REACTIVITIES OF KETENE LIGANDS ON POLYMETALLIC SYSTEMS

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Summary

Heterobimetallic $\mu \cdot \eta^2 \cdot (C,C) \cdot [M_1 - CH_2CO - M_2]$ and trimetallic $\mu_3 \cdot \eta^3 \cdot (C,C,O)$ -ketene complexes $[M_1 - CH_2(C=O \rightarrow M_3) - M_2]$ $(M_1 = Fe; M_2 = Fe, Ni, Mo, Co, Mn; M_3 = Fe, Zr)$ have been prepared as models for surface-bound ketene species responsible for the production of oxygenated organic compounds in the catalytic hydrogenation of carbon monoxide. Spectroscopic, electrochemical and crystallographic analyses have revealed cooperative metal-to-ketene ligand back-donation, although no interaction between the metal centers was detected. The bridging ketene ligand may be converted to various C_2 oxygenated functional groups via cationic oxycarbene complexes $[M_1 - CH_2C(OR) = M_2^+]$, and consequently the ketene species may act as C_2 templates in the actual catalytic reactions.

Results and discussion

Preparation and structural characterization of polymetallic μ -ketene complexes [1]

Heterobimetallic $\mu \cdot \eta^2 \cdot (C,C)$ -ketene complexes (1), dinuclear oxycarbene complexes (2) (the cationically activated form of 1) and trinuclear $\mu_3 \cdot \eta^3 \cdot (C,C,O)$ -ketene complexes (3) were prepared according to Scheme 1 [2].

A number of resonance structures including the ionic forms **B** and **C** in addition to the canonical forms **A** are available for each complex as shown in the scheme. The resonance contributors **B** and **C** arise respectively from back-donation of d-electrons from the alkyl-linked (M_1) and acyl-linked metal atoms (M_2) to the bridging ketene ligands. The extent of the contribution from **B** and **C** can be estimated from the following analyses.

The ¹³C NMR chemical shifts of the acyl carbon atoms of 1A $(M_1 = M_2 = Fp)$, 2A $(M_1 = M_2 = Fp)$, and the mononuclear complexes possessing the partial structures 1A and 2A are summarized schematically in Fig. 1 together with the v(C==O) data (peak values in parentheses). The acyl carbon of 1A appears in the same region as that of the acetyl complex 5 (the mononuclear counterpart of 1A and 1B) and removed from the aldehyde



Fig. 1. Comparison of ¹³C NMR and IR spectral data [δ (C=O) (ppm); v(C=O) (cm⁻¹)].

complex 6 (the mononuclear counterpart of 1A and 1C). ¹³C NMR spectroscopy reveals only the contribution of 1B. However, ¹³C NMR is less sensitive to the electronic state of the >C=0 part of the molecule than IR spectroscopy. For example, while the v(C=0) values for 6 and acetaldehyde are almost the same, the difference in v(C=0) values amounts to 75 cm⁻¹. The IR chart of 1A is reproduced in Fig. 2. Of the four CO stretching vibrations, two of the absorptions are assignable to the v(C=0) values of M_1 and M_2 (=Fp) when compared with those of the methyl and the acetyl complexes 5. These agreements imply that both metal centers exist as mononuclear electronic states, *i.e.* no interaction is observed between metal centers linked by the ketene ligand. On the other hand, v(C=0) for the ketene ligand is observed at lower energies by 35 cm⁻¹ in comparison to that



Fig. 2. IR chart of Fp-CH₂CO-Fp (1A).

of 5. The red shift of v(C=0) of the acyl complex of ca. 50 cm⁻¹ compared with normal organic carbonyl compounds is interpreted as arising from the oxycarbene resonance form corresponding to 1B [3]. The additional shift (Δv) observed for 1A could be caused by the contribution of the π -complex form 1C. A similar red shift has been observed for other heterobimetallic μ -ketene complexes.

The contribution of 1C is also demonstrated by X-ray crystallographic analyses [4]. An ORTEP drawing of 1A is reproduced in Fig. 3, while the structural parameters associated with the bridging ketene ligand are summarized in Table 1. These data show that the structure of 1 may be described primarily as an acyl complex 1A with a major contribution from 1B in accordance with the spectroscopic analyses.



Fig. 3. An ORTEP drawing of Fp-CH₂CO-Fp (1A).

Fe-C(1)-C(2)-M 0						
Complex ^a	FeC(1)	C(1)—C(2)	C(2)—O	C(2)—M	θ	
Fp-CH ₂ CO-Fp	2.07	1.48	1.22	2.01	75	
Fp-CH ₂ CO-NiCp(CO)	2.08	1.48	1.20	1.94	87	
Fp-CH ₂ CO-Mn(CO) ₅	2.08	1.48	1.21	2.17	63	
Fp-CH ₂ CH ₂ CO-Fp	2.07	1.54	1.20	2.00	78	

TABLE 1 Structural parameters for μ -ketene complexes (1)

*Bond lengths in Å; bond angles in degrees.

