

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

By FAUSTO CALDERAZZO,* DARIO VITALI, and GUIDO PAMPALONI
(*Istituto Chimica Generale, Via Risorgimento 35, 56100 Pisa, Italy*)

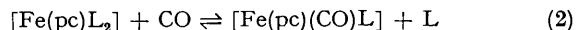
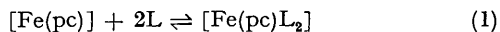
and INES COLLAMATI*

(*Laboratorio di Teoria e Struttura dei Composti di Coordinazione, C.N.R., Via Montorio Romano 36, 00131 Roma, Italy*)

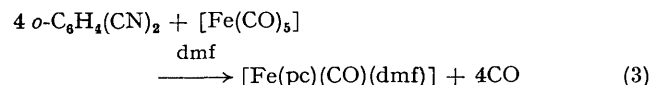
Summary The preparation and properties of some phthalocyanine (pc)-carbonyl derivatives $[\text{Fe}(\text{pc})(\text{CO})\text{L}]$ [$\text{L} =$ dimethylformamide (dmf), tetrahydrofuran, dimethyl sulphoxide, ammonia, and Pr^nNH_2] are reported, the first compound in the series being obtained directly from the reaction of $[\text{Fe}(\text{CO})_5]$ with $o\text{-C}_6\text{H}_4(\text{CN})_2$ in dmf.

IRON(II) phthalocyanine $[\text{Fe}(\text{pc})]$, has been extensively studied mainly as a model for the haem group.¹ It was reported to absorb CO in concentrated sulphuric acid² or in dimethyl sulphoxide (dmsO)³ solution. Equilibrium data for carbon monoxide binding by $[\text{Fe}(\text{pc})]$ 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 report⁵ in which carbonyl derivatives $[\text{Fe}(\text{pc})(\text{CO})\text{L}]$ ($\text{L} = \text{pyridine}$, piperidine , or 1-methylimidazole) have been isolated. However, preformed $[\text{Fe}(\text{pc})]$ 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 $[\text{Fe}(\text{pc})]$ have been reported with *trans* ligands containing group 6 donor atoms.



We report that the reaction of pentacarbonyl iron with $o\text{-C}_6\text{H}_4(\text{CN})_2$ 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 $[\text{Fe}(\text{pc})(\text{CO})(\text{dmf})]$ (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 - $[\text{Fe}(\text{pc})]$, as shown by i.r. spectroscopy. Lattice dmf[‡] and coordinated⁶ 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 $[\text{Fe}(\text{pc})]$ is quantitative at room temperature in neat dmf, thus showing that the reverse of equilibrium (2), with $\text{L} = \text{dmf}$, 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 $[\text{Fe}(\text{pc})]$ at moderate temperatures.

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 $[\text{Fe}(\text{pc})(\text{CO})(\text{thf})]$ (2) [ν_{CO} 1980 cm^{-1} (Nujol)] was isolated by recrystallising $[\text{Fe}(\text{pc})]$ from thf under CO.

When dimethyl sulphoxide (dmsO) was used, preliminary gas-volumetric measurements showed that $[\text{Fe}(\text{pc})]$ was only partially carbonylated at 20 °C in neat dmsO. Consistent with this, it was possible to isolate $[\text{Fe}(\text{pc})(\text{CO})(\text{dmsO})]$ (3) [ν_{CO} 1980 cm^{-1} (Nujol)] from treatment of $[\text{Fe}(\text{pc})(\text{dmsO})_2]$ (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 conclusive⁹ in establishing the mode of attachment of dmsO in (3) and (4).

In an extension of this work, the new amine-carbonyl derivatives $[\text{Fe}(\text{pc})(\text{CO})(\text{NH}_3)]$ and $[\text{Fe}(\text{pc})(\text{CO})(\text{Pr}^n\text{NH}_2)]$ [ν_{CO} 2000 cm^{-1} (Nujol) for both] were obtained by the action of CO on CH_2Cl_2 solutions of the dark green $[\text{Fe}(\text{pc})(\text{NH}_3)_2]$ and $[\text{Fe}(\text{pc})(\text{Pr}^n\text{NH}_2)_2]$, respectively, which were themselves obtained from $[\text{Fe}(\text{pc})]$ and NH_3 and Pr^nNH_2 , respectively, in benzene.

While this manuscript was in preparation, the ruthenium analogue $[\text{Ru}(\text{pc})(\text{CO})(\text{dmf})]$ 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).

¹ A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.

² I. Collamati, C. Ercolani, and G. Rossi, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 799.

³ S. Gaspard, R. Viovy, J. M. Brégeault, C. Jarjour, and S. Yolou, *Compt. rend.*, 1975, **281C**, 925.

⁴ D. V. Stynes and B. R. James, *J. Amer. Chem. Soc.*, 1974, **96**, 2733.

⁵ B. R. James, K. J. Reimer, and T. C. T. Wong, *J. Amer. Chem. Soc.*, 1977, **99**, 4815.

⁶ E. W. Randall, C. M. Silcox Yoder, and J. J. Zuckerman, *Inorg. Chem.*, 1966, **5**, 2240.

⁷ P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719.

⁸ E. G. Meloni, L. R. Ocone, and B. P. Block, *Inorg. Chem.*, 1967, **6**, 424.

⁹ F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.

¹⁰ N. P. Farrell, A. J. Murray, J. R. Thornback, D. H. Dolphin, and B. R. James, *Inorg. Chim. Acta*, 1978, **28**, L 144. We are indebted to Professor James for sending us copy of his paper prior to publication.