

Functionalisation of carbon dioxide by an iron(II) complex†

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Addition of carbon dioxide to *trans*-Fe(dmpe)₂(SCHNEt)H **2** affords the iminium carboxylate *trans*-Fe(dmpe)₂(SCHN⁺(Et)CO₂⁻)H **4**, which rearranges to the ferracycle *cis*-Fe(dmpe)₂(SCH₂N(Et)C(O)O-κS,O) **5**.

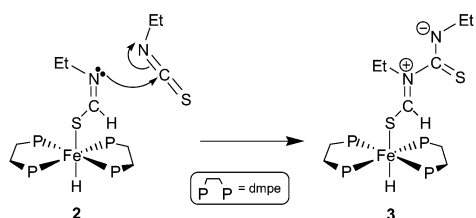
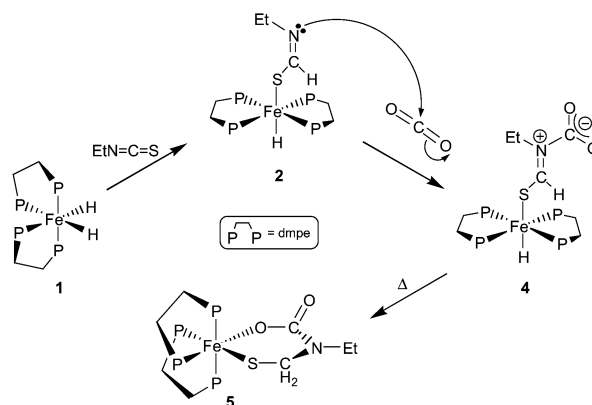
The fixation and functionalisation of carbon dioxide at transition metal centres has received much recent attention due to the potential of this greenhouse gas as an abundant and inexpensive source of carbon in the construction of more complex organic compounds.¹

We recently reported the insertion reaction between the iron hydride *cis*-Fe(dmpe)₂H₂ **1** (dmpe = Me₂PCH₂CH₂PMe₂) and the heteroallenes carbon dioxide (CO₂), carbon disulfide (CS₂), carbonyl sulfide (COS),² isocyanates (RNCO) and isothiocyanates (RNCS)³ to form η¹-bound (thio)formato and (thio)formimidato-type ligands. Insertion into both iron–hydride bonds of **1** occurred in the presence of excess heteroallene in each case except for that of ethyl or methyl isothiocyanate, where a N-to-C condensation of the heteroallene resulted from nucleophilic attack by the coordinated *N*-alkylthioformimidate of *trans*-Fe(dmpe)₂(SCHNR)H (R=Me, Et (**2**)) on another RNCS molecule to give the free zwitterion *trans*-Fe(dmpe)₂-(SCHN⁺(R)C(S)N⁻(R))H (R=Me, Et (**3**)) (Scheme 1).³

In this communication, we report initial studies on the reaction between CO₂ and *trans*-Fe(dmpe)₂(SCHNEt)H **2** to form an intermediate iron(II) iminium carboxylate zwitterion which rearranges, by insertion/cyclisation at the iron(II) centre, to form a novel heteroatomic ferracycle (Scheme 2).

Addition of CO₂ (1 atm) to a degassed solution of *trans*-Fe(dmpe)₂(SCHNEt)H **2**, formed *in situ* by the insertion reaction between *cis*-Fe(dmpe)₂H₂ **1** and EtNCS (Scheme 2), in toluene-*d*₈ at 300 K afforded the zwitterionic iminium carboxylate complex, *trans*-Fe(dmpe)₂(SCHN⁺(Et)CO₂⁻)H **4** as the major kinetic product (Scheme 2). The ³¹P{¹H} NMR spectrum of *trans*-Fe(dmpe)₂(SCHN⁺(Et)CO₂⁻)H **4** comprised a singlet resonance (δ 69.4) for the equivalent phosphorus donors. In the ¹H NMR spectrum, the hydride resonance (δ -25.20) appeared as a pentet (²J_{PH} 50 Hz), while the proton of the iminium fragment occurred as a singlet at δ 9.30. The iminium and carboxylate ¹³C nuclei resonated at δ 172.5 (unresolved ³¹P coupled multiplet) and 174.6, respectively.

An X-ray diffraction study of a red prismatic single crystal, grown from a concentrated toluene-*d*₈ solution at 300 K, confirmed the zwitterionic nature of **4** (Fig. 1).[‡] The dmpe

Scheme 1 Dimerization of EtNCS at an iron(II) centre.³Scheme 2 Reaction between **1** and EtNCS and CO₂ sequentially.

ligands adopted at least two complementary orientations, the populations of which were refined and fixed. The S(1)–C(1) bond length (1.670(2) Å) is extremely short for a C–S single bond (typically ~1.8 Å⁴). The C(1)–N(1), N(1)–C(2) and C–O bond lengths also suggest delocalisation of the zwitterionic charges throughout the dimer ligand.

