Carbon Dioxide Activation as an η^1-C Metallocarboxylate: Metallocarboxylate Ester Derivatives as a C_1 Template in Co-ordinated Ligand Reactions

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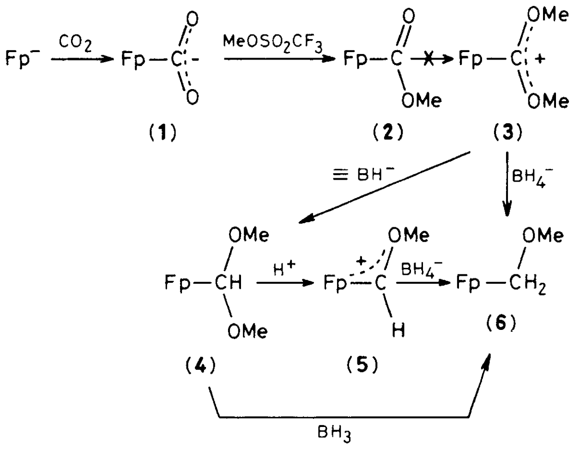
In tetrahydrofuran the reaction between Fp_2Mg [Fp = $Fe(CO)_2(\eta-C_5H_5)$] and CO_2 gives the symmetrical metallocarboxylate $(FpCO_2)_2Mg$, which can be alkylated to give the ester $FpCO_2Me$; its activated ester $FpC(OMe)_2^+$ serves as a C_1 template for reduction to $FpCH_2OMe$.

Stoicheiometric studies using transition organometallic complexes will provide valuable insight into reducing ligated CO_2[1] into other C_1 ligands. Homogeneous CO_2 fixation can be approached by converting an η^1-C metallocarboxylate, MCO_2^-, CO_2 complex into its metallocarboxylic ester (*i.e.*, alkoxycarbonyl)[2] derivative, which subsequently functions as a C_1 template in co-ordinated ligand transformations. Several of these (η^1-C)CO_2 adducts have been characterized, but only one can be alkylated and provides an ester.[3] Metallocarboxylates are instead transformed into 2:1 CO_2 adducts having metallacycle $MCO_2C(O)O$ or chelated $MC(O)OCO_2^-Na^+$ structures.[4] These facilitate the metal-induced reductive disproportionation of CO_2,[5] leaving CO and/or CO_3^{2-} bound to the metal. We now report (i) conditions for selectively ligating CO_2 as a metallocarboxylate $FpCO_2^-$ (**1**) [Fp = $Fe(CO)_2(\eta-C_5H_5)$] and converting it into a known[6] ester $FpCO_2Me$ (**2**) and (ii) reducing its activated ester $FpC(OMe)_2^+$ (**3**) into $FpCH_2OMe$ (**6**), Scheme 1.

Reaction conditions for selectively generating the metallocarboxylate (**1**) are critical. In previous studies it was found that treatment of Fp^-Na^+ in tetrahydrofuran (THF) with CO_2 gave only the 2:1 adduct $FpC(O)OCO_2^-Na^+$, which disproportionates[7] above −40 °C to release Na_2CO_3 and is protonated[8] to give $FpCO^+$. Attempted alkylation of this adduct with methyl iodide or trifluoromethanesulphonate affords only FpMe. By using the Mg^{II} counterion, however, we can now intercept the 1:1 CO_2 adduct as a metallocarboxylate $(FpCO_2)_2Mg$ (**1**). The chelated Mg^{II} blocks both deleterious CO_2 dissociation (which accounts for the above alkylation at Fe) and 2:1 CO_2 binding pathways.

Yellow-brown THF solutions of $(FpCO_2)_2Mg$ (**1**) were generated by purging the orange-yellow Fp_2Mg complex[9] with CO_2 (dried over P_2O_5) at −90 °C (5 min) and then warming to 25 °C. Treatment with methyl trifluoromethanesulphonate (2 equiv.) gave $FpCO_2Me$ (**2**) [71% by quantitative i.r.: ν(CO) 1648 cm^{-1}], unchanged Fp_2 (12%), and trace amounts of FpMe. The lower isolated yields of (**2**) reflect the interference of polymerized THF, induced by $MeOSO_2CF_3$, during the pentane extraction–crystallization procedure. Protonation (4 equiv. $HBF_4{\cdot}OEt_2$) of (**2**) *in situ*, however, afforded $FpCO^+BF_4^-$ (81% after reprecipitation from $MeNO_2$–Et_2O); although acidification of (**1**) also gave $FpCO^+$ (91% yield) (Scheme 2).

