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Preliminary communication

CONVERSION OF A DIIRON μ-KETENE COMPLEX, $FpCH_2COFp$ ($Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$), INTO BINUCLEAR CATIONIC OXYCARBENE COMPLEXES AND THEIR BIMODAL REACTIVITIES

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Summary

Reactions of a bimetallic μ-ketene complex, $FpCH_2COFp$, with electrophiles take place at the acyl oxygen atom to give cationic binuclear oxycarbene complexes. Bifunctionality of their cationic enol ether structure permits subsequent transformation both with nucleophiles and electrophiles.

Activation of a ketene molecule by metal coordination has long been studied and a variety of coordination modes have been revealed, e.g. mono- and polynuclear; η^2-(C,C)-, η^2-(C,O)- and μ_3-η^3-(C,C,O)-coordination [1,2,3]. However, reactivities of the ketene fragment in such systems hitherto examined are usually limited to C–C or C–O bond scission and degradation to C_2 oxygenates such as acetaldehyde and alkyl acetates [1]. Considering the expected role of the ketene unit in catalytic CO hydrogenation, it would be worthwhile to show the versatility of ketene ligand as a possible origin of various oxygenated functional groups. Herein we describe cationic activation of a μ-ketene complex, $FpCH_2COFp$ **1** *, and subsequent transformations to various C_2 products [4]. This work and the study on trinuclear osmium cluster, independently investigated by Geoffroy et al. [5], reveal the general reactivity of polynuclear μ-ketene complexes.

Treatment of a μ-ketene complex **1** with electrophiles (ROTf) ** in CH_2Cl_2 solution for 5 min (R = H and $SiMe_3$) –2 h (R = Me) afforded cationic oxycarbene complexes **2** (R = Me, 93%), **3** (R = H, 12%) and **4** (R = $SiMe_3$, 84%) as orange crystals after recrystallization from Et_2O/CH_2Cl_2 [6,7] (Scheme 1). Their structures

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

** $TfO = CF_3SO_3$.

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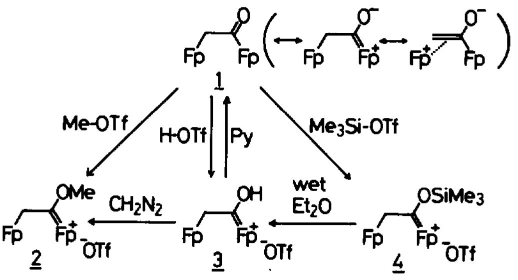
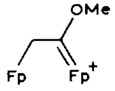
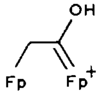
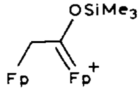
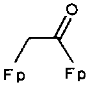
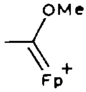
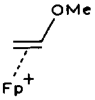


Fp= (η^5-C_5H_5)Fe(CO)$_2$, TfO= CF_3SO_3.

SCHEME 1.

TABLE 1

SELECTED ^{13}C NMR AND IR DATA OF BINUCLEAR OXYCARBENE COMPLEXES

Complex	^{13}C NMR (δ/ppm) [a]		IR (cm^{-1}) [a]
	CH_2	$\underset{\vert}{=\mathrm{C}}-\mathrm{O}$	ν(C≡O)
 (2)	30.14	299.07	2053, 2025, 1998, 1981
 (3)	32.24	302.74	2051, 2021, 1995, 1979
 (4)	36.50	305.25	2051, 2024, 1994, 1978
 (1)	29.62	259.00	2016, 1999, 1959, 1950
 (5)	46.81	334.30	2066, 2018
 (6)	26.44	147.13	2065, 2021