In solution at 300 K, *trans*-Fe(dmpe)₂(SCHN⁺(Et)CO₂⁻)H **4** quantitatively isomerised to a new compound **5** with a *cis* disposition of the dmpe ligands, and with no metal hydride (Scheme 2). Compound **5** was identified as the ferracycle *cis*-Fe(dmpe)₂(SCH₂N(Et)C(O)OκS,O) **5**.[‡] The complex was obtained cleanly as a single diastereomer. In the ¹H NMR spectrum, the two S–CH₂–N protons are diastereotopic and appear as doublets at δ 2.67 and 3.47 (²J_{HH} 14 Hz) respectively. The CH₂ protons of the ethyl group appear as doublets of quartets at δ 2.67 and 3.47 (²J_{HH} 14 Hz, ³J_{HH} 7 Hz).

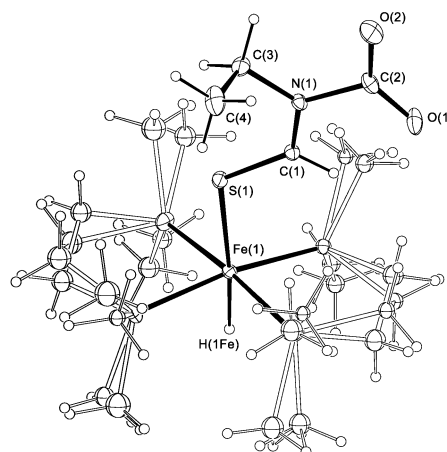


Fig. 1 ORTEP⁵ diagram of **4** showing 20% displacement ellipsoids and disorder in the dmpe ligands. Selected bond distances (Å) and angles (°): Fe(1)–S(1) 2.2925(10), S(1)–C(1) 1.670(2), C(1)–N(1) 1.321(3), N(1)–C(2) 1.518(3), C(2)–O(1) 1.232(3), C(2)–O(2) 1.226(3); Fe(1)–S(1)–C(1) 115.76(8), S(1)–C(1)–N(1) 127.16(17), N(1)–C(2)–O(1) 113.8(2), N(1)–C(2)–O(2) 113.3(2).

† Electronic supplementary information (ESI) available: experimental section. See <http://www.rsc.org/suppdata/cc/b1/b108492e/>

X-Ray diffraction analysis of a red columnar single crystal of *cis*-Fe(dmpe)₂(SCH₂N(Et)C(O)O-κS,O) **5** confirmed its ferracyclic structure, and determined its absolute stereochemistry (Fig. 2).[‡] The unit cell contained two crystallographically independent molecules. The six-membered ring is puckered, due in part to the planarity of the carbamate (O–C(O)–N) moiety. The metalloring bond lengths suggest essentially single bonds with a localised carbonyl moiety. Steric interaction between the methyl substituents on the axial phosphorus atoms and the groups which make up the sulfido–carbamate ferracycle most probably determines the configuration at the iron centre leading to the formation of a single diastereomer for this compound.

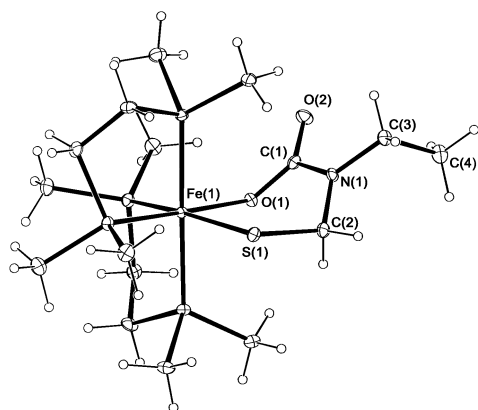
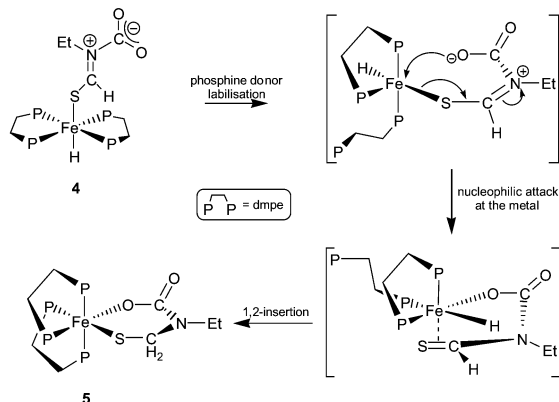


