Inorganica Chimica Acta, 32 (1979) L69–L70

An Adduct of *trans*-Diiodobis(1,2-dimethoxyethane)-nickel(II) and 1,2-Diiodotetrafluorobenzene

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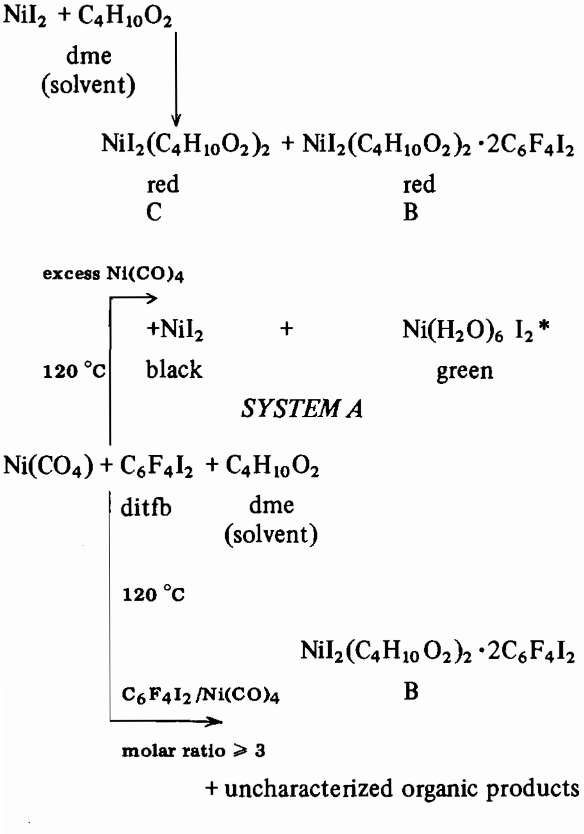
Received November 2, 1978

η^4-Cyclobutadiene- [1] and η^4-trimethylenemethyl- [2] transition metal complexes have been prepared by the reactions of transition metal carbonyls with appropriate organic halides in what are variously termed halide abstraction, metal insertion, oxidative substitution or, incorrectly, oxidative addition reactions and attempts to prepare transition metal–benzyne complexes by similar routes have been reported [3]. The reaction of tetracarboxylnickel(0) with 1,2-diiodobenzene in hexane gave a novel μ-1,2-phthalloyl complex which was originally thought to contain the benzyne ligand [3]. 1,2-Diiodotetrafluorobenzene (ditfb) with tetracarbonylnickel(0) gave an orange-red substance which was reported to undergo reversible colour changes on exposure to a nitrogen atmosphere and then to the air [3]. We have investigated the ditfb/tetracarbonylnickel(0) system and wish to report our preliminary results.



*occurs only if conditions are not anhydrous

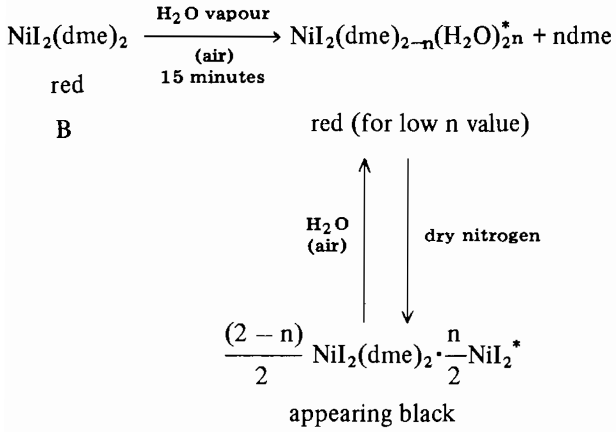
Scheme 1

An initially colourless 1,2-dimethoxyethane (dme) solution of ditfb and tetracarbonylnickel(0) under nitrogen in a Carius tube, on heating at 120 °C, assumed a dark red colour after a short time. On cooling the solution to room temperature after a reaction time of 16 hours an orange-red crystalline solid, A, of variable analyses, separated out.

Attempts to establish that A, which after a short exposure to air underwent the colour changes described above, contained a benzyne moiety by heating the orange-red solid, A, with Diels–Alder reagents such as 2,3,4,5-tetraphenylcyclopentadienone, 1,4-diphenylbutadiene and benzene all proved negative. On work-up the reaction mixture yielded the Diels–Alder reagent, nickel iodide hexahydrate and, significantly ditfb. The infra-red and mass spectra of A indicated the presence of ditfb and dme and the absence of carbonyl groups. In acetone the proton magnetic resonance spectrum of A, which was paramagnetic, consisted of a broad concentration dependent absorption. On addition of a drop of water to the deep red acetone solution of A, it was instantly decolourised, the broad pmr signal disappeared and a shoulder at approximately 3.4 ppm, with reference to TMS, appeared on the solvent resonance. This new resonance is attributed to dme which in deuterated acetone absorbs at 3.35 and 3.50 ppm.

