

Preliminary communication

**Metal-exchange reaction on cationic diiron
 $\mu\text{-}\eta^2\text{-(C,O)}$ -enolate complexes**

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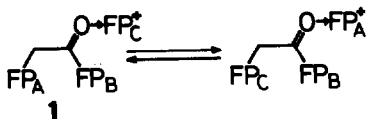
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Abstract

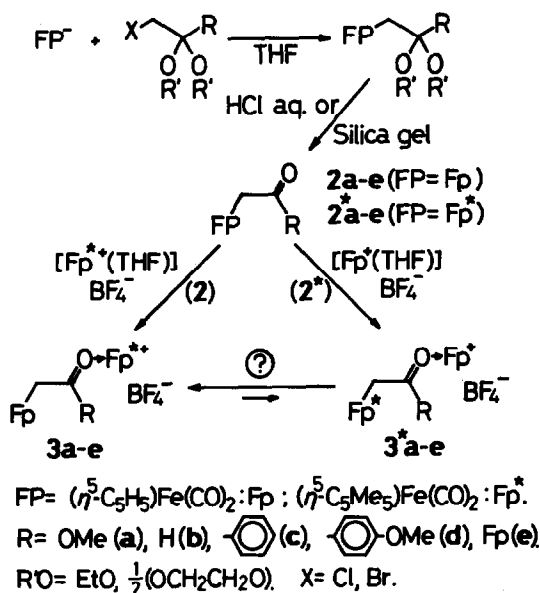
Several isomeric pairs of labeled cationic diiron $\mu\text{-}\eta^2\text{-(C,O)}$ -enolate complexes, $[\text{FP-CH}_2(\text{C}=\text{O} \rightarrow \text{FP}^+)\text{R}]\text{BF}_4^-$ [FP = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{Fp})$, $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2$ (Fp^{*}); R = OMe, H, C₆H₅, *p*-C₆H₄OMe, Fp], are prepared by the reactions of $\eta^1\text{-(C)}$ -enolate complexes $\text{FP-CH}_2(\text{C}=\text{O})\text{R}$, with $[\text{FP}^+(\text{THF})]\text{BF}_4^-$. An intramolecular metal-exchange reaction between the two FP groups bonded to the enolato ligand is observed for those containing electron-releasing substituents (R) such as aromatic or Fp group.

Sufficient development of the chemistry of transition metal enolates will lead to a new phase in organic synthesis, because the combination of their two potential reactivities, i.e. condensation at the enolate moiety with polar substrates such as organic carbonyl compounds and ligand insertion reactions with nonpolar substrates such as olefins, acetylenes and carbon monoxide, provides novel tools for highly selective C–C bond formation [1].

During our study of the chemistry of cationic trinuclear $\mu_3\text{-}\eta^3\text{-(C,C,O)}$ -ketene complexes (1), the labeling experiments indicated that the iron center bonded to the



methylene terminus (FP_A) is exchanged with that bonded to the acyl oxygen atom (FP_C) of the ketene ligand via an intramolecular process [2]. Since the local structure around FP_A in 1 is regarded as $\eta^1\text{-(C)}$ -enolate complex, the observed phenomenon is closely related to the reaction mechanism of transmetalation of the enolato ligand. To find out whether the third iron group (FP_B) is essential to the metal exchange reaction, we prepared several isomeric pairs of labeled diiron $\mu\text{-}\eta^2\text{-(C,O)}$ -enolate complexes (3 and 3^{*}) containing various substituents at the acyl carbon atom, and studied their reactions (Scheme 1).



Scheme 1.

The starting η^1 -(C)-enolate complexes (**2** and **2***) were prepared in 30-80 % yields by alkylation of ferrates, FP^- [$\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$; $\text{Fp}^* = (\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2$] [3], with acetals of various α -haloketones followed by acidic hydrolysis according to the Rosenblum's method [4,5*]. Owing to the "β-effect" [6] $\nu(\text{C}=\text{O})$'s were observed at lower frequencies by ca. 70 cm^{-1} compared with those of the corresponding methyl ketones (CH_3COR). The electron-donating ability of organic substituents (R) to the $>\text{C}=\text{O}$ group increases in the order: OMe (**a**) < H (**b**) < C_6H_5 (**c**) < *p*- $\text{C}_6\text{H}_4\text{-OMe}$ (**d**) < Fp (**e**), as estimated from the red shift of $\nu(\text{C}=\text{O})$ and the downfield shift of $\delta(\text{C}=\text{O})$ (Table 1).

