.077 (9). Bond angles (deg): Fe–C16–O1 = 124.3 (7), Fe–C16–C17 = 115.9 (6), O1–C16–C17 = 119.7 (8), C16–C17–C19 = 114.2 (7), C17–C19–O3 = 106.2 (7), C19–O3–Ti = 137.1 (5).

Scheme II



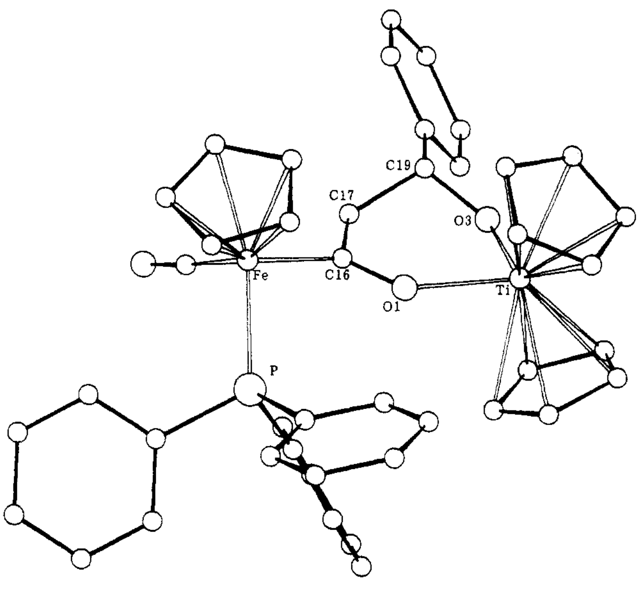


Figure 2. A view of complex 3. Bond distances (Å): Fe–P = 2.222 (2), Fe–cp = 1.740 (5), Fe–C16 = 1.925 (6), Fe–C18 = 1.752 (7), C16–O1 = 1.262 (7), C16–C17 = 1.532 (8), C17–C19 = 1.543 (8), C19–O3 = 1.397 (8), Ti–O3 = 1.842 (4), Ti–O1 = 2.065 (4), Ti–cp (mean) = 2.073 (7). Bond angles (deg): Fe–C16–O1 = 122.2 (4), Fe–C16–C17 = 122.1 (4), O1–C16–C17 = 115.4 (5), C16–C17–C19 = 117.1 (5), C17–C19–O3 = 109.5 (5), C19–O3–Ti = 129.0 (4), C16–O1–Ti = 135.6 (4), O1–Ti–O3 = 85.8 (2).

reported for the isostructural zirconium analogue.[5] Complex 1 reacts slowly at 44 °C with PhCHO.[8] The crystalline solid formed was analyzed by X-ray, IR, and ^{1}H NMR spectroscopies. Assignment of structures of the aldol diastereoisomers (2 and 4) was achieved in the following manner. The isolated solid was found to be the pure diastereoisomer 2, and the relative configuration of the chiral centers was rigorously determined by X-ray analysis, which established the *RR,SS* relative stereochemistry of the product. A careful analysis of the ^{1}H NMR spectrum was undertaken, and it is in agreement with the analogous analysis carried out on the organic products in the case of the $SnCl_2$-modified reaction of enolate A with PhCHO.[2] The reaction is highly stereospecific for the isolated yield.[2,6] The diastereoselectivity in our case is the opposite of what is observed by adding [ClTi(O-*i*-Pr)$_3$] to the lithium enolate, which produces an excess of the *RS,SR* diastereoisomer.[2] In addition, the reaction carried out on complex 1 does not require a large excess of the countercation or 2 equiv of base.[2,9]

The molecular structure of complex 2 is reported in Figure 1 with the most relevant bond distances and angles.[10] The structural parameters of such a complex are very close to those reported for the two separated iron[6] and titanium fragments.[11] The bridging ligand across two metal sites is rather flexible, and it does not impose any rigid mutual arrangement of the two metal sites. The transformation of 2 into 3 by removal of the chloride anion around titanium with use of a noncoordinating anion, BPh_4^-,[12] was carried out with the purpose of binding the