On comparison with the reference complex $Fp-CH_2CH_2CO-Fp$, which has no resonance form corresponding to 1C, the C(1)-C(2) bonds are substantially shortened and the C(2)-O bonds are slightly elongated, the latter being a reflection of the existence of 1C. The overall conformation of the $M_1-CH_2CO-M_2$ section of the molecule is determined by 1C so that the overlap between the electron-rich Fe-CH₂ bond and the electron-deficient p-orbital projecting perpendicular to the O-C(2)-C(1) plane is maintained at a maximum value. (The dihedral angles (θ) between the $M_1-C(1)-C(2)$ plane and the O-C(2)-C(1) plane lie in the range 64 - 88°.)

To check the possibility that carbonylation may be catalyzed by oxidants [5] (vide infra), the electrochemical properties of the heterobimetallic μ -ketene complexes (1) have been examined by cyclic voltammetry (CV). The cyclic voltammogram of 1A obtained in acetonitrile at -20 °C (Fig. 4) contains two anodic waves $(E_{pa1} = 0.31 \text{ V}, E_{pa2} = 0.94 \text{ V})$ and one cathodic wave $(E_{pc} = -1.1 \text{ V})$ over the range 1.1 - 1.4 V [versus Ag/Ag⁺: all the CV values were measured using Ag wire as a pseudoreference electrode [6] with the $E_{\rm p}$ values being converted to the more general Ag/Ag⁺ system; $E_{\rm p}({\rm Ag}/{\rm Ag})$ Ag^+) = $E_p(Ag \text{ wire}) - 0.44 \text{ V}]$. The E_{pa} values of 1A are compared with those of the mononuclear complexes FpMe (5) and (6) since the E_{pa2} value of 1A and the E_{pa} values of 6 were irreversible under the measurement conditions employed. Since the E_{pa2} value appears in the same voltage region as the E_{pa} values of 6, E_{pa1} and E_{pa2} have been tentatively assigned to the anodic waves of the acyl metal center (M_2) and the alkyl-linked metal center (M_1) , respectively. However, the fact that the oxidation of M_1 is preceded by that of M_2 which possesses a more electron-withdrawing acyl ligand seems curious. To confirm these assignments we have also examined the CV values of the diiron μ -ketene complexes labeled as Fp^{*}[†]. The E_{pa1} values of 1A and 1B and the E_{pa2} values of 1B and 1C appear in the same voltage region (Fig. 4). Since the common structures of 1A and 1B, and of 1B and 1C are CH_2CO-Fp

[†]We have not, as yet, succeeded in preparing Fp--CH₂CO--Fp*.



Fig. 4. Cyclic voltammetry charts for 1A - C (measurement conditions: acetonitrile at -20 °C; Ag wire pseudo-reference electrode; $[1] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ $[Bu_4 \text{NPF}_6] = 0.15 \text{ mol dm}^{-3}$; sweep speed = 200 mV s⁻¹).

and Fp^* — CH_2CO , respectively, the E_{pa1} and E_{pa2} values may be attributed to oxidation of M_2 and M_1 . Similar results may be obtained for other heterobimetallic μ -ketene complexes, although in those cases the corresponding peaks may be somewhat broad. The E_p values are summarized in Table 2.

These results may be interpreted by taking 1C into account. While the $Fp-CH_2$ part of the molecule can apparently be regarded as an alkyl complex, the electron density at the metal center is less relative than that of the acetyl complex because of the existence of 1C. The latter plays an important

TABLE 2	
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Comparison of the E_p values (V) of μ -ketene complexes (1) and similar heterobimetallic complexes^a

Complex	$E_{ m pa2}$	$E_{\rm pa1}$	<i>E</i> _{pc}	$E_{\rm pa}({\rm M}-{\rm COCH}_3)$
Fp-CH ₂ CO-Fp (1A)	0.94	0.31	-1.1	0.72 (Fp)
$Fp^{*}-CH_{2}CO-Fp$ (1B)	0.71	0.35	-1.1	
Fp*CH2COFp* (1C)	0.66	0.11	1.39	0.53 (Fp*)
Fp-CH, CO-NiCp(CO)	0.64	0.36	0.83	0.80
Fp-CH ₂ CO-MoCp(CO) ₂ (PPh ₃)	ь	0.12	-0.59	0.28
Fp-CH ₂ CO-Co(CO) ₃ (PMe ₂ Ph)	1.04	0.54	1.16	0.71

^aE_p(V): FpMe [0.53], Fp-CH₂CHO (6) [1.01], Fp*-CH₂CHO [0.70].