The above data indicated that A probably contained an adduct of nickel iodide and ditfb and that dme was present as a ligand. Because of the variable analyses of A, however, a more positive conclusion as to the identity of the red solid could not be made.

A systematic study of the elemental composition of A prepared using a wide range of molar ratios of the reactants showed that, at low concentrations, if the molar ratio of ditfb/$Ni(CO)_4$ were ⩾3, an orange-red solid, B, of constant composition corresponding to $NiI_2(dme)_2(ditfb)_2$ crystallised from the solution. *Anal*: calculated for $C_{20}H_{20}F_8I_6NiO_4$, C, 18.51; H, 1.54; F, 11.72; I, 58.78%. Found, C, 18.65; H, 2.03; F, 11.72; I, 60.11% (see Scheme 1). This formulation for B was confirmed by its preparation from black anhydrous nickel iodide and ditfb in 1:2 molar ratio in dme. After gently heating the mixture to effect solution and allowing it to cool orange-red crystals analysing as B were obtained. *Anal*: calculated for $C_{20}H_{20}F_8I_6NiO_4$, see above. Found, C, 18.65; H, 2.03; F, 10.99; I, 58.25%.



*at surface of solid only n will be ever increasing as reversible cycles are repeated

Scheme 2

In the hope that an investigation of the properties of *trans*-$NiI_2(dme)_2$, C, would lead to a better understanding of the nature of A and B, C was prepared by recrystallising anhydrous nickel iodide from dme [6] (see Scheme 1).

The infra-red spectrum of C closely resembled that of B in the 1000–1200 cm^{-1} region and to a very good approximation the spectrum of B was simply the sum of those of ditfb and C thus confirming that B was and adduct of *trans*-$NiI_2(dme)_2$ and ditfb.

That C is only slightly soluble in dme (see preparation of C) explains the variable composition of systems A. The latter were produced in reaction systems in which tetracarbonylnickel(0) and ditfb were invariably in high concentration and the ditfb/$Ni(CO)_4$ molar ratios were much lower than 3 which ratio was optimal for the production of pure B. For example a typical reaction system would have concentrations of ditfb at 0.5 mol dm^{-3} and $Ni(CO)_4$ at mol dm^{-3}. Such a system will inevitably lead to the formation of $NiI_2(dme)_2$ possibly even to the exclusion of that of the adduct (scheme 1).

Although the nature of the adduct, B, is not yet fully understood two possibilities appear to exist. B may be either an inclusion system or a charge transfer complex (the iodide ion is known to act as an electron donor to acceptors such as 1,3,5-trinitrobenzene [6] and hexafluorobenzene is a good electron acceptor [7]. It may therefore be possible that ditfb is capable of acting as an acceptor with the iodide ligands of C as electron donor).

Further studies to elucidate the nature of B through the preparation and investigation of the properties of similar adducts, with different transition metal complex and organic moieties, to those of B, are currently underway in these laboratories. Attempts are also being made to identify the organic products of the reaction of tetracarbonylnickel(0) with ditfb in dme and to elucidate the reaction mechanism of that reaction.

Finally comments on the cause of the colour changes reported in the initial studies of systems A and the inorganic products arising from the $Ni(CO)_4$/ditfb reaction [3] are in order. If solid B or C is exposed to the atmosphere the dme ligands at or near the surface of the solids are substituted by water molecules. The partially hydrated solids retain their orange-red colour as the pale green hexaaquonickel(II) ion absorbs light much less strongly than B or C and presumably the hydrated layer is very thin (scheme 2).

On subjecting the superficially hydrated crystals to a dry nitrogen atmosphere the surface is dehydrated leaving a thin layer of the strongly absorbing black anhydrous nickel iodide at the surface. The crystals now appear black. On re-exposure to the air the surface layer is re-hydrated and the solids again appear to be orange-red in colour. Interestingly similar observations, but with reversible green to black colour changes, may be made by subjecting hexaaquonickel(II) iodide to a dry nitrogen atmosphere and then to the air!

The green and black products of the $Ni(CO)_4$/ditfb reaction referred to in reference [3] are not observed at the reactant concentrations and ratios (typical concentrations were: $Ni(CO)_4$, 0.05 mol dm^{-3}; ditfb 0.15 mol dm^{-3}) used in the work described here and were probably respectively hydrated and anhydrous nickel iodide which could arise through using excess $Ni(CO)_4$ in a highly concentrated reaction system (Scheme 2) (in the early work [3], typical reactant concentrations were $Ni(CO)_4$, mol dm^{-3}; ditfb, 0.5 mol dm^{-3}).

Acknowledgements

Acknowledgements are made to the North Yorkshire and West Yorkshire Education Authorities for maintenance grants to C.J.P. and D.M.S. respectively and to the Chemical Society for a Research Fund Grant (EWG).

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