

# A Novel Route to Thiocarbonyl–Metal Complexes via Electron Transfer to $(\eta^2\text{-CS}_2\text{R})$ -Metal Cations

Daniel Touchard,<sup>a</sup> Chantal Lelay,<sup>a</sup> Jean-Luc Fillaut,<sup>b</sup> and Pierre H. Dixneuf<sup>b</sup>

<sup>a</sup> Institut Universitaire de Technologie, 44606 Saint-Nazaire, France

<sup>b</sup> Laboratoire de Chimie de Coordination organique, campus de Beaulieu, Université de Rennes, 35042 Rennes, France

The reduction with sodium-amalgam of the cations  $[\text{Fe}(\eta^2\text{-CS}_2\text{Me})(\text{CO})_2\text{L}_2]\text{PF}_6$  (**1**), containing basic phosphines L ( $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PBU}^n_3$ ), gives rise to low-valent thiocarbonyl–iron complexes  $\text{Fe}(\text{CS})(\text{CO})_2\text{L}_2$  (**3**).

Low-valent thiocarbonyl–metal complexes have already been prepared *via* four main routes:<sup>1</sup> (i) the desulphurization of  $(\eta^2\text{-CS}_2)$  metal complexes by phosphines,<sup>1,2</sup> (ii) the reaction of thiophosgene with metal carbonyl anions,<sup>3,4</sup> (iii) the addition of hydride to  $\text{M}(\eta^2\text{-CS}_2\text{R})^+$  cations *via*  $\text{M}(\text{H})(\eta^1\text{-CS}_2\text{R})$  intermediates,<sup>5,6</sup> and (iv) the addition of NaSH to dihalogenocarbene–metal complexes.<sup>7</sup> We now report a novel route to thiocarbonyl–metal complexes by reduction of  $\text{M}(\eta^2\text{-CS}_2\text{R})^+$  cations with sodium-amalgam and the preparation of low-valent thiocarbonyl–iron(0) complexes.

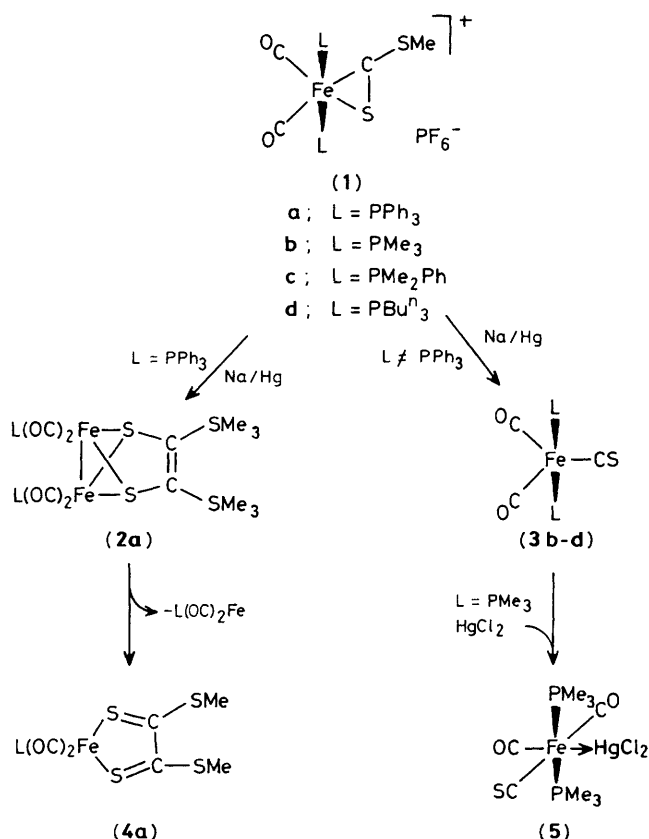
Although a route to cationic thiocarbonyl–iron(II) complexes has been described,<sup>1,8</sup> only two  $\text{Fe}^0\text{CS}$  derivatives have been obtained so far: the unstable  $\text{Fe}(\text{CS})(\text{CO})_4$  complex by the reaction of  $\text{Fe}(\text{CO})_4^{2-}$  with thiophosgene<sup>4</sup> and  $\text{Fe}(\text{CS})(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2$  by treatment of the corresponding  $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2$  derivative with  $\text{PBU}^n_3\text{-CCl}_4$ ,<sup>9</sup> a reaction which seems restricted to the use of the weak electron donor  $\text{P}(\text{OPh})_3$  as ligand.

