Preparation and Intramolecular Metal-exchange Reaction of Cationic Trinuclear μ_3-η^3-(C,C,O)-Ketene Complexes

Munetaka Akita,* Takashi Kawahara, and Yoshihiko Moro-oka*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Co-ordination of the acyl oxygen atom in a di-iron μ_2-η^2-(C,C)-ketene complex, Fp–CH_2CO–Fp [Fp = (η^5-C_5H_5)Fe$(CO)_2$] to Lewis acidic organometallic centres produces cationic trinuclear μ_3-η^3-(C,C,O)-ketene complexes, the two metal components of which exchange with each other *via* an intramolecular process.

We have previously[1] described an indirect preparative method for a variety of heterobimetallic μ_2-η^2-(C,C)-ketene complexes, Fp–CH_2CO–ML_n [Fp = (η^5-C_5H_5)Fe$(CO)_2$]. Increased nucleophilicity of the acyl oxygen atom as judged by the shift of ν(C=O) prompted us to attempt to introduce a third metal component, producing trinuclear μ-ketene complexes.[2]

Treatment of a di-iron μ-ketene complex, Fp–CH_2CO–Fp (**1**), with an iron cation, [Fp^+(thf)]BF_4^- (**2**),[3] in dichloromethane for 3 h at 25 °C afforded deep purple red microcrystals (**3**) (65%) after recrystallization from Et_2O–CH_2Cl_2 (Scheme 1). N.m.r. spectra (^1H and ^{13}C) show that (**3**) contains three non-equivalent Fp groups and a μ-ketene bridge.† In particular, a quaternary carbon signal at δ 297.46 indicates the presence of an oxycarbene structure[4] similar to that in a dinuclear methoxycarbene complex, Fp–$CH_2C(OMe)$=Fp^+ $CF_3SO_3^-$ (δ 299.07).[5] These spectral features reveal that (**3**) is a cationic trinuclear μ_3-η^3-(C,C,O)-ketene complex, with the largest contribution from an oxycarbene structure (**4**) [see possible resonance forms (**3**)—(**5**)]. Addition of a slight excess of PPh_3 to a CH_2Cl_2 solution of (**3**) regenerated (**1**) accompanied by [$Fp^+(PPh_3)$]BF_4^- in quantitative yield.

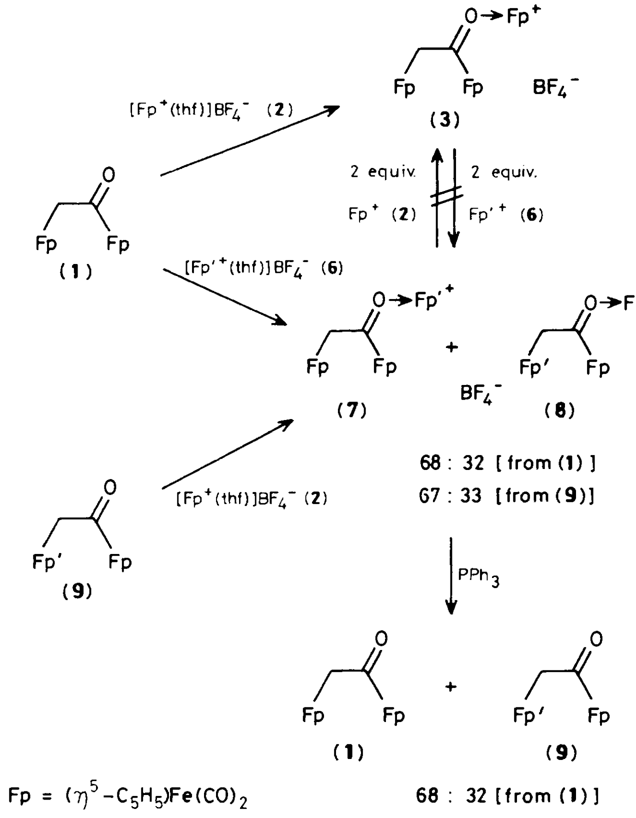
When the complex (**1**) was similarly treated with a 'labelled' cation, [Fp'^+(thf)]BF_4^- (**6**) [Fp′ = (η^5-C_5H_4Me)Fe$(CO)_2$], a mixture of two isomeric tri-iron μ-ketene complexes, (**7**) and (**8**), was obtained in 68:32 ratio as revealed by n.m.r. analyses‡ (Scheme 1). Spectra recorded during the reaction indicated that (**7**) was formed initially, and that the isomer (**8**) was formed subsequently, presumably *via* an exchange reaction§ between Fp_A and Fp_C on the ketene skeleton. The