^bDecomposed.

role in one-electron oxidation, although, until now, the contribution of **1C** has only been detected via small additional changes in the IR spectral data and molecular structure. Labeling experiments have also shown that no interaction occurs between the two metal centers even after one-electron oxidation.

The cathodic wave $(E_{\rm pc})$ of 1A which disappears on reverse sweep (initial reduction) is apparently coupled with $E_{\rm pa1}$ on the basis of the linear relationship between $\Delta E (E_{\rm pc} - E_{\rm pa})$ and the scan speed [7]. While reduction of a 19e intermediate Fp—CH₂CO—Fp⁺(NCMe) (8) [6] or of a 17e α -ketoacyl intermediate Fp—CH₂CO—CO—Fe⁺Cp(CO)(NCMe) (9) [8] might be possible to evaluate $E_{\rm pc}$, attempts to observe or isolate the associated intermediate were unsuccessful.

Structural characteristics similar to those present in our system have been observed generally for μ - η^2 -(C,C)-ketene complexes reported previously by other research groups, with a few exceptions [2c]. Thus, it is essential to consider the significant contribution of **1C** in addition to **1B** in discussing the reactivities of bridging ketene ligands. As a result, the acyl oxygen atom experiences substantial nucleophilic activation through cooperative metal-toligand back-donation. In fact, reactions with organic and organometallic electrophiles readily take place at the acyl oxygen atom to produce the adducts 2 and 3 shown in Scheme 1. Disappearance of v(C=0) absorptions in the IR spectrum in the range $1700 - 1400 \text{ cm}^{-1}$ and of acyl carbon signals appearing in the very low field region of the NMR spectrum [δ (C=O) for 3 occurring at 290 - 300 ppm] indicate the formation of O-C and O-M bonds with considerable covalency and an enhanced electrophilic carbene character. On the basis of comparison of the v(C=0) values with those for 4 (the mononuclear counterpart of 2B and 3B) and 7 (the mononuclear counterpart of 2C and 3C) (Fig. 1), the structures of 2 and 3 may be described primarily in terms of the oxycarbene complexes 2B and 3B incorporating fairly large contributions from 2C and 3C, which is demonstrated unequivocally by the upfield shift of δ (C=O) by ca. 30 ppm as a result of 7. The corresponding $v(C \equiv 0)$ absorptions for 2 and 3 which appear between those for the neutral and cationic mononuclear complexes also indicate that the positive charge is widely delocalized over a number of metal centers.

Reactivities of ketene ligands relevant to the catalytic hydrogenation of carbon monoxide [2a]

Decarbonylation

Interconversion between the μ -ketene complex and a μ -methylene complex has been reported in some instances occurring via a decarbonylation or carbonylation process [1]. Although we have attempted the decarbonylation of 1 under a variety of reaction conditions [photolysis, thermolysis and reaction with RhCl(PPh₃)₃ (an effective decarbonylating agent)], we have failed to obtain the μ -methylene complex but rather elimination of the ketene molecule (actually trapped as an acetate ester in quantitative yields in the presence of alcohol) was observed where $M_2 = Fe$ or Ni.

Carbonylation

Carbonylation of 1 has also been attempted under various reaction conditions, for example (i) under CO pressure at elevated temperatures, (ii) under an atmosphere of CO in the presence of a catalytic amount of oxidant $([Cp_2Fe]^+)$ or Lewis acid (AlX₃) and (iii) reaction with PR₃ in refluxing acetonitrile. Irrespective of the reaction conditions employed, no indication of the formation of a μ -malonyl complex was obtained.

In order to evaluate the migration ability of the ketene ligand, we have studied the oxidative alcoholysis of the μ -ketene complexes (1). The results obtained are summarized in Table 3. In each case, the Fe—CH₂ bonds were directly cleaved by bromine without CO insertion and only trace amounts of the malonate ester were obtained. These results can be interpreted in terms of decreased nucleophilicity at the migrating center (CH₂) caused by the adjacent electron-withdrawing group (C=O). Electrochemical analyses (vide supra) indicate that oxidizing agents do not catalyze the migration of the methylene group to give a malonyl complex nor a malonate ester [5] because the acyl-linked metal centers are oxidized first.

Reduction

Although 1 was unaffected by dihydrogen even under drastic conditions, the use of Pd/C as a catalyst effected the hydrogenolysis of 1 at atmospheric pressure to give the acetyl complex 4, *i.e.* the weaker M—C bond in 1 is cleaved preferentially. Similarly, Fp— CH_2CH_2CO —Fp afforded CH_3CH_2CO —Fp on catalytic hydrogenation.

