# Novel Route to Tetrathiafulvalene Derivatives *via* Carbon Disulphide–Iron Complexes

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The (1,3-dithiol-2-ylidene)iron compounds (**2**), arising from ($\eta^2$-$CS_2$)Fe complexes, give rise to tetrathiafulvalene derivatives either by addition of iodine or by thermolysis; the dimerisation of the carbene ligand requires a vacant co-ordination site on Fe and is inhibited by an increase in CO pressure which allows the formation of the new carbene–iron derivative (**5**).

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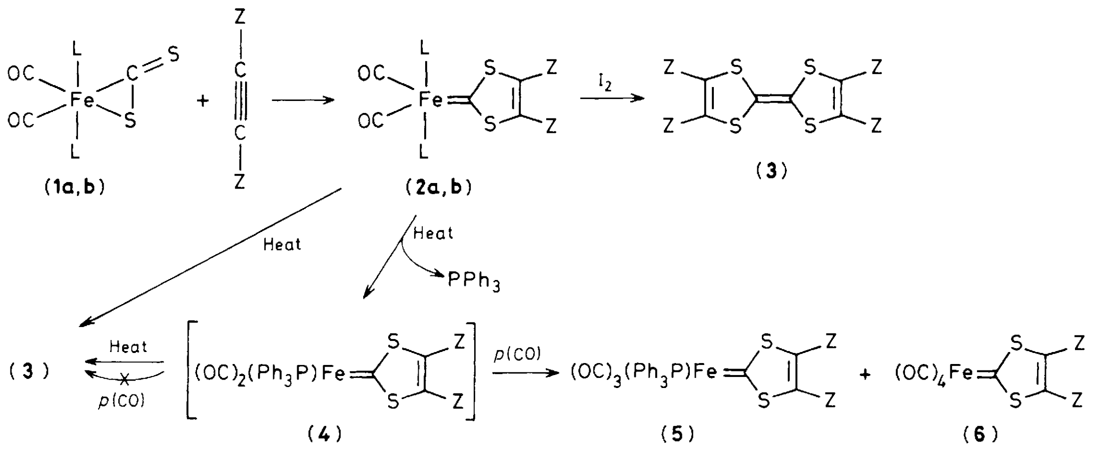
The discovery that charge transfer complexes, containing tetrathiafulvalene (TTF) as a one electron donating component, exhibit high electrical conductivity[1] has stimulated numerous attempts to design appropriate synthetic routes to TTF derivatives.[2] To date, such syntheses have generally involved coupling reactions of 1,3-dithiolium salts[3] and of unstable 1,3-dithiol-2-ylidene phosphoranes[4] or alternatively desulphurisation of 1,3-dithiol-2-thiones using phosphites[5] or metal carbonyls.[6] The direct synthesis of TTF compounds from $CS_2$ and alkynes has recently been reported[7] but the conditions (>4000 atm; 100 °C) were extreme. In this communication we report the facile generation of TTF derivatives in one step from the ($\eta^2$-$CS_2$)iron complexes (**1**) readily accessible in high yield (80—85%) from $Fe(CO)_5$ and $CS_2$.[8]

Electrophilic alkynes readily add to ($\eta^2$-$CS_2$)iron complexes to give the carbene–iron compounds (**2**)[9] which react with oxygen to give dithiolene complexes plus a small amount of the corresponding TTF.[10] We have discovered that the addition of iodine to the carbene–iron complexes (**2**)[9] leads to the formation of the TTF (**3**)[5a] in 55—83% yield (Scheme 1). Moreover, the TTF synthesis can be carried out in one pot directly from the readily available ($\eta^2$-$CS_2$)Fe compounds (**1a**)[11] and (**1b**).[8] To a solution of (**1a**) or (**1b**) (2 mmol) in toluene (10 ml) under $N_2$ was added one equivalent of dimethyl acetylenedicarboxylate. After 1 h at 25 °C an excess of iodine in toluene was added and the mixture was left for 2 days at room temperature. Silica gel chromatography and subsequent work-up afforded (**3**) in 55 and 83% yield from (**1a**) and (**1b**) respectively. Similarly, TTF (**3**, Z = H and $CO_2Et$)[5a] was isolated from (**1b**) and $HC_2CO_2Et$, albeit in lower yield (29%). Formation of (**3**) from (**2a**) and $I_2$ was accompanied by the generation of $FeI_2(CO)_2\{P(OMe)_3\}_2$ identified by solution i.r. spectroscopy [$\nu$(C≡O), $C_7H_8$, 2050—2000 $cm^{-1}$].[12] Precise mechanistic details are not yet available but comparative studies show that the reaction with $I_2$ is faster for (**2b**) than (**2a**); this is consistent with the relative electron donor properties and lability of the ligands L in (**2a**) and (**2b**).[9]

