Synthesis and Reactivity of Organometallic Nickel(II) Complexes Obtained by Oxidation of Nickel(0) Complexes with Halogenated Organic Compounds

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Reaction of the complexes $[Ni(dpb)_2]$ [dpb = 1,4-bis(diphenylphosphino)butane] and $[Ni(dpp)_2]$ [dpp = 1,3-bis(diphenylphosphino)propane] with RCOX (R = Ph or Et; X = Cl or Br) in benzene, in molar ratio 1 : 1, at room temperature, produces nickel(II)-acyl complexes. The spontaneous decomposition of these species produces nickel(II) dihalogenodiphosphino-complexes, nickel(0) monocarbonyldiphosphino-complexes, and benzophenone or diethyl ketone.

Reaction of $[Ni(dpb)_2]$ with PhBr gives [NiBr(Ph)(dpb)], which undergoes ready carbonylation with CO in benzene to give benzoyl bromide.

THE complexes $[Ni(dpp)_2]$ [dpp = 1,3-bis(diphenylphosphino)propane] and $[Ni(dpb)_2]$ [dpb = 1,4-bis(diphenylphosphino)butane] are known to react easily with thiocarbamoyl chloride to give $[Ni(diphosphine)(CSNMe_2)Cl]$.[1] Moreover both $[Ni(dpp)_2]$ and $[Ni(dpb)_2]$ are known to be easily oxidized to Ni^{II} complexes by cyanogen [2] and hydrogen cyanide [3] and both complexes are efficient catalysts in the homogeneous-phase addition of HCN to butadiene to give pent-3-enenitrile.[4]

We report here the reactions of $[Ni(dpp)_2]$ and $[Ni(dpb)_2]$ with a variety of halogen-containing organic compounds, with particular regard to acyl halides.

EXPERIMENTAL

All operations were conducted under argon at room temperature or as otherwise stated. I.r. spectra were recorded on a Perkin-Elmer 457 instrument, equipped, for spectra in solution, with permanent NaCl or CsCl 0·5-mm cells. Spectra in the visual range were obtained with an Optica CF4R instrument. G.l.c. analyses were performed on a Hewlett–Packard 5750 instrument; a molecular sieves column (2 m long, 4 mm diam.) was used for carbon monoxide detection and a Carbowax W (10%) column (2 m long, 4 mm diam.) for the detection of chlorobenzene and benzaldehyde.

Materials.—Benzene was purified and dried by a standard method. All other solvents were C. Erba solvents (R.P.E. grade) and were used as received. The acyl halides were C.Erba reagents and were purified by distillation under vacuum.

Complexes.—$[Ni(dpp)_2]$ and $[Ni(dpb)_2]$ were prepared according to published methods,[5] as well as $[NiCl_2(dpp)]$,[6] $[NiBr_2(dpb)]$,[7] and $[NiCl_2(dpb)]$.[8]

Preparation of [NiBr(Ph)(dpb)].—The complex $[Ni(dpb)_2]$ (1 g) was dissolved in bromobenzene (80 ml) at room temperature to give a red solution. This was warmed at 40 °C for 14 h with stirring; after *ca.* 3 h a yellow, very fine precipitate began to separate. This was filtered off and washed with benzene (3 × 70 ml), m.p. 220 °C (decomp.) [Found (data referring to samples of different batches): C, 63·55 (62·95); H, 5·5 (5·15); Br, 12·6. Calc. for NiBr(Ph)(dpb): C, 63·6; H, 5·15; Br, 12·45%]. The complex was diamagnetic.

General Method used for Studying the Reactions between the Nickel(0) *Complexes and the Acyl Halides.*—The reaction vessel was a three-necked flask, equipped with a vacuum stopcock and a gas-tight rubber cap. The Ni^0 complex (0·2—1·0 mmol) was added (by means of a Teflon container previously held in a special valve for solids, fitted on the third neck) to a benzene solution (20—40 ml) of the acyl halide present in equimolar amounts with Ni^0. The i.r. spectrum of the acyl halide solution before addition of Ni^0 represented the reference spectrum.

Addition of $[Ni(dpb)_2]$ led immediately to clear red solutions ($[Ni(dpb)_2]$ is rather soluble in benzene) and addition of $[Ni(dpp)_2]$ gave yellow suspensions, which became red solutions within 10—20 min. Small amounts of the reacting solution could be sucked off through the rubber cap and several i.r. spectra of the solution could be recorded at various times. The events which could be visually estimated for the various reactant pairs are described in the following section.

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[6] G. R. Van Hecke and W. D. Horrocks, *Inorg. Chem.*, 1966, **5**, 1968.

