Reaction of Pentacarbonyliron with Phthalonitrile in Dimethylformamide and Isolation of Carbonyl Derivatives of Iron(II) Phthalocyanine Stabilised by Group 6 Donor Atoms

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Summary The preparation and properties of some phthalocyanine (pc)–carbonyl derivatives [Fe(pc)(CO)L] [L = dimethylformamide (dmf), tetrahydrofuran, dimethyl sulphoxide, ammonia, and $\mathrm{Pr^nNH_2}$] are reported, the first compound in the series being obtained directly from the reaction of $[\mathrm{Fe(CO)_5}]$ with o-$\mathrm{C_6H_4(CN)_2}$ in dmf.

Iron(II) phthalocyanine [Fe(pc)], has been extensively studied mainly as a model for the haem group.[1] It was reported to absorb CO in concentrated sulphuric acid[2] or in dimethyl sulphoxide (dmso)[3] solution. Equilibrium data for carbon monoxide binding by [Fe(pc)] in solution in the presence of nitrogen-containing bases have been measured.[4]

As far as the solid state is concerned, we are aware of only one report[5] in which carbonyl derivatives [Fe(pc)(CO)L] (L = pyridine, piperidine, or 1-methylimidazole) have been isolated. However, preformed [Fe(pc)] must be used and rigorous adjustment of the amine:Fe molar ratio is required since equilibria (1) and (2) are almost invariably unfavourable for the formation of the carbonyl derivative with high amine concentrations. No carbonyl derivatives of [Fe(pc)] have been reported with *trans* ligands containing group 6 donor atoms.

$$[\mathrm{Fe(pc)}] + 2\mathrm{L} \rightleftharpoons [\mathrm{Fe(pc)L_2}] \qquad (1)$$

$$[\mathrm{Fe(pc)L_2}] + \mathrm{CO} \rightleftharpoons [\mathrm{Fe(pc)(CO)L}] + \mathrm{L} \qquad (2)$$

We report that the reaction of pentacarbonyl iron with $o\text{-}C_6H_4(CN)_2$ in dimethylformamide (dmf) at 110—140 °C, followed by cooling to room temperature and filtration under CO at atmospheric pressure led to the carbonyl derivative [Fe(pc)(CO)(dmf)] (**1**),† in yields as high as 70%; see equation (3). Compound (**1**), presumably a hexacoordinate-complex of iron (II) with CO and *O*-bonded dmf in the axial positions, was obtained as diamagnetic red-violet crystals after crystallization from dmf under CO. It is stable in air for several minutes, rapidly modified by air in solution or as a finely divided suspension, indefinitely stable under CO [ν_{CO} (Nujol) 1970 cm^{-1}] and thermally (70—90 °C) decomposed *in vacuo* to a mixture of α- and β-[Fe(pc)], as shown by i.r. spectroscopy. Lattice dmf‡ and coordinated[6] dmf were shown to be present by amide carbonyl stretching vibrations at 1682 and 1650 cm^{-1}, respectively. Gas-volumetric measurements have shown that carbonylation of [Fe(pc)] is quantitative at room temperature in neat dmf, thus showing that the reverse of equilibrium (2), with L = dmf, is substantially suppressed. Reaction (3) is the only known direct method for preparing a carbonyl derivative of a metal phthalocyanine. Moreover, in view of the ready thermal displacement of both CO and dmf from (**1**) reaction (3) can be regarded as a new and alternative[7,8] method for preparing [Fe(pc)] at moderate temperatures.

$$4\, o\text{-}\mathrm{C_6H_4(CN)_2} + [\mathrm{Fe(CO)_5}] \xrightarrow{\mathrm{dmf}} [\mathrm{Fe(pc)(CO)(dmf)}] + 4\mathrm{CO} \qquad (3)$$

Neat tetrahydrofuran (thf) displaces dmf (as shown by i.r. measurements) from (**1**) and CO evolution was not detected, thus suggesting that a thf–carbonyl species, characterised by a carbonyl absorption at 1995 cm^{-1} (thf), is stable under these conditions, *i.e.* equilibrium (2) is completely shifted to the right in thf. The red-violet [Fe(pc)(CO)(thf)] (**2**) [ν_{CO} 1980 cm^{-1} (Nujol)] was isolated by recrystallising [Fe(pc)] from thf under CO.

When dimethyl sulphoxide (dmso) was used, preliminary gas-volumetric measurements showed that [Fe(pc)] was only partially carbonylated at 20 °C in neat dmso. Consistent with this, it was possible to isolate [Fe(pc)(CO)(dmso)] (**3**) [ν_{CO} 1980 cm^{-1} (Nujol)] from treatment of [Fe(pc)(dmso)$_2$] (**4**) in CH_2Cl_2 with CO, *i.e.* in the absence of a large excess of dmso. I.r. spectra in the 800—1200 cm^{-1} region were not conclusive[9] in establishing the mode of attachment of dmso in (**3**) and (**4**).

In an extension of this work, the new amine–carbonyl derivatives [Fe(pc)(CO)(NH$_3$)] and [Fe(pc)(CO)(Pr^{n}NH$_2$)] [ν_{CO} 2000 cm^{-1} (Nujol) for both] were obtained by the action of CO on CH_2Cl_2 solutions of the dark green [Fe(pc)(NH$_3$)$_2$] and [Fe(pc)(Pr^{n}NH$_2$)$_2$], respectively, which were themselves obtained from [Fe(pc)] and NH_3 and Pr^{n}NH$_2$, respectively, in benzene.

While this manuscript was in preparation, the ruthenium analogue [Ru(pc)(CO)(dmf)] was reported.[10]

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† Satisfactory elemental analyses were obtained for all the compounds.

‡ Retention of (presumably) lattice solvent, in variable amounts depending on the drying procedure, was also observed with compounds (**2**), (**3**), and (**4**).

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