The tetrathiafulvalene (**3**) was also obtained *via* thermolysis of (**2b**) in a yield that increased with temperature. Thus from (**2b**), prepared *in situ* by addition of the alkyne to (**1b**), (**3**) was isolated in 35% (autoclave, tetrahydrofuran, 100 °C, 8 h), 57% (toluene reflux, 110 °C, 8 h), and 83% (decalin, 150 °C, 4 h) yield. Formation of (**3**) from (**2b**) does not result from dimerisation of a free carbene since heating of (**2b**) in a toluene–methanol mixture did not afford the stable derivative $\overline{\text{MeOCH-SC(CO}_2\text{Me)=C(CO}_2\text{Me)S}}$ obtained in trapping experiments of the free carbene with methanol.[5a] Moreover, heating of (**2a**) in refluxing toluene (10 h) failed to generate (**3**). These results demonstrate that a likely first step in the transformation (**2b**) → (**3**) is loss of a labile $PPh_3$ ligand leading to the 16-electron species (**4**), a sequence favoured by



Scheme 1. Z = $CO_2Me$; **a**, L = $P(OMe)_3$; **b**, L = $PPh_3$.

an increase in temperature. In support of this, when (**2b**) was heated in toluene (110 °C) for 0.5 h a violet-red, air sensitive complex, identified by microanalysis and spectroscopy as the carbene–iron complex (**5**) [m.p. 124—125 °C, *M* (benzene) 615, calculated 620; i.r. (Nujol) 1970, 1890, and 1740 $cm^{-1}$, n.m.r. ($C_6D_6$), $\delta$ (36 °C): $^1H$, 3.23 (s, $CO_2Me$); $^{13}C$, 216.2 (d, $^2J_{P-C}$ 28.0 Hz, CO), 158.5 (s, >C=O), 151.5 (s, >C=C<), and 53.0 p.p.m. (s, $CH_3$)] was isolated *via* silica gel column chromatography. Compound (**5**), formally derived from (**2b**) *via* displacement of a $PPh_3$ group could not be obtained *via* the general route to (1,3-dithiol-2-ylidene)iron complexes owing to the inaccessibility of the corresponding ($\eta^2$-$CS_2$)iron precursor.[9] An improved synthesis of the new compound (**5**) (yield 55%) involved heating (**2b**) in an autoclave (toluene, 100 °C, 3.5 h) at an initial CO pressure of 20 atm followed by column chromatography. When the reaction mixture was heated at 100 °C for 8 h (**5**) and a small amount of (**6**) (5%), were obtained. It is noteworthy that (**3**) was not formed with (**5**) and (**6**) when (**2b**) was heated (110 °C, 8 h) under CO (20 atm). In sharp contrast however, heating of pure (**5**) in toluene under a nitrogen atmosphere afforded (**3**). These observations confirm that a key step in the formation of (**3**) is the generation of the 16-electron intermediate (**4**). Since evidence for the presence of free carbene in these reactions is lacking an appropriate pathway to the TTF derivatives may involve the transfer of one carbene ligand of (**4**) to the iron atom of another molecule of (**4**), *via* a binuclear $\mu$-alkylidene intermediate similar to that suggested by Casey[13] for the coupling reaction of carbene–chromium complexes.

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