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[8] B. Corain and G. Puosi, *J. Catalyst*, 1973, **30**, 403.

The qualitative analysis of the final reaction products was carried out by several techniques. Thus, absence of chlorobenzene and carbon monoxide was ascertained by g.l.c.; benzophenone and diethyl ketone were determined by an accurate estimate of their $\nu_{C=O}$ stretching bands and comparison of the observed values with those of standard ketone solutions. In order to limit the uncertainties, known controlled amounts of the proper ketone were also added to the final reaction solutions in order to verify the appearance of a single defined $\nu_{C=O}$ band. The nature of the obtained $[NiX_2(diphosphine)]$ complexes has been ascertained by elemental analysis and by comparison of their Nujol mull spectra (as far as 250 cm^{-1}) with those of authentic samples.

The quantitative estimate of benzophenone and diethyl ketone was only approximate because of partial overlap of the $\nu_{C=O}$ band with other bands. The quantitative analysis of [Ni(CO)(dpp)(dpp)] [9] was carried out assuming for the $\nu_{C=O}$ band of this complex a molar extinction coefficient equal to that of the very similar complex [Ni(CO)(dpb)(dpb)] which is known as a solid pure sample.[9] The quantitative analysis of $[NiCl_2(dpp)]$ could be carried out accurately on dissolving the red crystals obtained upon filtration with a known volume of CH_2Cl_2 and using a spectrophotometric determination at 470 nm.

RESULTS AND DISCUSSION

Reaction between $[Ni(dpp)_2]$, $[Ni(dpb)_2]$, *and Acyl Halides.*—The scope of the reactions carried out in the present research and the nature of the final reaction products either isolated (and characterized) or identified upon the basis of i.r. spectroscopic evidence are summarized in the Table. In all cases but one, the final inorganic reaction products are the insoluble complexes $[NiX_2(diphosphine)]$ (X = Cl or Br; diphosphine = dpp or dpb) and the soluble compounds [Ni(CO)(diphosphine-*P*)(diphosphine-*PP'*)] [9] in which one diphosphine acts as a bidentate ligand and the other one as a unidentate. Benzophenone and diethyl ketone (depending on the nature of the acyl halide) are the organic products identified.

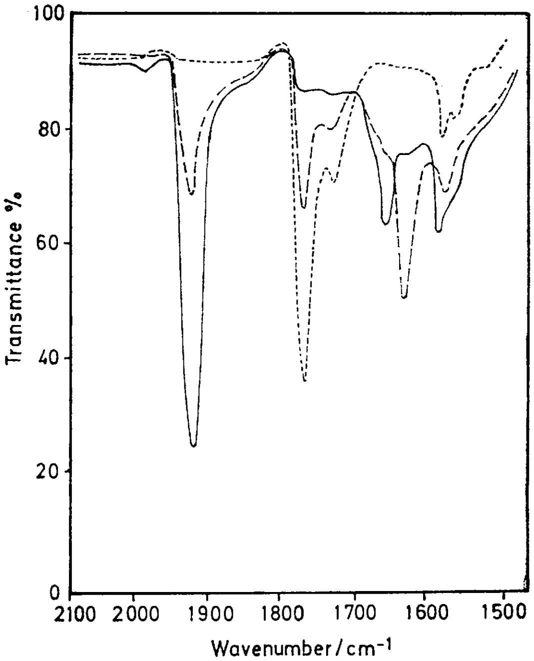
Ni^0	Acyl halide	Products
$[Ni(dpp)_2]$	PhCOCl	$[NiCl_2(dpp)]$ [Ni(CO)(dpp)(dpp] Ph_2CO
$[Ni(dpp)_2]$	EtCOCl	$[NiCl_2(dpp)]$ [Ni(CO)(dpp)(dpp)] Et_2CO
$[Ni(dpp)_2]$	PhCOBr	[NiBr(COPh)(dpp)]
$[Ni(dpb)_2]$	PhCOCl	$[NiCl_2(dpb)]$ [Ni(CO)(dpb)(dpb)] Ph_2CO
$[Ni(dpb)_2]$	EtCOCl	$[NiCl_2(dpb)]$ [Ni(CO)(dpb)(dpb)] Et_2CO
$[Ni(dpb)_2]$	PhCOBr	$[NiBr_2(dpb)]$ [Ni(CO)(dpb)(dpb)] Ph_2CO

Note: molar ratios Ni^0/acyl halide = 1.

The data reported in the Table have to be considered qualitative and only for the reaction between $[Ni(dpp)_2]$ and PhCOCl are quantitative data available.