The ligand exchange reaction of the labile cationic iron complexes, $[\text{FP}^+(\text{THF})]\text{BF}_4^-$ [8], with **2** or **2*** proceeded during 1-2 h in dichloromethane to give the first examples of dinuclear μ - η^2 -(C,O)-enolate complexes (**3** and **3***) as deep red crystals or oils (40-60 % yields). The shift of the $\nu(\text{C}=\text{O})$ to lower energies by ca. 100 cm^{-1} indicates the coordination of the $>\text{C}=\text{O}$ group to a Lewis acid (Table 1). While the adducts (**3a**, **3*b** and **3*a**, **3*b**) were isolated as isomerically pure forms, only one isomer, **3**, was ultimately observed for c-e series irrespective of the starting complexes. Primary products **3*c**-**3*e** could not be isolated pure but were observed by spectroscopic methods. When the reaction was monitored by ^1H NMR spectroscopy, the isomerization of **3*e** to **3e** was complete within 2 h but it took more than 12 h in the cases of **3*c** and **3*d**. The isomerization was further confirmed by the treatment with PPh_3 which removes the FP group from $>\text{C}=\text{O}$. The reactions of equilibrated mixtures obtained from **3c**-**3e** and **3*c**-**3*e** gave **2c**-**2e** as sole products. Thus, introduction of electron-releasing substituents brings about the metal-exchange reaction on the cationic diiron μ - η^2 -(C,O)-enolate com-

* Reference marked with an asterisk indicates a note in the list of references.

Table 1

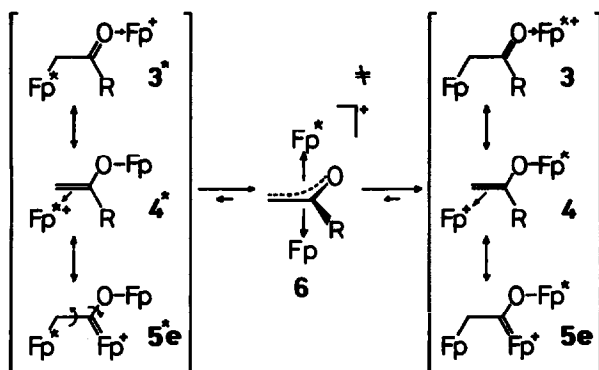
IR and ^{13}C -NMR data for the C=O of the enolate complexes **2**, **2***, **3** and **3***.

R	$\nu(\text{C=O}) / \text{cm}^{-1}$ ^a [$\delta(\text{C=O}) / \text{ppm}$] ^b				
	2	3	Exchange reaction ($t_{1/2}$) ^c	3*	2*
MeO (a)	1675	1562 [197.9]	No	1560 [199.2]	1677 [183.1]
H (b)	1650 [201.3] ^d	1558 [208.1]	No	1546 [206.6]	1641 [199.1]
C_6H_5 (c)	1621	1521 [220.4]	Yes (5 h)	–	1618 [204.9]
<i>p</i> - C_6H_4 -OMe (d)	1616 [205.0]	1514 [220.0]	Yes (3 h)	–	1619 [204.1]
Fp (e) ^e	1612 ^f [253.3] ^f	1443 [295.5]	Yes (0.5 h)	–	1607 [250.6]

^a Observed in CH_2Cl_2 . ^b Observed in C_6D_6 (**2** and **2***) and in CDCl_3 (**3** and **3***). ^c Approximate half-lives of **3*** in CD_2Cl_2 solutions ($[\text{3}^*] = \text{ca. } 0.4 \text{ M}$) at 24°C . ^d ref. 7 (in CDCl_3). ^e Fp = $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2$. ^f ref. 5. Satisfactory spectral and analytical data were obtained for all the isolated complexes.

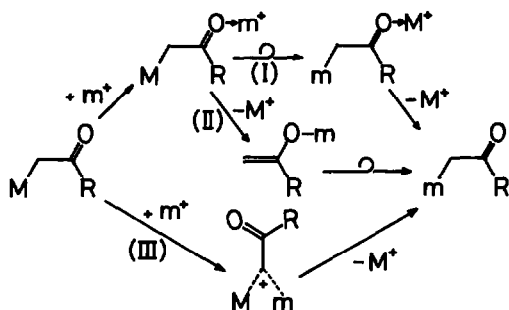
plexes, and the equilibrium lies towards **3** in which the methylene carbon is bonded to the Fp group rather than the Fp* group.

On the assumption that there is a transition state such as **6** which is an oxa-analogue of the structurally characterized diiron μ -allyl complex, $[(\text{Fp-CH}_2\text{CH=CH}_2)\text{Fp}^+]\text{BF}_4^-$ [**9***], and by considering possible resonance forms, **4** and **5** (Scheme 2), these results may be interpreted as follows: (i) Electron-releasing substituents increase donation from the bridging enolato (oxaallyl) ligand to both metal centers and consequently stabilize **6**. (ii) Additional oxycarbene resonance forms (**5e** and **5*e**) cause drastic changes in $\nu(\text{C=O})$ and $\delta(\text{C=O})$, and rotation around the C–C and C–O bonds facilitates successive transformation to **6**. It is difficult for normal organic substituents to cause π -electron delocalization to the extent brought about by Fp. (iii) The main factor which determines the equilibrium is thought to be the stronger π -interaction in **4** in which the more Lewis acidic metal



Scheme 2.

center (Fp) is coordinated by the more electron-donating vinyl ether ligand bearing the Fp* group. The observed tendency is consistent with that of the transmetalation of alkyl ligands ($MR + mX \rightarrow mR + MX$: M is more electropositive than m) [10]. Hence, path I is proposed as one of possible reaction pathways for the transmetalation of the η^1 -(C)-enolato ligand (Scheme 3).



Acknowledgement

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References

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