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Preliminary communication

ACID-CATALYZED LIGAND SUBSTITUTION ON THE COMPLEX $Ni^0(CO)[P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2]_2$

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Summary

Triphenylphosphite reacts with the nickel(0) complex, $Ni(CO)(DPB)_2$, (DPB = 1,4-bis(diphenylphosphino)butane) in dichloromethane with quantitative displacement of one DPB molecule; the rate is enhanced by acids.

The mechanism of ligand substitution reactions in the coordination sphere of coordinatively saturated metal(0) complexes is usually dissociative [1]. However, exchange of labelled CO with $Fe(CO)_5$ was also found to be acid catalyzed with CF_3COOH, an efficient catalyst [1]. We have now observed that the complex Ni(CO)(DPB)(DPB—P) (I), in which one DPB ligand is thought to act as a monodentate ligand [2], undergoes quantitative displacement of DPB upon treatment with a tenfold excess of $P(OC_6H_5)_3$ in CH_2Cl_2 under argon at room temperature, and that the process is catalyzed by CF_3COOH and H_2SO_4.

A very slow reaction takes place when a 10^{-2} *M* solution of I is made 10^{-2} *M* in $P(OC_6H_5)_3$ (distilled twice at 1 mmHg). The relevant changes in the IR spectrum of the solution are shown in Fig. 1a. The same spectral pattern is observed with a tenfold excess of ligand, but the reaction is considerably faster and leads to the complete disappearance of the 1907 cm^{-1} band (ν(CO) of the reacting complex) (Fig. 1b). Spectral data are consistent with the occurrence of reaction 1.

$$\underset{\nu(CO)\ 1907\ cm^{-1}}{Ni(CO)(DPB)(DPB\text{—}P)} + P(OC_6H_5)_3 \rightleftharpoons \underset{\nu(CO)\ 1942\ cm^{-1}}{Ni(CO)(DPB)[P(OC_6H_5)_3]} + DPB \qquad (1)$$

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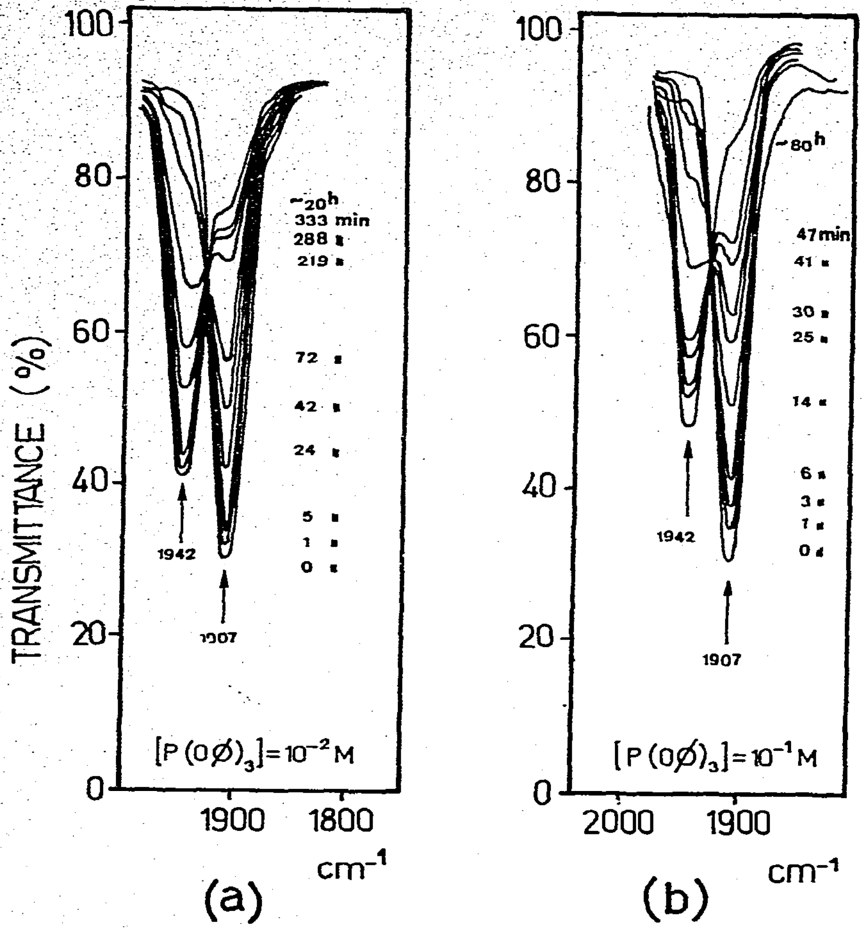