In all cases reported in the Table the dissolution of the reacting Ni^0 complex is accompanied by a more or less pronounced decrease of the intensity of the band due to the $\nu_{C=O}$ of the employed acyl halide and by the development of a medium intensity band in the region 1620—1650 cm^{-1} (1630 for $[Ni(dpp)_2]$/PhCOCl; 1650 for $[Ni(dpp)_2]$/EtCOCl; 1630 for $[Ni(dpb)_2]$/PhCOCl; 1645 for $[Ni(dpb)_2]$/EtCOCl; 1630 for $[Ni(dpp)_2]$/PhCOBr; 1620 for $[Ni(dpb)_2]$/PhCOBr).

The range 1620—1650 cm^{-1} is known to be typical of the $\nu_{C=O}$ values of metal–co-ordinated COR groups (R = alkyl, phenyl) [10-12] and it has been found [12] that the well characterized complexes $[Ni(X)(Ac)(PMe_3)_2]$ (X = Cl, Br, or I) display these bands in the region 1635—1650 cm^{-1}. On the basis of the i.r. features and of the existence of the above-mentioned acetyl Ni^{II} complexes, we propose that the primary reaction products are always the halogenoacyl complexes [Ni(X)(COR)(diphosphine)]. Only in the case of the system $[Ni(dpp)_2]$/PhCOBr, however, the primary acyl complex appears to be stable for at least 40 h; in the other cases the acyl complex represents only an unstable intermediate which decomposes spontaneously to give the stable final reaction products listed in the Table.



$[Ni(dpp)_2]$ + PhCOCl; benzene; *t ca.* 21 °C; cell path = 0·5 mm; [PhCOCl] = 2×10^{-2}M; molar ratio = 1 : 1. - - - - Solution containing PhCOCl (2×10^{-2}M), — — — reaction mixture after 90 min, —— reaction mixture after 20 h

The red solutions containing the complexes [Ni(X)(COR)-(diphosphine)] are apparently unstable and the precipitation of the dihalogenonickel(II) complex (they are all scarcely soluble) and the simultaneous increase in intensity of the i.r. band due to the C≡O stretch of the monocarbonyl Ni^0 complex can be observed after 20—120 min (depending on the reactants). In all cases the $\nu_{C=O}$ band due to the ketone is easily detectable after several hours.

For the reaction between $[Ni(dpp)_2]$ and PhCOCl quantitative data could be obtained. It is seen that 1 mol. equiv. of Ni^0 produces 0·5 (±0·05) mol. equiv. of $[NiCl_2(dpp)]$ and *ca.* 0·5 and 0·3 mol. equiv. of [Ni(CO)-(dpp)(dpp)] and benzophenone respectively. Carbon

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[9] B. Corain, M. Bressan, and G. Favero, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 197.

[10] C. D. Cook and G. S. Jauhal, *Canad. J. Chem.*, 1967, **45**, 301.

[11] S. P. Dent, C. Fahorn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1972, **46**, C68.

[12] H. F. Klein, *Angew. Chem. Internat. Edn.*, 1973, **12**, 402.

monoxide and chlorobenzene were carefully excluded as reaction products by gas chromatographic analysis. The relevant i.r. spectra are reported in the Figure. On recording the i.r. spectrum of the reacting solution as far as 250 cm^{-1}, it can be seen that, when the 1630 cm^{-1} band reaches its highest intensity, a very weak but significant band appears at 340 cm^{-1}; the intensity of the latter decreases to zero when the absorption at 1630 cm^{-1} has completely disappeared. The band at 340 cm^{-1} can be attributed to the ν_{Ni-Cl} of a Cl^- ligand *trans* to a substituted phosphine in a square planar Ni^{II} complex.[13]

The presence in solution of an acyl-metal complex is chemically supported by the observation that addition of CF_3CO_2H (2×10^{-2}M against an estimated 1×10^{-2}M concentration of the acyl complex) to the solution during the accumulation of the species absorbing at 1630 cm^{-1}, leads to partial decomposition of this species and to the formation of substantial amounts of benzaldehyde (*ca.* $0{\cdot}2 \times 10^{-2}$M) as seen by g.l.c. analysis.* Addition of chlorobenzene (2×10^{-2}M to 2×10^{-1}M) to the same solution has no effect on the intensity of the 1630 cm^{-1} band.