---

† For (**3**), δ_H (CD_2Cl_2) 2.44 (2H, s, CH_2), and 4.89, 5.07, and 5.30 (5H × 3, s, 3cp); δ_C (CD_3NO_2) 33.33 (CH_2), 88.18 (2cp), 88.76 (cp), and 213.10, 215.44, and 217.50 (CO).

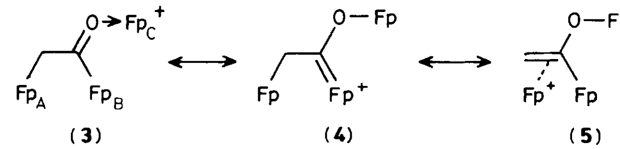
‡ For (**7**), δ_H (CD_2Cl_2) 1.85 (3H, s, Me), 2.45 (2H, s, CH_2), and 4.92 and 5.05 (5H × 2, s, cp); δ_C (CD_3NO_2) 12.85 (Me), 34.50 (CH_2), 213.74, 215.98, and 217.69 (CO), and 297.90 (carbene); for (**8**) δ_H (CD_2Cl_2) 1.94 (3H, s, Me), 2.34 (2H, s, CH_2), and 4.89 and 5.31 (5H × 2, s, cp); δ_C (CD_3NO_2) 13.53 (Me), 36.91 (CH_2), 213.47, 215.82, and 218.17 (CO), and 296.63 (carbene). Other signals cannot be resolved owing to overlapping.

§ Di-iron complexes joined by μ_2-η^3-allyl ligands such as [$FpCH_2CH$=CH_2]Fp^+ BF_4^- have been reported to be fluxional. The higher exchange barrier observed for (**7**) and (**8**) as compared with such systems is presumably caused by the requirement of activation of a σ-co-ordinated C=O group to a π-co-ordinated C=O prior to isomerization.[6]

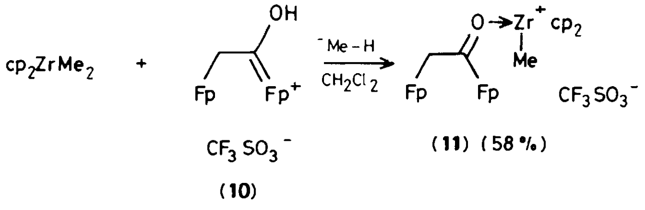


Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$
Fp′ = $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2$

Scheme 1



isomerization was further confirmed by addition of PPh_3, producing a 68:32 mixture of (**1**) and (**9**), identified by comparison with authentic samples.[7] This result also reveals that PPh_3 attacks Fp_C, co-ordinated by the acyl oxygen atom. On the other hand, the reaction of the 'labelled' μ-ketene complex (**9**) with (**2**) afforded a mixture of two isomers of similar composition [(**7**):(**8**), 67:33] and the action of PPh_3 produced (**1**) and (**9**) in 67:33 ratio (Scheme 1). Furthermore, when the isolated tri-iron complexes (**3**) and (**7**) + (**8**) were treated with 2 equiv. of the iron cations (**6**) and (**2**), respectively, in CH_2Cl_2 for 12 h, incorporation of the externally added cation into the trinuclear system occurred to only a small extent¶ (Scheme 1). Thus, it is concluded that the metal-exchange reaction follows an intramolecular process and finally attains equilibrium. Since (**3**) and (**5**) are formally regarded as a co-ordination complex of metal *C*-enolate[8] and a π-complex of a metal *O*-enolate,[9] respectively, trinuclear