Fig.1. Spectral changes observed during the reaction between Ni(CO)(DPB)(DPB—P) and $P(OC_6H_5)_3$. $[Ni^0] = 10^{-2}$ *M*; (a) $[P(OC_6H_5)_3]$ 10^{-2} *M* and (b) 10^{-1} *M*. Cell path 0.5 mm.

The observed increase in ν(CO) is consistent with coordination of $P(OC_6H_5)_3$ to nickel(0) and this [3], coupled with the finding that the reaction is almost quantitative (≈90%) when the ligand to nickel ratio is 1, confirms the validity of eq. 1.

If the reaction is carried out with I(10^{-2} *M*) and twice-distilled $P(OC_6H_5)_3$ (10^{-1} *M*) in the presence of CF_3COOH 1×10^{-4}–4×10^{-4} *M*, the rate of disappearance of I is greatly enhanced (see Fig. 2) with the spectral features remaining the same as those in the absence of acid. Sulfuric acid is also effective but significantly less than CF_3COOH. With 10^{-2} *M* CF_3COOH ligand substitution is instantaneous.

We suggest a mechanism based on (a) protonation of I [4], (b) replacement of DPB—P by L in the obtained labile nickel(II) hydrido complex, and (c) reductive elimination of H^+ to give the final product; this represents a "fast" route for ligand substitution which is an alternative to the "classic" ligand substitution mechanism [1].

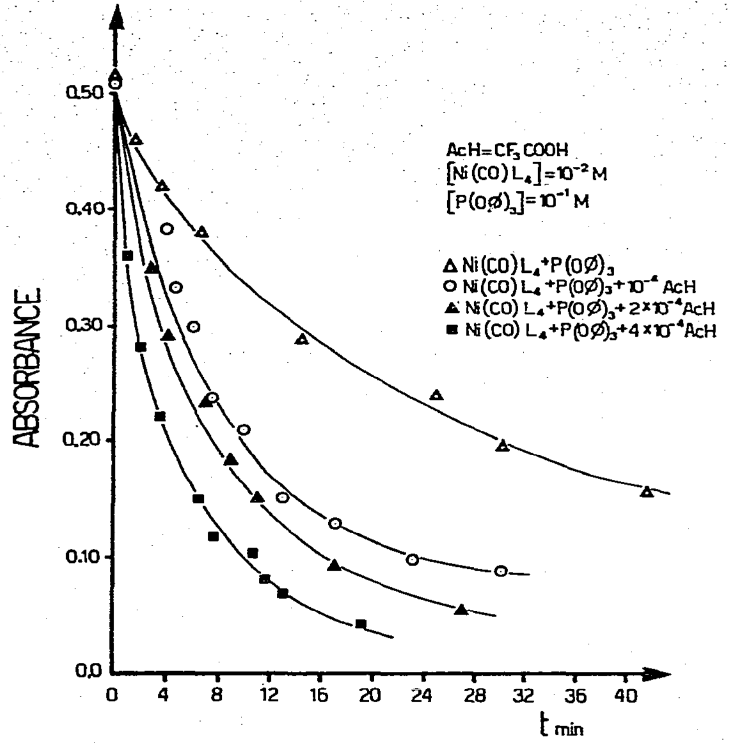

Fig.2. Effect of added CF$_3$COOH on the rate of disappearance of Ni(CO)(DPB)(DPB—P) in the presence of P(OC$_6$H$_5$)$_3$. Changes of absorbance at 1907 cm^{-1} versus time under the specified conditions.

This is the first example of an acid-catalyzed ligand substitution in ML$_n$ complexes (in which the metal is Ni, Pd, Pt and L a neutral ligand). Further studies on the reaction are in progress.

References

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