Synthesis, Structure, and Fluxional Behavior of κ^1-*O*-Enolatoiron(II) Complexes Derived from 1,3-Dicarbonyl Compounds

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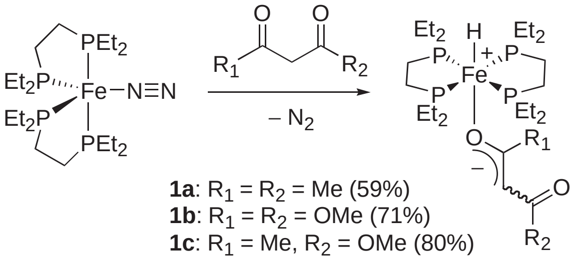
Highly nucleophilic κ^1-*O*-enolatoiron(II) complexes *trans*-FeH(OCR^{1}CHCOR^2-κ^1*O*)(DEPE)$_2$ (**1a**: R^1 = R^2 = Me, **1b**: R^1 = R^2 = OMe, **1c**: R^1 = Me, R^2 = OMe) are prepared by the reaction of Fe(N$_2$)(DEPE)$_2$ with 1,3-dicarbonyl compounds.

Transition-metal enolates have attracted considerable attention as key intermediates in chemo-, regio-, and stereospecific C–C bond forming reactions under neutral and mild conditions.[1] We previously demonstrated for the first time that zwitterionic structure of the enolato ligands in RuH[NCCHC(O)OR-κ^1*N*]-(DPPE)$_2$, and RuH(OCMeCHCOMe-κ^1*O*)(DPPE)$_2$, which is provided by strong coordination of the cyano substituent or enforced monodentate coordination of the enolate by the bidentate ligands, significantly increases the nucleophilicity of the enolato ligands playing important roles in C–C bond forming steps of Murahashi aldol and Michael reactions.[2] On the other hand, *O,O′*-chelating enolato ligand in RuH(OCMeCHCOMe-κ^2*O,O′*)(PPh$_3$)$_3$ showed no nucleophilicity at all. Thus, κ^1-*O*-enolato formulation is indispensable for these catalytic reactions. Since then, such κ^1-*O*-enolato structure is also regarded to play an important role in the catalytic reactions, but detailed spectroscopic inspections of these enolate ligands have unprecedented to date. Herein, we report synthesis, structure, and fluxional behavior of the highly nucleophilic κ^1-*O*-enolatoiron(II) complexes derived from 1,3-dicarbonyl compounds.

Treatment of Fe(N$_2$)(DEPE)$_2$[3] with 1,3-dicarbonyl compounds such as acetylacetone, dimethyl malonate and methyl acetoacetate in benzene at room temperature for 23 h gave *trans*-FeH(OCR^{1}CHCOR^2-κ^1*O*)(DEPE)$_2$ (**1a**: R^1 = R^2 = Me, **1b**: R^1 = R^2 = OMe, **1c**: R^1 = Me, R^2 = OMe) in 59, 71, and 80% yields, respectively, accompanied by evolution of molecular nitrogen in 94, 106, and 102% yields, respectively (Eq 1).[4] These complexes were characterized by IR and NMR spectroscopy, elemental analysis and X-ray analysis.



1a: R$_1$ = R$_2$ = Me (59%)
1b: R$_1$ = R$_2$ = OMe (71%)
1c: R$_1$ = Me, R$_2$ = OMe (80%)

(1)

The molecular structure of **1c** is depicted in Figure 1 showing essentially octahedral geometry at Fe.[5] The enolato ligand coordinates to the iron center by the κ^1-*O* fashion through carbonyl oxygen of the ketone moiety presumably to avoid the steric repulsion between the MeO group and four P nuclei. This is the first molecular structure of late-transition metal κ^1-*O*-enolato complex of 1,3-dicarbonyl.

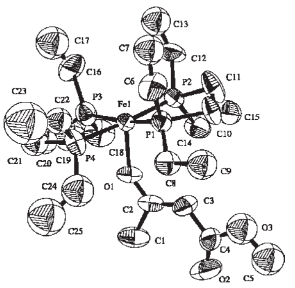


Figure 1. Molecular Structure of *trans*-FeH(OCMeCHCO$_2$Me-κ^1*O*)(DEPE)$_2$ (**1c**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

