A Novel Preparative Method for Heterobimetallic μ-η^2-(C,C)-Ketene Complexes, Fp–CH_2CO–ML_n [Fp = (η^5-C_5H_5)Fe$(CO)_2$]

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A variety of heterobimetallic μ-η^2-(C,C)-ketene complexes, Fp–CH_2CO–ML_n, are prepared through acylation of metal anions, ML_n^-, by Fp–CH_2CO–Cl.

Ketene species, of all the possible primary coupling products among surface species [*e.g.* CH_x (x = 0—3), CO], have been most frequently postulated as the origin of oxygenated products in the catalytic transformation of syngas.[1] However, the well-known μ-methylene complexes[2] are not commonly carbonylated into μ-ketene complexes[3] presumably owing to the extraordinary stability of the dimetallacyclopropane skeleton. Here we report an indirect preparative method for the first examples of heterobimetallic μ-ketene complexes.

μ-Ketene complexes were prepared by acylation of metal anions, ML_n^-, by iron-substituted acetyl chloride (**2**) which was generated *in situ* by the treatment of the carboxylic acid (**1**)[4] with oxalyl dichloride (Scheme 1). Purification by column chromatography gave μ-ketene complexes, (**3**)—(**8**), as yellow to orange-red crystals accompanied by dimetallic complexes free from the ketene ligand, Fp–ML_n. This method turned out to be widely applicable to all the metal anions used.

Spectral features (Table 1) assignable to Fp and ML_n moieties of (**3**)—(**8**) exhibit very close similarities to those of Fp–Me and MeCO–ML_n possessing the partial structures of the alkyl side and the acyl side of μ-ketene complexes, respectively. For example, the ^{1}H and ^{13}C n.m.r. spectra of (**3**)† are consistent with the formal structure, Fp_A–CH_2CO–Fp_B, and the triplet ^{13}C n.m.r. signal [^2J(C–H) 3.0 Hz]

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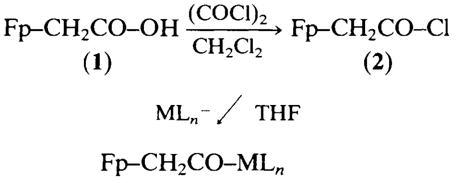
† Compound (**3**) ^{1}H n.m.r. (in C_6D_6) δ 2.57 (2H, s), 4.17 (5H, s, Fp_A), 4.37 (5H, s, Fp_B); ^{13}C n.m.r. (in C_6D_6) δ 86.97, 216.95, other signals are reproduced in Table 1.

Table 1. Spectral data of Fp–CH_2CO parts of heterobimetallic μ-ketene complexes, Fp–CH_2CO–ML_n.[a]

	^1H n.m.r./δ		^{13}C n.m.r./δ				I.r./cm^{-1}
ML_n	Cp(Fp)	CH_2CO	Cp(Fp)	CO(Fp)	CH_2	C=O	ν(C=O)
$Fe(CO)_2Cp$ **(3)**	4.17 (s)	2.57 (s)	85.34 (d, 179.4)[b]	217.19	30.01 (t, 136.1)[b]	253.28 (t. 3.0)[c]	1612
$Fe(CO)_2(\eta^5\text{-}C_5H_4Me)$ **(4)**	4.18 (s)	2.62 (s)	85.33 (d, 180.7)[b]	217.35	29.92 (t, 136.1)[b]	255.07 [f]	1611
$Mo(CO)_2(PPh_3)Cp$ **(5)**	4.19 (s)	3.25 (d, 2.2)[d]	85.07 (d, 178.2)[b]	217.81	32.23 (t, 134.9)[b]	262.82 (d, 10.7)[e]	1585
Ni(CO)Cp **(6)**	4.11 (s)	2.39 (s)	85.43 (d, 180.7)[b]	216.39	26.28 (t, 138.0)[b]	234.68 (t, 3.7)[c]	1649
$Mn(CO)_5$ **(7)**	4.06 (s)	2.47 (s)	85.67[g] (d, 181.3)[b]	216.29	30.78 (t, 136.6)[b]	260.12	1581
$Co(CO)_3(PMe_2Ph)$ **(8)**	4.19 (s)	2.85 (d, 2.2)[d]	85.67[g] (d, 179.0)[b]	216.29	29.29 (dt, 27.5,[e] 136.6[b])	200.35 (d, 27.6)[e]	1620

[a] ^1H (100 MHz) and ^{13}C (125 MHz) n.m.r. spectra were recorded in [$^2H_6$]benzene unless otherwise noted and i.r. spectra in CH_2Cl_2. Values in parentheses are multiplicity and coupling constant, J in Hz. [b] ^1J(C–H). [c] ^2J(C–H). [d] J(H–P). [e] J(C–P). [f] Broad triplet (see footnote ‡). [g] In [^2H]chloroform.