We have already shown that the reduction of cation (**1a**), with sodium-amalgam,<sup>10</sup> led to the red product (**2a**) arising from the C–C coupling of the one-electron reduced species of (**1a**). The reduction under similar conditions of the analogous cation (**1b**), but containing the basic phosphine  $\text{PMe}_3$ , occurred in a quite different way. A solution of (**1b**)<sup>11</sup> (2 mmol) in 50 ml of dry tetrahydrofuran (THF) was poured, under an inert atmosphere, onto 20 g of 1% sodium-amalgam. The solution turned slowly from orange to yellow. After 4 h at room temperature a yellow complex was obtained by crystallization in pentane in 30–35% yield (m.p. 180–182 °C) and identified as (**3b**) (Scheme 1) {i.r.(Nujol):  $\nu(\text{CO})$  1930, 1870,  $\nu(\text{CS})$  1215  $\text{cm}^{-1}$ ;  $m/z$ : 307.985 [calc. for  $\text{M}^+(\text{C}_9\text{H}_{18}\text{FeO}_2\text{P}_2\text{S})$ : 307.985];  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ , 80 MHz):  $\delta$  1.31 (d,  $\text{PMe}_3$ ,  $^2J_{\text{PH}}$  8.8 Hz);  $^{31}\text{P}$  n.m.r. ( $\text{CDCl}_3$ , 32.38 MHz):  $\delta$  37.7 p.p.m. (s,  $\text{PMe}_3$ );  $^{13}\text{C}$  n.m.r. ( $\text{C}_6\text{D}_6$ , 75.469 MHz):  $\delta$  324.6 (t, CS,  $^2J_{\text{PC}}$  37 Hz), 213.3 (t, CO,  $^2J_{\text{PC}}$  25 Hz), 19.6 (t,  $\text{PMe}_3$ ,  $^1J_{\text{PC}}$  32 Hz)}. It is noteworthy that (**3b**) was not observed during the attempted desulphurization of  $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PR}_3)_2$  by phosphines.<sup>11</sup> By addition of 0.9 equiv. of  $\text{HgCl}_2$  to a solution of (**3b**) in diethyl ether a stable light yellow precipitate was obtained (85%) and identified as the donor–acceptor adduct  $\text{Cl}_2\text{Hg} \leftarrow \text{Fe}(\text{CS})(\text{CO})_2(\text{PMe}_3)_2$  (**5**)<sup>†</sup> [i.r.(Nujol):  $\nu(\text{CO})$  1995, 1965,  $\nu(\text{CS})$  1280  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  n.m.r. ( $\text{CDCl}_3$ , 32.38 MHz): 13.9 p.p.m.,  $^2J(^{31}\text{P}\text{-}^{199}\text{Hg})$  620.1 Hz], containing equivalent  $\text{PMe}_3$  groups *cis* to the  $\text{Fe} \rightarrow \text{Hg}$  bond.<sup>12</sup>

Under similar conditions, complex (**1c**) led to two complexes isolated in low yields: the yellow derivative (**3c**)<sup>†</sup> (8% yield) [i.r.(Nujol):  $\nu(\text{CO})$  1960, 1895,  $\nu(\text{CS})$  1230  $\text{cm}^{-1}$ ] and a blue product identified as  $\text{L}(\text{OC})_2\text{Fe-S-C}(\text{SMe})\text{-C}(\text{SMe})\text{=S}$  (**4c**) ( $\text{L} = \text{PMe}_2\text{Ph}$ , 9%). The analogous product (**4a**)<sup>†</sup> ( $\text{L} = \text{PPh}_3$ ) has already been reported to be formed by decomposition of (**2a**),<sup>10</sup> during the reduction of (**1a**) with Na/Hg.