^{1}H NMR spectrum of **1b** at 80 °C (Figure 2) shows two singlets assignable to the methoxy and methine appeared at δ 3.37 (6H) and 4.03 (1H). At this temperature, a sole quintet at δ −35.90 (1H) in the ^{1}H NMR and a singlet at δ 88.59 in the ^{31}P{^{1}H} NMR are observed showing that **1b** has a hydride with four equivalent P ligands. When lowering the temperature, the methoxy signal decoalesced into two resonances suggesting the two methoxy groups being magnetically unequal. The methoxy and carbonyl resonances in the ^{13}C NMR was not observed at room temperature, probably owing to significant broadening but at −20 °C a couple of methoxy and carbonyl signals appeared at δ 48.8, 52.4, and δ 170.0, 174.8, respectively. The methine carbon appeared at δ 61.6 (s, $J_{\text{C–H}}$ = 155 Hz). These ^{13}C NMR data suggest κ^1-*O* coordination of the enolato moiety

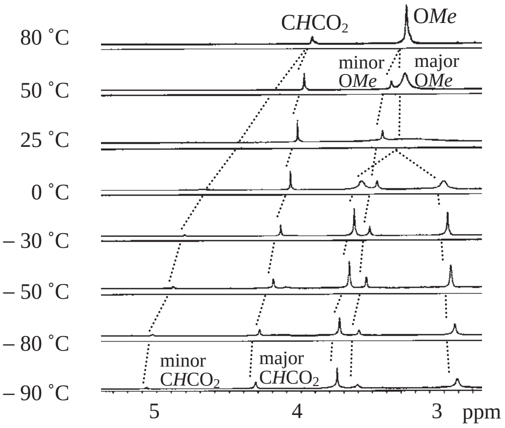
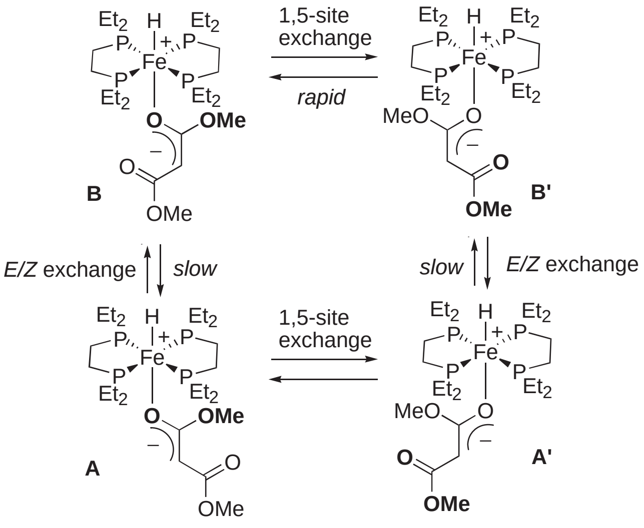


Figure 2. Variable temperature NMR spectra of **1b** in toluene-d_8.



Scheme 1. Fluxional behaviors in **1b**.

with significant contribution of oxo-π-allyl structure. Meanwhile, a set of signals attributable to the minor species was also appeared both in the ^{1}H and ^{31}P{^{1}H} NMR spectra at low temperature and the major/minor ratio was estimated as 1.0/0.13 at $-50\,^{\circ}$C.[6]

Magnetically inequivalence of two methoxy signals in the major isomer is consistent with the monodentate coordination of the enolato ligand as observed in the solid-state structure for **1c**. Coalescence of these signals at high temperature indicates apparent 1,5-site exchange of the Fe atom between two carbonyl oxygens (Scheme 1). The methoxy group in the minor isomer appeared as a singlet in this whole temperature range, suggesting involvement of rapid intramolecular site-exchange process. Thus, the minor species are assignable to a rapidly equilibrating mixture of (*Z*)-isomers **B** and **B′**. The major isomers are assigned as slowly equilibrating mixture of (*E*)-isomers **A** and **A′**. Line broadening behavior of these two processes in the VT NMR suggests that slow (*E*)/(*Z*) isomerization between **A** and **B** (and between **A′** and **B′**) takes place accompanied by fast 1,5-site exchange process as shown in Scheme 1. It should be noted that one of the methoxy resonances for the (*E*)-enolato ligand (δ 2.91 at $-90\,^{\circ}$C) and the major singlet in ^{31}P{^{1}H} NMR tend to broaden at $-90\,^{\circ}$C, while the counterpart remains sharp. These features in the ^{1}H and ^{31}P{^{1}H} NMR spectra can be accounted for by the slow rotation of the enolato ligand around the Fe–O bond, where the methoxy group close to Fe is affected by its magnetic anisotropy. Thus, the fluxional behavior of enolato complex **1b** is visualized as (a) (*E*)/(*Z*) isomerization of the enolato ligand (between **A** and **B**, and **A′** and **B′**), (b) rapid 1,5-shift of iron(II) between carbonyl oxygens, and (c) very rapid rotation of the enolate moiety around the Fe–O axis.