μ-ketene complexes may be regarded as intermediates in the interconversion of *C*- and *O*-enolates.[10—12]

The heteronuclear μ_3-η^3-(C,C,O)-ketene complex (**11**) was also accessible by an alkane elimination reaction between cp_2ZrMe_2 (containing polar M–C bonds) and a hydroxycarbene complex (**10**),[5] a conjugate acid of (**1**). The zirconoxycarbene carbon resonance (δ 312.99),** appearing 15 p.p.m. to lower field than that of (**3**), indicates the increased contribution of an oxycarbene structure due to the oxygenophilicity of Zr.

These results suggest that an oxycarbene structure like (**4**) should be taken into account when discussing the reactivity of ketene species generated on a heterogeneous catalyst system consisting of a transition metal component and acidic support such as Rh/ZrO_2, which is known to catalyse selective conversion of syngas to C_2-oxygenates;[13] it is probable that the oxycarbene species pivots around the metal–carbene bond. We are now studying the introduction of other metal cations and attempting to elucidate the exchange reaction mechanism.

We are grateful to the Asahi Glass Foundation for Industrial Technology and the Ministry of Education, Science, and Culture for financial support.

Received, 16th March 1987; Com. 329

References

1 M. Akita, A. Kondoh, and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1986, 1296.
2 J. S. Holmgren, J. R. Shapley, S. R. Wilson, and W. T. Pennington, *J. Am. Chem. Soc.*, 1986, **108**, 508.
3 S. J. LaCroce and A. R. Cutler, *J. Am. Chem. Soc.*, 1982, **104**, 2312.
4 C. P. Casey, W. H. Miles, and H. Tukada, *J. Am. Chem. Soc.*, 1985, **107**, 2924.
5 M. Akita, A. Kondoh, T. Kawahara, and Y. Moro-oka, *J. Organomet. Chem.*, 1987, **323**, C43.
6 W. Priester, M. Rosenblum, and S. B. Samuels, *Synth. React. Inorg. Met.-Org. Chem.*, 1981, **11**, 525.
7 M. Akita, A. Kondoh, T. Kawahara, T. Takagi, and Y. Moro-oka, *Organometallics*, submitted for publication.
8 E. R. Burkhart, J. J. Doney, R. G. Bergman, and C. H. Heathcock, *J. Am. Chem. Soc.*, 1987, **109**, 2022.
9 M. D. Curtis, S. Thanedar, and W. M. Butler, *Organometallics*, 1984, **3**, 1855.
10 S. S. Labadie and J. K. Stille, *Tetrahedron*, 1984, **40**, 2329.
11 M. Kawanisi, S. Kozima, K. Kobayasi, and T. Hitomi, *Rep. Asahi Glass Found. Ind. Technol.*, 1984, **44**, 109.
12 K. Kobayashi, M. Kawanisi, T. Hitomi, and S. Kozima, *Chem. Lett.*, 1984, 497.
13 G. S. Ferguson and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1986, **108**, 8293, and references cited therein.

¶ The extent of incorporation was determined after conversion of the reaction mixture into (**1**) and (**9**) with PPh_3. The reaction of (**3**) led to the formation of (**1**) and (**9**) in 96:4 ratio, and the reaction of a 66:34 mixture of (**7**) and (**8**) gave (**1**) and (**9**) in 68:32 ratio.

** For (**11**), δ_H (CD_3NO_2) 0.50 (3H, s, Me–Zr), 2.95 (2H, s, CH_2), 5.15 (10H, s, 2cpFe), and 6.38 (10H, s, cp_2Zr); δ_C (CD_3NO_2) 31.47 (Me), 33.39 (CH_2), 88.12, 89.04 (2cpFe), 114.12 (cp_2Zr), and 214.69 and 217.86 (CO).