

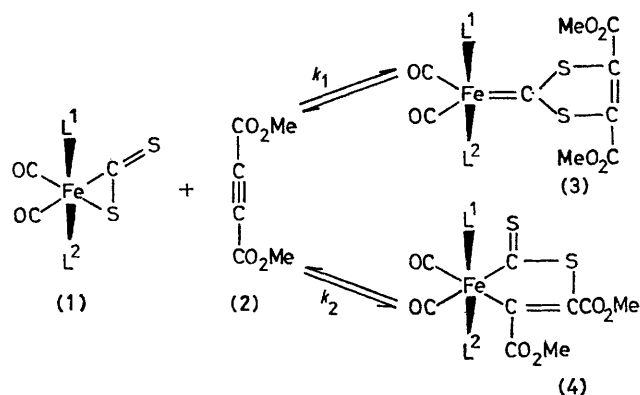
## Versatility of Cycloaddition of Electrophilic Alkynes to $\eta^2$ -CS<sub>2</sub> Metal Complexes. Reversible Isomerisation of 1,3-Dithiol-2-ylideneiron and Heterometallic Complexes

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**Summary** The 1,3-dithiol-2-ylideneiron(0) complexes (**3**) isomerise to heterometallics (**4**), the equilibrium constant and rate constant increasing with donor strengths of the ligands on iron.

We have shown recently<sup>1</sup> that 1,3-dithiol-2-ylideneiron compounds may be formed directly by addition of a variety of activated alkynes to the  $\eta^2$ -CS<sub>2</sub> iron complex (**1a**). This new type of addition is in contrast to that observed by Wakatsuki *et al.*<sup>2</sup> who isolated a heterometallic derivative resulting from treatment of dimethyl acetylenedicarboxylate with an  $\eta^2$ -CS<sub>2</sub> rhodium complex. We now provide evidence for isomerisation of 1,3-dithiol-2-ylideneiron complexes (**3**) to heterometallics (**4**) and we note that the relevant equilibrium constant and rate constant are strongly dependent on the electron-donating effect of the phosphorus ligands L<sup>1</sup> and L<sup>2</sup> (Scheme).



SCHEME

When a benzene solution of the  $\eta^2$ -CS<sub>2</sub> iron derivatives (**1a–e**)<sup>3</sup> is treated at room temperature under an inert atmosphere with 1 equiv. of the alkyne (**2**), the carbene complexes (**3a–e**) are formed within a few seconds. The complexes (**3**) were characterised by their mass spectra, two C≡O i.r. absorption bands at low frequencies, and only one CO<sub>2</sub>Me <sup>1</sup>H n.m.r. signal [*e.g.*, C<sub>6</sub>D<sub>6</sub> solution of the brown, air-sensitive compound (**3e**) has  $\nu(\text{C}\equiv\text{O})$  at 1890 and 1835 cm<sup>-1</sup>, and a singlet at  $\delta$  3.45 (6H, CO<sub>2</sub>Me)]. Whereas the compounds (**3a**) and (**3b**) are stable, (**3e**) is rapidly converted into the metalocyclic isomer (**4e**), and complexes (**3c**) and (**3d**) lead to an equilibrium mixture [(**3c**):(**4c**) 85:15 and (**3d**):(**4d**) 18:82, respectively]. Complexes (**4c–e**) were characterised by their mass