It is also noted that the enolato-complex **1b** (5.0 mol %) smoothly catalyzed double-Michael addition of dimethyl malonate with 2 equiv. of methyl acrylate in benzene-d_6 under neutral and mild conditions, at 30 °C for 3 h in 100% yield.

In summary we revealed the molecular structure and fluxional behaviors of κ^1-*O* enolatoiron(II) complexes having high nucleophilicity.

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References and Notes

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4 Physical and spectroscopic data for **1b** are given as an example: 71% yield. *E* isomer: ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ 89.9 (br, 4P, *DEPE*), ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ -35.44 (qui, $J_{\text{P–H}} = 48$ Hz, Fe–*H*), 0.80 (br, 12H, –*Me* (DEPE)), 1.06 (m, 4H, $\mathrm{PC}H_2$Me (DEPE)), 1.09 (br, 12H, –*Me* (DEPE)), 1.48 (m, 8H, –P($\mathrm{C}H_2$)$_2$P–, $\mathrm{PC}H_2$Me), 1.77 (m, 4H, $\mathrm{PC}H_2$Me), 2.16 (m, 8H, –P($\mathrm{C}H_2$)$_2$P–, $\mathrm{PC}H_2$Me), 3.4 (br, 6H, –O*Me*), 4.1 (s, 1H, –*C*HCO$_2$Me). ^{13}C NMR (74.45 MHz, C_6D_6, 298 K): δ 8.6 (q, $J_{\text{C–H}} = 126$ Hz, –*Me* (DEPE)), 9.2 (q, $J_{\text{C–H}} = 125$ Hz, –*Me* (DEPE)), 19.8 (t, $J_{\text{C–H}} = 128$ Hz, –P*C*H$_2$Me), 22.7 (br. t, $J_{\text{C–H}} = 118$ Hz, –P*C*H$_2$Me and P*C*$_2$H$_4$P), 61.6 (d, $J_{\text{C–H}} = 155$ Hz, –*C*HCO$_2$Me). ^{13}C NMR (74.5 MHz, $C_6D_5CD_3$, 273 K): δ 8.6 (s), 9.3 (s), 19–21 (overlapped with signals due to $C_6D_5CD_3$) 22.4 (m), 48.8 (s, O*Me*), 52.4 (s, O*Me*), 61.6 (s), 170.0 (s, *C*=O), 174.8 (s, *C*=O). *Z* isomer: ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ 87.8 (s, 4P, *DEPE*). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ -35.46 (qui, $J_{\text{P–H}} = 48$ Hz, Fe–*H*), 0.8 (obscured by the major species, –*Me* (DEPE)), 1.1 (obscured by the major species, $\mathrm{PC}H_2$Me, –*Me* (DEPE)), 1.5 (obscured by the major species, –P($\mathrm{C}H_2$)$_2$P), 1.8 (obscured by the major species, $\mathrm{PC}H_2$Me), 2.2 (obscured by the major species, –P($\mathrm{C}H_2$)$_2$P–, $\mathrm{PC}H_2$Me), 3.51 (s, 6H, –O*Me*), 4.1 (obscured by the major species, –*C*HCO$_2$Me). E. A.; Calcd for $C_{25}H_{56}O_4P_4Fe$: C, 50.01; H, 9.40%. Found: C, 50.03; H, 9.64%. IR(KBr, cm^{-1}): 1859 (*w*, $\nu_{\text{Fe–H}}$), 1688 (*s*, $\nu_{\text{C=O}}$), 1552 (s, $\nu_{\text{C=O}}$), 1072 (s, $\nu_{\text{C–O}}$).

5 Crystallographic data for **1c**: monoclinic, *Cc* (*No.* 9), $a = 10.987(7)$ Å, $b = 16.403(7)$ Å, $c = 18.326(5)$ Å, $\beta = 97.95(3)^{\circ}$, $V = 3270(2)$ Å^3, $Z = 4$, $T = 20.0\,^{\circ}$C, $D_{\text{calcd}} = 1.187$ g/cm^3, Total reflection = 4081, Unique reflection = 3742, $F_{000} = 1264.00$, $\mu = 6.78$ cm^{-1}, R (R_{w}) = 0.0746 (0.0988), GOF = 0.9.

6 Contrary to **1b**, no distinguishable isomers were detected for **1a** and **1c**.

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