The nature of the final reaction products reported in the Table leads to the conclusion that the decomposition route of the nickel(II)–acyl complexes described in this paper is quite new in the chemistry of metal–acyl complexes and must be compared with the other two well documented types of decomposition, *i.e.* the decarbonylation of the acyl ligand with reductive elimination ($Rh^{III} \longrightarrow Rh^{I}$, elimination of PhCl) observed for the complex $[RhCl_2(COPh)(PPh_3)_2(S)]$ [14] and the decarbonylation without reductive elimination observed for the complex $[PtCl(Ac)(PPh_3)_2]$ [10] and for $[Ni(Cl)(Ac)(PMe_3)_2]$.[12]

Reaction between $[Ni(dpb)_2]$ *and Bromobenzene. Reaction of* $[NiBr(Ph)(dpb)]$ *with Carbon Monoxide.*— $[Ni(dpb)_2]$ Reacts with PhBr at 50 °C to give a yellow microcrystalline product, the analysis for which leads to its formulation as $[NiBr(Ph)(dpb)]$. $[Ni(dpp)_2]$ does not react under the same conditions. The compound is air stable in the solid state and thermally quite stable. It is almost insoluble in common organic solvents and its i.r. Nujol mull spectrum displays a strong band at 1550 cm^{-1}. This band is characteristic also of the complexes $[PtCl(Ar)(PEt_3)_2]$ (Ar = aryl) (1561—1574 cm^{-1}) [15] and of $[Ni(CN)(Ph)(deb)]$ [16] [deb = 1,4-bis(diethylphosphino)butane] (1565 cm^{-1}) and is presently attributed to a C=C aromatic stretching mode due to the σ-bonded $C_6H_5^-$ ligand. No band attributable to a ν_{Ni-Br} in a Ni^{II} square planar (the complex is diamagnetic) complex can be identified in the region 340—310 cm^{-1} [13b] and it is possible that a band, present also in bromobenzene, at 320 cm^{-1} (with shoulder at *ca.* 310 cm^{-1}) does obscure a ν_{Ni-Br} band expected at *ca.* 310 cm^{-1} for a Ni^{II} bromo-complex, in which the bromine atom is *trans* to a carbanion as a ligand.[17] The complex is likely to be polymeric in nature (possibly dimeric) bearing the dpb molecules as bridges between square planar moieties.[7] A benzene suspension of $[NiBr(Ph)(dpb)]$ (210 mg in 15 ml) reacts slowly with CO to give after 40 h a pale yellow solution. I.r. spectra of the solutions in equilibrium with the sparingly soluble Ni^{II} complex during the reaction show the steady formation of $[Ni(CO)_2(dpb)]$ [9] and benzoyl bromide. At the end of the reaction, the yield of benzoyl bromide is quantitative (based on the Ni^{II} employed) and the i.r. spectrum of the solution shows the presence of $[Ni(CO)_2(dpb)]$ ($\nu_{C=O}$ at 1995 and 1940 cm^{-1}). The quantitative estimate of this latter complex is impossible, as it is not known as a pure compound.[9]

The results can be explained in terms of an ' insertion ' of CO into the Ni^{II}–C(sp^2) bond followed by reductive elimination of PhCOBr promoted by carbon monoxide, with concomitant formation of $[Ni(CO)_2(dpb)]$ (see Scheme).

As far as we know, this is one of the very few examples of reaction of CO with a Ni^{II} complex containing a nickel–carbon σ bond.[12,18,19]

$$[Ni(dpb)_2] + PhBr \longrightarrow [NiBr(Ph)(dpb)] + dpb$$

$$\begin{tikzcd} {[NiBr(Ph)(dpb)] + CO} \arrow[r] & {[NiBr(COPh)(dpb)]\ \text{postulated intermediate (see ref. 12)}} \arrow[d, "CO"] \\ & {[Ni(CO)_2(dpb)] + PhCOBr} \end{tikzcd}$$

$\nu_{CO} = 1995$, 1940 $\qquad \nu_{CO} = 1790$

SCHEME

CONCLUSIONS

The complexes $[Ni(dpp)_2]$ and $[Ni(dpb)_2]$ have shown to be able not only to cleave several C(sp^2)–X bonds, but to produce Ni^{II} organometallic species of various stabilities and reactivities. In particular, the nickel(II)–acyl complexes offer an entirely new example of spontaneous decomposition of transition-metal acyl compounds. The complex $[NiBr(Ph)(dpb)]$ appears to be stable, in a general sense, but prone to reductive elimination in the presence of CO, and, for this reason, $[Ni(dpb)_2]$ appears as a promoter of a two-stage synthesis of benzoyl bromide from bromobenzene and carbon monoxide.

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* 1M = 1 mol dm^{-3}.

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