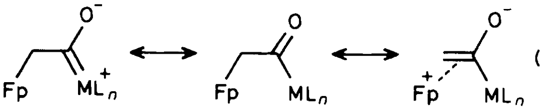
$$\underset{(1)}{\text{Fp–}CH_2CO\text{–OH}} \xrightarrow[CH_2Cl_2]{(COCl)_2} \underset{(2)}{\text{Fp–}CH_2CO\text{–Cl}} \xrightarrow{ML_n^- \,/\, THF} \text{Fp–}CH_2CO\text{–}ML_n$$

ML_n = $CpFe(CO)_2$	**(3)**	27%
$(\eta^5\text{-}C_5H_4Me)Fe(CO)_2$	**(4)**	13%
$CpMo(CO)_2(PPh_3)$	**(5)**	35%
CpNi(CO)	**(6)**	37%
$Mn(CO)_5$	**(7)**	74%
$Co(CO)_3(PMe_2Ph)$	**(8)**	66%

Fp = $CpFe(CO)_2$, Cp = $\eta^5\text{-}C_5H_5$, THF = tetrahydrofuran

Scheme 1

appearing at δ 253.28 unequivocally designates the presence of the ketene ligand.‡ Four C≡O stretching vibrations observed in CH_2Cl_2 [**(3)** 2016, 1999, 1959, 1950 cm^{-1}; **(4)** 2017, 1997, 1960, 1943 cm^{-1}] are divided into two groups. A pair of absorptions of the highest and the third highest frequencies should be assigned to the ν(C≡O) of the Fp_B part (*cf.* Fp–COMe 2015, 1960 cm^{-1}) and the remaining two absorptions to those of the Fp_A part (*cf.* Fp–Me 2003, 1948 cm^{-1}). In addition, the ν(C=O) absorption of the ketene ligand [**(3)** 1612 cm^{-1}; **(4)** 1611 cm^{-1}] is at lower frequencies by 35 cm^{-1} when compared with that of Fp–COMe (1647 cm^{-1}). Furthermore, no indication of bridging carbonyl ligands (^{13}C n.m.r., i.r.) was observed which are characteristic of dinuclear carbonyl cyclopentadienyl iron complexes with a metal–metal bond such as $Cp_2Fe_2(CO)_4$ and $Cp_2Fe_2(CO)_3(\mu\text{-}CR_2)$.



(1)

Similar observations for all the other heterobimetallic μ-ketene complexes **(5)**—**(8)**, Fp–CH_2CO–ML_n (Table 1), verify that (a) the metal centres, Fe and M, exist as mutually independent mononuclear states and no evidence for metal–metal interaction can be detected, (b) the μ-ketene part acts as a dianionic bidentate ligand and makes two σ bonds between CH_2 and Fe and between CO and M, and (c) the shift of ν(C=O) absorption indicates the contribution of a π-complex[5] in addition to the well-established oxycarbene structure[6] (equation 1).

Hydridic reduction ($LiAlH_4$)[7] of **(3)**, as an example, resulted in the formation of C-3 products [propane (5%) in the gas phase and propan-1-ol (48%) in the acidified liquid phase] as major components (total yield of other components <15%). Decarbonylation of **(3)** by $Rh(PPh_3)_3Cl$[8] or irradiation did not produce a μ-methylene complex but a phosphine-substituted μ-ketene complex, Fp–CH_2CO–Fe(CO)(PPh_3)Cp (45%),§ or $Cp_2Fe_2(CO)_4$ (90%) and CH_2=C=O which was trapped as ethyl acetate (94%) in the presence of EtOH (3 equiv.). Compound **(3)** was not susceptible to carbonylation to lead to a μ-malonyl complex under various conditions [CO (50 atm), 120 °C, 12 h, in toluene; CO (1 atm), oxidants or

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‡ While similar coupling is observed for **(6)** (Table 1), these signals for **(5)**, **(7)**, and **(8)** are obscured by the interaction with ^{31}P, ^{55}Mn, and ^{59}Co nuclei. The acyl carbon of **(4)** does not exhibit a sharp triplet signal but a very broad triplet-like signal (^2J *ca.* 3 Hz) and the reason is not clear at the present time.

§ ^1H N.m.r. (in C_6D_6) δ 2.81 [1H, dd, J(H–H) 11.1, J(P–H) 0.9 Hz, one of diastereotopic methylene protons], 2.96 [1H, d, J(H–H) 11.1 Hz, another methylene proton], 4.14 (5H, s, Fp), 4.44 [5H, d, J(P–H) 1.3 Hz, CpFe(CO)(PPh_3)], 6.92—7.12 (9H, m, Ph), 7.61—7.89 (6H, m, Ph). I.r. (KBr disk) ν(C≡O) 1995, 1943 (Fp), 1903 [CpFe(CO)(PPh_3)]; ν(C=O) 1553 cm^{-1}.

Lewis acids; $+PR_3$, 48 h, in refluxing MeCN][9] because of the electron-withdrawing character of the substituent adjacent to the migrating centre ($FpCOCH_2$). Oxidative methanolysis of (**3**) (Br_2, 1 atm CO, MeOH) afforded $Br–CH_2CO–OMe$ (87%) accompanied by a trace amount of a carbonylated product, $MeO–OC–CH_2CO–OMe$ (5%).

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