spectra, two C≡O i.r. absorption bands at high frequencies, two CO<sub>2</sub>Me n.m.r. signals, and, for (**4d**) and (**4e**), by <sup>13</sup>C n.m.r. spectroscopy [*e.g.*, compound (**4e**), yellow solid, m.p. 180 °C; C<sub>6</sub>D<sub>6</sub> solution shows  $\nu(\text{C}\equiv\text{O})$  at 2030 and 1970 cm<sup>-1</sup>, and two singlets at  $\delta$  3.46 and 3.78 (each 3H, CO<sub>2</sub>Me); <sup>13</sup>C n.m.r.  $\delta$  50.8 and 51.5 (MeO), 140.2 (t, <sup>2</sup>J<sub>F-C</sub> 5 Hz) and 159.0 (t, <sup>3</sup>J<sub>F-C</sub> 3 Hz) (<sup>13</sup>C=C), 176.4 and 176.5 (C=O), and 196.6 (t, <sup>2</sup>J<sub>F-C</sub> 24 Hz), 207.9 (t, <sup>2</sup>J<sub>F-C</sub> 19 Hz), and 212 p.p.m. (t, <sup>2</sup>J<sub>F-C</sub> 15 Hz) for two non-equivalent CO and one co-ordinated C=S].

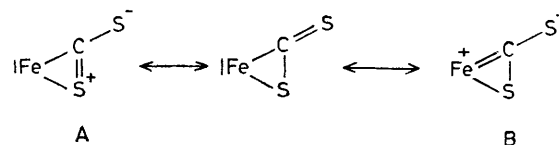
TABLE

	a	b	c	d	e
L <sup>1</sup>	P(OMe) <sub>3</sub>	PPh <sub>3</sub>	P(OMe) <sub>3</sub>	PMe <sub>2</sub> Ph	PMe <sub>3</sub>
L <sup>2</sup>	P(OMe) <sub>3</sub>	PPh <sub>3</sub>	PMe <sub>3</sub>	PMe <sub>2</sub> Ph	PMe <sub>3</sub>
( <b>3</b> ):( <b>4</b> ) <sup>a</sup>	100:0	100:0	85:15	18:82	0:100
Rate <sup>b</sup>	—	—	Very slow	Slow	Fast

<sup>a</sup> Measured by <sup>1</sup>H n.m.r. spectroscopy using C<sub>6</sub>D<sub>6</sub> solutions at 37 °C. <sup>b</sup> With 0.3 mol l<sup>-1</sup> of (**3c**), (**3d**), and (**3e**) in C<sub>6</sub>D<sub>6</sub> solution at 37 °C, equilibrium was reached after *ca.* 48, 20, and 1 h, respectively.

The ratio of the complexes (**3**):(**4**) (Table) shows that basic phosphorus ligands L destabilize the carbene complex; this is attributed to the strong donor character of the nucleophilic carbene ligand.<sup>4,5</sup> By contrast, complexes of iron(II), such as (**4**), are stabilised by powerful donor ligands.

The isomerisation (**3e**) → (**4e**) was easily monitored by the CO<sub>2</sub>Me <sup>1</sup>H n.m.r. signal; the rate increased with the concentration of the carbene complex (**3e**), thus ruling out a simple intramolecular rearrangement. Addition of (**1d**) to (**3e**) gave rise to (**1e**) and (**3d**) indicating the reversibility of the carbene complex formation. These facts suggest that the multistep transformation (**3**) → (**4**) may proceed *via* the retrocycloaddition (**3**) → (**1**), followed by the 1,3-dipolar addition (**1**) → (**4**) as shown in the Scheme with  $k_1 > k_2$ .



An accurate X-ray structure determination for [Fe(CO)<sub>2</sub>( $\eta^2$ -CS<sub>2</sub>)(PMe<sub>3</sub>)(PPh<sub>3</sub>)] indicated that bond lengths were best described by the 1,3-dipolar canonical forms A and B,<sup>3</sup> and accounts for the effect of electron-donating ligands L stabilising form B and increasing  $k_2$ .

The present study shows that by selection of suitable ligands L, it is possible to inhibit or effect the isomerisation of a 1,3-dithiol-2-ylidenemetal complex to the isomeric heterometalloycycle.

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<sup>1</sup> H. Le Bozec, A. Gorgues, and P. Dixneuf, *J. Amer. Chem. Soc.*, 1978, submitted for publication.

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