While 1 appears to be robust toward reduction via hydridic reagents, the action of a stronger reagent (LiAlH₄) resulted in the formation of a complex mixture of products containing both hydrocarbons and alcohols. These results are summarized in Table 4, where C_3 products are derived from CO ligands attached to metal atoms.

TABLE 3

Oxidative methanolysis of μ -ketene complexes (1)

Fp-CH ₂ CO-M-	(i) Br ₂ /CO/CH ₂ Cl ₂ (ii) MeOH	\rightarrow Br-CH ₂ CO-OMe + MeOOC-CH ₂ CO-OMe			
M		Products (% yield)			
		Br-CH ₂ CO-OMe	MeOOC-CH ₂ CO-OMe		
Fp		87	5		
NiCp(CO)		89	0.3		
$MoCp(CO)_2(PPh_3)$		57	0		
$Co(CO)_3(PMe_2Ph)$		79	0		
$Mn(CO)_5$		13	0		

*Reaction conditions: under CO (1 atm) at -20 °C. Yields were determined by GLC methods.

TABLE 4

Product distribution obtained on reduction of 1 by LiAlH₄^a

Μ	Produc	ets					
	Hydrocarbons(%)					Alcohols ^b (%)	
	CH4	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₄ H ₈	C ₂ H ₅ OH	C ₃ H ₇ OH
Fp	2	tr ^c	tr	tr	2	34	25
NiCp(CO)	6	.0	4	7	0	14	12
$MoCp(CO)_2(PPh_3)$	4	0	9	tr	0	14	1
$Co(CO)_3(PMe_2Ph)$	3	3	1	2	0	8	2
Mn(CO) ₅	5	10	11	10	tr	2	1

Fp-CH ₂ CO-M-	THF	hydrocar	bons +	alcohols

"Yields determined by GLC methods.

^bDetermined after hydrolysis.

 $^{c}tr = trace (<1\%).$

Reactivity of 2*

As discussed above, 2 is activated as an electrophile capable of reaction with milder nucleophiles, with the contribution of 2B and 2C being actually reflected in the regiochemistry. Hard nucleophiles such as hydrides attack the most electrophilic carbone carbon in 2B to give $H_2C=CH(OMe)-Nu$ (vinyl ether, being equivalent to acetaldehyde when Nu = H), and soft nucleophiles (L) such as phosphines, alkoxides and carbanions attack the cationic center in 2C to release $H_2C=C(OR)$ —Fp and [Fp⁺(L)], respectively.

Catalytic hydrosilation of metal acyl complexes [9]

In contrast to the reduction of coordinated CO ligands, the efficient reduction of acyl functional groups remains a problem to be solved.

Acyl ligands are usually converted to α -alkoxyalkyl ligands by means of a cationic activation-hydridic reduction sequence $[M \rightarrow CO \rightarrow R \rightarrow M^+ \rightarrow$ $C(OR') \rightarrow M \rightarrow CH(OR') \rightarrow R$ as exemplified by the case of the μ -ketene complex. However, we have applied catalytic hydrosilation to the reduction of acyl ligands, and succeeded in obtaining the one-pot transformation of such to α -siloxyalkyl ligands. The results obtained are listed in Table 5. In those cases where the acyl complex contains electron-donating substituents or ancillary ligands which stabilize the [M⁺=CHR] intermediate, overreduction occurred to produce $M-CH_2-R$.

Application of this method to the reduction of μ -ketene ligands is now under investigation.

^{*}Since the reaction of 3 with nucleophiles (including that with hydrides) occurred at M_a to regenerate 1, it was not possible to employ 3 as a model for the reduction of a ketene ligand.

TABLE 5

Catalytic hydrosilation of acyl metal complexes

$ \begin{array}{ccc} \overset{\text{RhCl}(PPh_3)_3 \text{ cat.}}{\longrightarrow} M - CH - R &+ & M - CH_2 - R \\ & & & & (11) \\ & & O - SiHPh_2 \\ & & (10) \end{array} $	
R	Products
Ме	10
Ме	11
Ph	11
Ме	10
Ме	10
	$ \begin{array}{cccc} R & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & &$

Conclusions

On the basis of the results obtained, we can now construct a network of reactions involving the various C_2 oxygenated functional groups such as ketene, acetyl, ethyl, etc (Scheme 2). If we assume that the reaction of 1 with R^+ is equivalent to the electrophilic activation of a ketene species by a Lewis acidic support, the ketene species generated on a heterogeneous catalyst surface should play an important role in the actual catalytic hydrogenation of carbon monoxide.



Scheme 2.

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