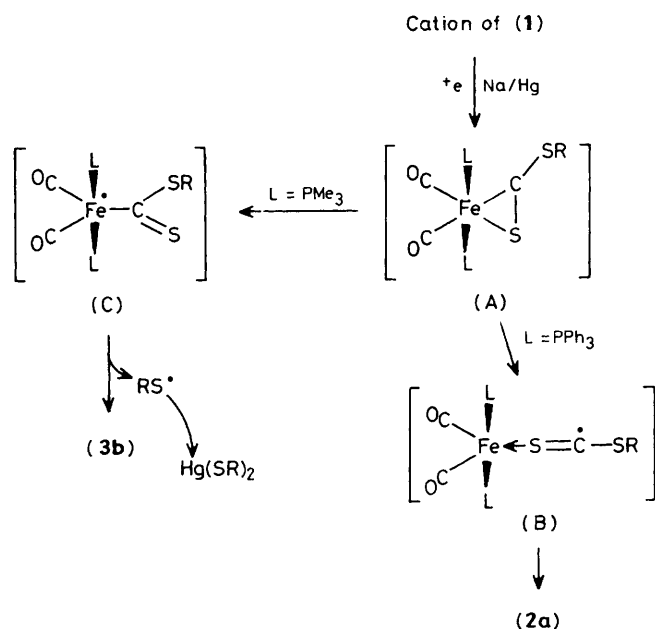
The thiocarbonyl–iron(0) complexes (**3**) can be directly obtained by reduction, with an excess of Na/Hg, of the readily accessible cation (**1a**)<sup>11</sup> in THF, but in the presence of 2.3 equiv. of the tertiary alkylphosphines  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ , and  $\text{PBU}^n_3$ . Thus the complexes (**3b**) (28%), (**3c**) (8%), and (**3d**) (9%) [i.r.(Nujol):  $\nu(\text{CO})$  1945, 1885,  $\nu(\text{CS})$  1225  $\text{cm}^{-1}$ ] were isolated. In these reactions the formation of (**2a**), the reduction product of (**1a**) with Na/Hg,<sup>10</sup> was not observed; therefore the substitution of the  $\text{PPh}_3$  groups of (**1a**) by alkylphosphines is faster than the reduction of (**1a**). This reaction is an example of radical-promoted substitution of phosphines by more basic ligands and can be related to the substitution reaction of carbonyl ligands by phosphines in radical ions.<sup>13</sup>

This formation of thiocarbonyl–iron(0) complexes directly from (**1a**) has been used to produce an  $\text{FeCS}$  derivative where the  $\text{Fe}(\eta^2\text{-CS}_2)$  precursor was not available. The reaction of a mixture of (**1a**) (1.3 mmol) and *dppe* ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) (1.5 mmol) in THF with Na/Hg led to the isolation of  $\text{Fe}(\text{CS})(\text{CO})_2(\text{dppe})$  (**6**)<sup>†</sup> (6% yield) [i.r.(Nujol):  $\nu(\text{CO})$  1970, 1930,



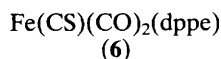
Scheme 1

<sup>†</sup> All new compounds reported have microanalytical, mass spectral, and spectroscopic data in accord with their assigned structures.



- a; L = PPh<sub>3</sub>  
 b; L = PMe<sub>3</sub>  
 c; L = PMe<sub>2</sub>Ph

Scheme 2



1915,  $\nu(\text{CS})$  1235  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  n.m.r. ( $\text{CDCl}_3$ , 297 K, 32.38 MHz) broad signal at 35.6 p.p.m.]

The reduction of cations (1a–c) with Na/Hg in THF shows the versatility of the behaviour of the reduced species, (A) (Scheme 2) according to the nature of the ancillary phosphorus groups L. A reasonable explanation of these results is as follows. With the relatively poor donor groups L = PPh<sub>3</sub>, (1a) is reduced irreversibly at  $-0.74$  V vs. saturated calomel electrode (s.c.e.) $\ddagger$  and the intermediate (A) undergoes homolytic cleavage of the Fe–C bond to afford the radical (B), precursor of (2a).<sup>10</sup> With the donor groups L = PMe<sub>3</sub>, (1b) is reduced irreversibly at  $-1.04$  V vs. s.c.e. $\ddagger$  and the inter-

$\ddagger$  Cathodic potential of the cyclic voltammogram of 20 mg of (1) in 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> acetonitrile solution using Platine as a working electrode. Scan rate: 100 mV s<sup>-1</sup>.

mediate (A) may lead to the metal centred radical (C) with a strong Fe–C bond. The homolytic cleavage of the C–S(R) bond is then expected to give the RS<sup>•</sup> radical which can be trapped by Hg<sup>0</sup>,<sup>14</sup> or its elimination can be assisted by Hg<sup>0</sup>, to form Hg(SR)<sub>2</sub>. Actually with (1c) (L = PMe<sub>2</sub>Ph) both processes occurred to give (3c) (A) → (C) and (4c) via (2c) (A) → (B). Indeed (1c) is reduced at  $-0.94$  V vs. s.c.e., $\ddagger$  at a potential between those of (1a) and (1b).

The reaction (1) → (3) is then expected to be used for the preparation of other MCS complexes, when the reduction of the corresponding  $\text{M}(\eta^2\text{-CS}_2\text{R})^+$  cations takes place at negative potential ( $\lesssim -1$  V vs. s.c.e.), e.g. when donor groups are bonded to the metal centre. It is noteworthy that this method is complementary of the desulphurization reaction of  $\text{M}(\eta^2\text{-CS}_2)$  precursors by phosphines which by contrast readily occurs<sup>1</sup> when ancillary ligands are not basic.

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