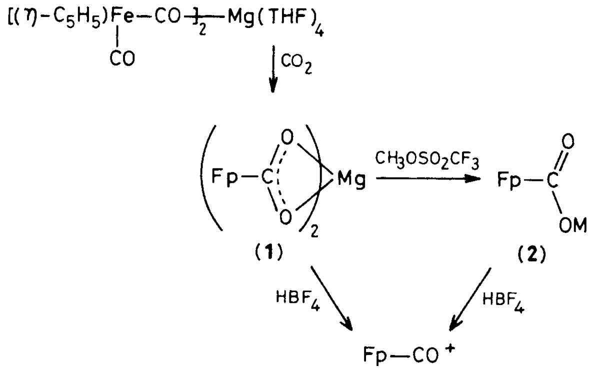


Scheme 1

The proposed chelate structure for the Mg^{II} metallocarboxylate (**1**) is in accord with its i.r. spectra and chemical reactivity. A symmetrical carboxylate structure conforms with its solution i.r.[10] [$\nu(CO_2^-)_{asym}$ 1560 (br) cm^{-1}] absorption,† which disappears upon alkylation. No evidence was found for reductive disproportionation at room temperature: solutions, although unstable at 25 °C, remained homogeneous as Fp_2 and FpH (1:1) quantitatively formed. Extensive CO_2 dissociation from (**1**) did not occur since its reaction with methyl iodide (2 equiv., −50 °C to +25 °C; MeOH quench after 5 min at 25 °C) afforded only 13% FpMe (isolated yield) and a trace of (**2**).

The connection between $FpCO_2Me$ (**2**) and its activated ester $FpC(OMe)_2^+$ (**3**) is presently indirect, since attempted alkylation of (**2**) gave only $FpCO^+$. Neutral alkoxycarbonyls are not alkylated at the acyl-O unless a 2,5-dioxacyclopentylidene complex (*e.g.*, $FpCOCH_2CH_2O^+$)[11] results. Instead alkoxide abstraction generally ensues.[2] Therefore (**3**) was procured by an unrelated procedure of Angelici.[11]

Reduction of $FpC(OMe)_2^+$ (**3**) in CH_2Cl_2 (−80 °C) with one equivalent of $LiHBEt_3$ afforded the formyl acetal complex $FpCH(OMe)_2$ (**4**)‡ (82% yield) after pentane extraction.



Scheme 2

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† Selected i.r. data in THF (ν/cm^{-1}), (**1**) as Mg^{II} salt: 2015s, 1959s (CO) and 1560m (br) (CO_2); Mg^{II} derivative of $FpCH_2CO_2H$ (ref. 14), $(FpCH_2CO_2)_2Mg$: 2018s, 1953s (CO) and 1604m (br) (CO_2) [closely resembles $\nu(CO_2)$ of (**1**) in appearance]; (KBr) 2018s, 1959s (CO) and 1590m (br), 1435m (br) (CO_2); (**2**): 2012s, 1974s (CO) and 1674m (C=O).

‡ Compound (**4**) (yellow oil): ^1H n.m.r. ($CDCl_3$) δ 6.48 (s, 1 H, FeCH), 4.78 (s, 5 H, $\eta-C_5H_5$), and 3.28 (s, 6 H, OCH_3): ^{13}C n.m.r. (gated decoupled) δ 216.3 (CO), 115.8 (d sept., ^1J 166, ^3J 5 Hz, FeCH), 85.8 (d quint., $\eta-C_5H_5$), and 54.8 p.p.m. (d quart., ^1J 142, ^3J 5 Hz, OCH_3). A satisfactory elemental analysis was obtained.

Solutions of (**4**) are remarkably stable at room temperature (<10% decomposition after 16 h) in contrast with the extremely unstable formyl complex FpCHO.[12] Another recent synthesis of (**4**) entails methoxide addition to the methoxymethylidene salt (**5**).[13] Several reductive procedures are available for converting (**3**) or (**4**) into $FpCH_2OMe$ (**6**), Scheme 1. A CH_2Cl_2 solution of $BH_3{\cdot}SMe_2$ (1.5 equiv.) thus causes the conversion of (**4**) into (**6**) (93% yield isolated after chromatography), whereas treatment of (**3**) with $PPh_3Me^+BH_4^-$ (1.0 equiv.) gives a mixture of (**6**) (61%), FpMe (2%), and FpH (assayed as FpCl, 10%). Finally, $HPF_6{\cdot}OEt_2$ protonates (**4**) to give (**5**) (90%), and our previously reported[12] BH_4^- reduction of (**5**) then yields (**6**).

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