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(8) Procedure for 2: 1 (3.03 g, 4.54 mmol) was reacted with benzaldehyde (0.46 mL, 4.51 mmol) in THF (75 mL). The suspension was stirred at room temperature for 2 days and then heated at 44 °C for 7 h. The resulting solution was reduced to 20 mL; then Et_2O (50 mL) was added. An orange crystalline solid formed (yield 1.47 g, 42%). IR spectrum (Nujol): $\nu(CO)$ 1903, $\nu(CO)_{acyl}$ 1621 cm^{-1}. ^{1}H NMR (ABX-type spectrum) for the [$FeCOCH_2CH(Ph)OTi$] fragment (200 MHz, CD_2Cl_2): δ_A 3.13 (dd, 1 H, J_{AX} = 16.60 Hz, J_{AB} = 3.20 Hz); δ_X 3.58 (dd, 1 H, J_{XB} = 9.80 Hz, J_{XA} = 16.60 Hz); δ_{Cp-Fe} 4.50 (d, 5 H, J_{Cp-P} = 1.20 Hz); δ_B 5.58 (dd, 1 H, J_{BX} = 9.80 Hz, J_{BA} = 3.20 Hz); δ_{Cp-Ti} 6.17 (s, 5 H); $\delta_{Cp'-Ti}$ 6.22 (s, 5 H); δ 7.22–7.55 (m, 20 H). Anal. Calcd for $C_{43}H_{38}ClFeO_3PTi$: C, 66.82; H, 4.96; Cl, 4.59; P, 4.01. Found: C, 66.72; H, 5.10; Cl, 4.45; P, 3.88.

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(10) Structure of 2: $C_{43}H_{38}ClFeO_3PTi$, monoclinic, space group $P2_1/n$, a = 15.329 (1) Å, b = 13.191 (2) Å, c = 18.829 (1) Å, β = 103.75 (1)°, V = 3698.2 (7) Å^3, Z = 4, ρ_{calcd} = 1.388 g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 7.59 cm^{-1}, crystal dimensions 0.18 × 0.26 × 0.50 mm^3. The structure was solved by the heavy-atom method and refined anisotropically for all non-hydrogen atoms. All the hydrogen atoms were directly located from a difference Fourier map and introduced into the final refinement as fixed contributors (U_{iso} = 0.08 Å^2); 1998 unique observed reflections ($I > 1.5\sigma(I)$) collected at room temperature ($6 < 2\theta < 46°$) were used (R = 0.041).

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acyl function back to titanium as in the cyclic transition state C′. Figure 2 gives a picture of the X-ray structure of **3**, with some relevant structural parameters.[13] The cyclization of **2** to **3** requires mainly a rotation of ~111° around the C17–C19 bond, as indicated by the values for the C16–C17–C19–O3 torsion angle: 168.1 (7) and 56.9 (7)° for **2** and **3**, respectively. The structural parameters of **3** do not reveal any significant deviation from those of some known derivatives of iron[6] and titanium[11] in the same coordination environment. The metallacycle adopts a half-chair conformation, being folded by 45.3 (4)° along the C17···O3 line (the folding is defined by the dihedral angle between the C17–C19–O3 and C17, C16, O1, Ti, O3 planes). The conformation of the metallacycle is expected to be very close to that of the cyclic transition state, the bond sequence being the same and the cyclization changing nothing in the stereochemistry of the two chiral centers. A geometrical difference between C′ and **3** may exist only because of the different coordination numbers of titanium, which is pentacoordinate in C′ and tetracoordinate in **3**.

Complexes **2** and **3** confirm general assumptions, which have never been structurally proved before, on the role of the countercation in metal enolates. They exclude metal–enolate aggregations or equilibria as playing any role and show how a transition-metal moiety such as $[(cp)_2Ti(Cl)]$ orients the substrate toward the enolate and determines the geometry of the transition state. The design of transition-metal moieties to be used as countercations, keeping in mind geometry requirements at the metal and metal–oxygen bond strength, might be important in enolate chemistry.

Attempts to understand the steric control exerted by the second metal site by using the structural information from complexes **1**–**3**, the introduction of a second chiral metal, and the parallel use of the bimetallic keto form of the iron anion are in progress.

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Supplementary Material Available: Tables of X-ray data, fractional atomic coordinates, anisotropic thermal parameters, and bond distances and angles for complexes **2** and **3**, a table of bond distances for **1**, and a figure showing the structure of complex **1** (18 pages); listings of observed and calculated structure factor amplitudes for complexes **2** and **3** (19 pages). Ordering information is given on any current masthead page.