Fig. 2 ORTEP⁵ diagram of one of the molecules of **5** showing 20% displacement ellipsoids. Selected bond distances (Å) and angles (°): Fe(1)–O(1) 2.053(2), C(1)–O(1) 1.286(3), C(1)–O(2) 1.246(3), C(1)–N(1) 1.385(3), N(1)–C(2) 1.446(3), C(2)–S(1) 1.833(3), Fe(1)–S(1) 2.3354(13); Fe(1)–O(1)–C(1) 123.34(18), N(1)–C(2)–S(1) 115.8(2).

cis-Fe(dmpe)₂(SCH₂N(Et)C(O)OκS,O) **5** is formally the product of hydride migration from the iron(II) centre to the iminium carbon of *trans*-Fe(dmpe)₂(SCHN⁺(Et)CO₂[−])H **4** with formation of a six-membered ferracycle. The mechanism of the transformation **4** to **5** probably involves loss of one of the coordinated phosphines, with intramolecular attack by the carboxylate group to eliminate a thioaldehyde. The formation of an intermediate thioaldehyde is speculative and there is no direct spectroscopic evidence for this species. Subsequent addition of the metal hydride to the pendant thioaldehyde would form the cyclic product **5** (Scheme 3).

The net result of the overall sequence of reactions is the reduction of the unsaturated isothiocyanate Et–N=C=S to an iron-coordinated, *N*-substituted thiolate Et–N(X)–CH₂–S–Fe by sequential migration of two hydrides from a metal centre to



Scheme 3 Proposed mechanism for the transformation **4** to **5**.

the electrophilic carbon of the heteroallene. CO₂ is involved in the reaction initially as an electrophile but is important in the formation of the heterocyclic product. The formation of the carboxylate **4** produces a tethered ligand which is conveniently disposed (*via* a six-membered transition state) to provide a driving force for the formation of a thioaldehyde and subsequent hydride migration. Further studies of the scope, mechanism and applications of this novel addition/cyclisation reaction of metal hydrides with heteroallenes are ongoing.

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Notes and references

[‡] *Selected crystal data*: full sphere data were collected at 150(2) K on a Bruker SMART 1000 to 56° 2θ with Mo radiation. Data integration and reduction were undertaken with SAINT and XPREP,⁶ and subsequent computations were carried out with the teXsan⁷ and WinGX⁸ graphical user interfaces. A Gaussian absorption correction was applied to the data.^{6,9} A subsequent empirical correction was determined with SADABS¹⁰ for **4**. The data reduction included the application of Lorentz and polarisation corrections. The structures were solved by direct methods with SIR97,¹¹ and extended and refined with SHELXL-97.¹²

4: C₁₆H₃₉FeNO₂P₄S, *M* = 489.27, triclinic, space group *P* $\bar{1}$ (no. 2), *a* = 9.973(5), *b* = 14.680(8), *c* = 8.748(5) Å, α = 104.586(8), β = 99.791(8), γ = 81.837(8)°, *V* = 1214.8(11) Å³, *D*_c = 1.338 g cm^{−3}, *Z* = 2, *R*1(*F*) 0.0391, *wR*2(*F*²) 0.1000, GOF(all) 1.059. The equatorial ligand system is disordered with the bidentate ligands adopting two orientations. Complementary populations of the two equatorial ligand orientations were refined and then fixed in both cases. The partially occupied non-hydrogen sites were modelled with isotropic displacement parameters, whereas the rest of the non-hydrogen sites were treated anisotropically. A riding atom model was used for hydrogen atoms with the exception of H(1) and the hydride H(1Fe), both of which were located and modelled with refined positional and isotropic displacement parameters.

5: C₁₆H₃₉FeNO₂P₄S, *M* = 489.27, monoclinic, space group *P* $\bar{1}$ /*n* (no. 14), *a* = 17.989(9), *b* = 12.561(6), *c* = 20.303(10) Å, β = 94.604(8)°, *V* = 4573(4) Å³, *D*_c = 1.421 g cm^{−3}, *Z* = 8, *R*1(*F*) 0.0366, *wR*2(*F*²) 0.0489, GOF(all) 0.983. The asymmetric unit contains two crystallographically independent molecules. The non-hydrogen atoms were modelled with anisotropic displacement parameters and a riding atom model was used for the hydrogen atoms. CCDC reference numbers 169564 and 169565. See <http://www.rsc.org/suppdata/cc/b1/b108492e/> for crystallographic data in CIF or other electronic format.

[§] *Selected spectral data for 5*: ³¹P{¹H} NMR: δ 45.3 (ddd, ²*J*_{PP} 32, 40, 226 Hz), 57.9 (ddd, ²*J*_{PP} = 36, 52, 226 Hz), 60.3 (dt, ²*J*_{PP} 28, 36 Hz), 65.2 (dt, ²*J*_{PP} 28, 52 Hz). ¹³C{¹H}: δ 45.9 (m, *J*_{CP} 3, 5 Hz, FeS–CH₂–N), 166.1 (p, ³*J*_{CP} 3 Hz, FeO(C=O)N).

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