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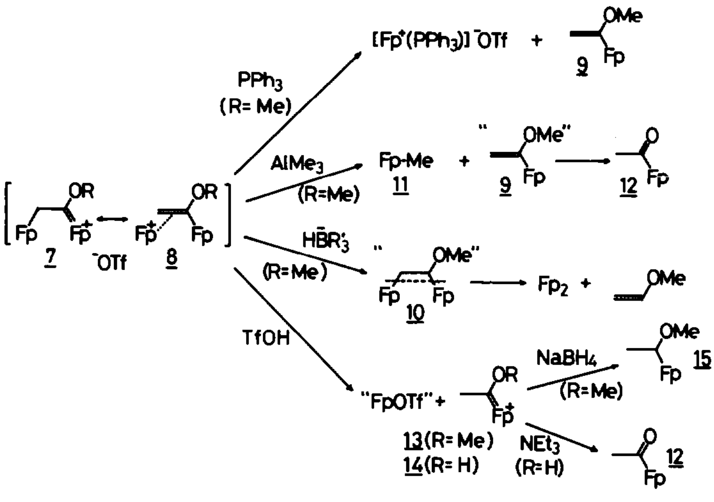
[a] ^{13}C NMR and IR spectra were recorded in CD_2Cl_2 and CH_2Cl_2, respectively, except **1** (^{13}C NMR in $CDCl_3$). All counter anions were trifluoromethanesulfonate (TfO$^-$).



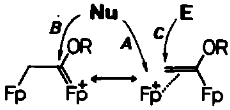
SCHEME 2.

were confirmed by ^{13}C NMR signals appearing around 300 ppm (Table 1), which shifted from the mononuclear α-alkoxycarbene region (5) [8] toward the methine carbon region of cationic vinyl ether complex **6** by ca. 30 ppm but were still in lower field compared with the acyl-carbon signal of **1**. In addition, ν(C≡O) absorptions shifted to frequencies higher than those of **1** (Table 1), and ν(C=O) absorption of the ketene linkage disappeared. These spectral features reveal that the electron-donating, alkyl-side Fp group brings about delocalization of the positive charge over the two iron centers [1,5]. Increased contribution of a π-complex (**8**) [1] was demonstrated by immediate liberation of an α-methoxyvinyl complex **9** [9] promoted by the action of PPh_3 (Scheme 2).

Although the three oxycarbene complexes obtained were thermally stable, the siloxycarbene complex **4** was very sensitive to moisture and was readily desilylated to the hydroxycarbene complex **3** (72% from **1**) in wet ether. Its OH group turned out to be so acidic that **3** was neutralized by pyridine to regenerate **1** in a quantitative yield, and was converted to the methoxy analogue **2** (68%) by treatment with diazomethane (Scheme 1).

Reflecting its cationic character, the ketene part in the methoxycarbene complex **2** was expected to show enhanced reactivity toward nucleophiles compared with that of the parent complex **1**, which was reduced by strong hydridic reagents with difficulty to give C_3 products [1]. When **2** was subjected to reduction with various borohydride reagents ($NaBH_4$, $LiHBEt_3$, $NaBH_3CN$ etc.), Fp_2 and methyl vinyl ether (an enol ether of acetaldehyde) were liberated in > 90% yields, even at −78°C, perhaps through a transient μ-methoxyethylene complex **10**, which may arise from initial hydride atttack at the cationic carbene center in structure **7** [6] (Scheme 2). When **2** was treated with an alkylating agent such as trimethylaluminum, nucleophilic attack took place at the alkyl-side Fp to give a methylated product **11** and an acetyl complex **12**, actually a hydrolyzed product of α-methoxyvinyl complex **9**.

On the other hand, the enol ether part in structure **8** suffered successive electrophilic attacks at the methylene terminus. Protonation (2–3 equiv. TfOH) of **2**



SCHEME 3.

and **3** in CH_2Cl_2, during 12 h gave mononuclear α-oxyethylidene complexes **13** and **14**, which were characterized by comparison of their ^1H NMR and IR spectral data with those of authentic samples, and by subsequent conversion to the isolable forms **15** and **12**, respectively [6,7,8] (Scheme 2).

Thus, owing to their unique structure, reaction of the binuclear cationic alkoxycarbene complexes occurs with soft nucleophiles such as phosphine and alkylaluminum at the alkyl-side Fp (path *A*), with hard nucleophiles such as hydride at the carbene center (path *B*), and with electrophiles at the methylene terminus (path *C*) [5] (Scheme 3). Consequently, cationic activation of the ketene ligand in **1** serves as a template for producing C_2 functional groups [10] such as acetaldehyde and **9–15**, of which further transformations to ethyl, ethylidene and ethylene complexes have been previously reported [6,11].

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