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[12] Procedure for **3**: to a THF suspension (100 mL) of **2** (1.47 g, 1.90 mmol) was added $NaBPh_4$ (0.68 g, 2.0 mmol). A red solution suddenly formed, and a white solid precipitated. The suspension was stirred for 4 h at room temperature, and the white solid was removed by filtration. The IR spectrum of the solution showed the shift of the acylic function from 1621 cm^{-1} down to 1581 cm^{-1} and of the carbonylic one from 1903 cm^{-1} in **2** up to 1945 cm^{-1}. The solution after partial evaporation gave, by addition of Et_2O (30 mL), a red crystalline solid (yield 1.36 g, 68%). The solid recrystallized from CH_2Cl_2/hexane contains CH_2Cl_2 of crystallization. ^1H NMR (ABX-type spectrum) for the $[FeCOCH_2CH(Ph)OTi]$ fragment (200 MHz, CD_2Cl_2): δ 2.58 (q,* 1 H, $J_{XA} = 10.51$ Hz, $J_{XB} = 17.81$ Hz, $J_{H-P} = 0.80$ Hz), 4.09 (q,* 1 H, $J_{BX} = 17.30$ Hz, $J_{BA} = 2.20$ Hz, $J_{H-P} = 0.60$ Hz), 4.67 (d, 5 H, cp–Fe, $J_{cp-P} = 1.20$ Hz), 5.16 (d,* 1 H, $J_{AB} = 2.00$ Hz, $J_{AX} = 10.41$ Hz), 6.29 (s, 5 H), 6.24 (s, 5 H), 6.44–7.55 (m, 40 H). An asterisk indicates that each peak is split into a doublet derived from coupling with phosphorus. Anal. Calcd for $C_{68}H_{60}BCl_2FeO_3PTi$: C, 71.53; H, 5.30; Cl, 6.21; P, 2.71. Found: C, 71.29; H, 5.30; Cl, 6.10; P, 2.67.

[13] Structure of **3**: $C_{68}H_{60}BCl_2FeO_3PTi$, monoclinic, space group $P2_1/n$, $a = 15.300$ (1) Å, $b = 14.196$ (2) Å, $c = 27.105$ (2) Å, $\beta = 100.77$ (12)°, $V = 5783.5$ (7) Å^3, $Z = 4$, $\rho_{calcd} = 1.311$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 5.52 cm^{-1}, crystal dimensions 0.37 × 0.48 × 0.61 mm^3. The structure was solved by the heavy-atom method and refined anisotropically for all non-hydrogen atoms. All the hydrogen atoms were directly located from a difference Fourier map and introduced into the final refinement as fixed contributors ($U_{iso} = 0.08$ Å^2); 4187 unique observed reflections ($I > 2\sigma(I)$) collected at room temperature ($6 < 2\theta < 46°$) were used ($R = 0.049$). All calculations were carried out with use of SHELX 76.

Catalytic Hydration of Alkynes with Zeise's Dimer

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Summary: **Pt(II) in the form of Zeise's dimer has been shown to be an efficient and facile hydration catalyst or catalyst precursor for the hydration of alkyl-substituted alkynes.**

Unactivated alkynes are an abundant hydrocarbon resource, and hydration represents an excellent means of functionalization. Classically, they are hydrated to ketones or aldehydes by use of Hg(II) complexes with added catalytic amounts of H_2SO_4 or pTsOH.[1,2] Further, Regen,[3] in 1982, reported that phenylmercuric hydroxide was a highly selective reagent for the hydration of nonconjugated terminal alkynes. In this latter methodology, it was not necessary to employ acid but the reaction required stoichiometric amounts of mercury. Other metals have also been employed to hydrate acetylenes and alkynes, including copper(I),[4] silver(I),[4] palladium(II),[4] ruthenium(III),[4] rhodium(III),[4] and osmium(II).[5] These hydrolyses are accelerated by protonic acids and give a variety of products from acetylene such as crotonaldehyde and polymers thereof, in addition to the simple hydration products.

In regard to platinum-facilitated addition reactions with alkynes, Clark and Chisholm concentrated on the addition of methanol to cationic complexes.[6,7] Trogler[8] has reported the analogous hydration of nitriles with a hydridoplatinum(II) hydroxide complex. Finally, in a paper by Chatt[9] in 1961, dealing with the preparation of alkyne

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