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Phosphine Site Exchange in $[NiX(PMe_3)_4]X$ *via* an I_a Mechanism with a 20-electron Transition State

By PIERRE MEIER and ANDRÉ E. MERBACH*
(*Institut de Chimie Minérale et Analytique, Université de Lausanne,* 3, *Place du Château,*
CH-1005 *Lausanne, Switzerland*)

and MICHÈLE DARTIGUENAVE and YVES DARTIGUENAVE*
(*Laboratoire de Chimie de Coordination du CNRS et Université P. Sabatier,* 205, *route de Narbonne,*
F-31030 *Toulouse, France*)

Summary In the stereononrigid, low-spin, 18 electron, trigonal-bipyramidal complexes $[NiX(PMe_3)_4]X$ (X = halide) axial–equatorial PMe_3 interchange has been shown by ^{31}P n.m.r. spectroscopy to follow an I_a mechanism with a 20 electron transition state involving attack by the X^- ion.

AMONG the different mechanisms postulated to explain stereochemical nonrigidity in low spin five-co-ordinate d^8 complexes (18 electron) with monodentate phosphine ligands, the ones more commonly cited are the Berry pseudo-rotation process in $[ML_5]^{n+}$ and $[NiXL_4]BF_4$[1,2] and the tetrahedral jump process in the hydride $[MHL_4]^{m+}$ complexes.[3] In both cases the processes occur with no modification of the number of electrons in the transition state, in agreement with the 18 e rule.[4] We report here an exception to this rule, occurring in the low-spin d^8 five-co-ordinate trigonal-bipyramidal (TBP) complexes $[NiX(PMe_3)_4]X$ (X = halide).

The $^{31}P\{^1H\}$ Fourier transform n.m.r. spectra of CH_2Cl_2–CD_2Cl_2 (1 : 1) solutions of $[NiX(PMe_3)_4]X$, obtained by adding 1 mol equiv. of PMe_2 to the five-co-ordinate $NiX_2(PMe_3)_3$ complexes, show, at 173 K, a sharp singlet at −14·5 p.p.m. for X = Cl, −15·6 p.p.m. for X = Br, and −18·4 p.p.m. for X = I, upfield from external H_3PO_4 (62·5%), indicating a fast intramolecular phosphine exchange. On the other hand, A_2X_2 spectra can be resolved at 163 K when the counterion is BF_4^-; +1·0 (P_{ax}) and −28·8 (P_{eq}) p.p.m. for X = Cl (J_{PP} 82·5 Hz), −2·6 and −29·2 p.p.m. for X = Br (J_{PP} 79 Hz), and −5·2 and −29·2 p.p.m. for X = I (J_{PP} 76·5 Hz), in agreement with a trigonal bipyramidal structure with X in an equatorial position, as determined by *X*-ray diffraction in the solid state[2] for the $[NiBr(PMe_3)_4]BF_4$ complex.

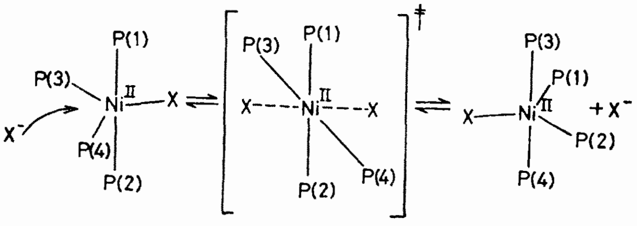
This indicates that the ionic halide X^- is involved in the exchange process. At 114 K in chlorodifluoromethane, the PMe_3 exchange in $[NiCl(PMe_3)_4]Cl$ is almost frozen on the n.m.r. time scale, giving the two triplets in the spectrum as expected for the TBP cation $[NiCl(PMe_3)_4]^+$, +1·5 and −28·6 p.p.m. with J_{PP} 79·0 Hz. However, when the halide is Br or I, the 114 K spectra are broad singlets showing that the PMe_3 exchange is still fast. The exchange rate increases in the order $Cl<Br<I$, that is, in the order of increasing nucleophilicity of the anion.

TABLE. Determination of the rate $1/\tau_c$ of the axial–equatorial PMe_3 exchange in a 0·02 M solution of $[NiBr(PMe_3)_4]BF_4$ in CH_2Cl_2–CD_2Cl_2 (1 : 1), at 169 K as a function of $[NBu_4]Br$ concentration.

$[NBu_4]Br/\mathrm{M}$	$10^{-4}\ 1/\tau_c/s^{-1}$[a]	$10^{-7}k_2/l\ mol^{-1}\ s^{-1}$
0·0	$<10^3$	—
$2{\cdot}16 \times 10^{-3}$	$4{\cdot}6 \pm 0{\cdot}5$	$2{\cdot}1 \pm 0{\cdot}3$
$4{\cdot}88 \times 10^{-3}$	$12{\cdot}5 \pm 1{\cdot}1$	$2{\cdot}6 \pm 0{\cdot}3$
$7{\cdot}14 \times 10^{-3}$	$18{\cdot}0 \pm 2$	$2{\cdot}5 \pm 0{\cdot}3$

[a] $1/\tau_c = \{d[NiBr(PMe_3)_4]/dt\}/[NiBr(PMe_3)_4] = k_2\ [Br^-]$.

A second order rate-law has been observed (Table) for the PMe_3 axial–equatorial interchange in the $[NiBr(PMe_3)_4]^+$ cation, thus indicating the participation of the ionic bromide to the transition state; see Scheme. This implies an associative interchange mechanism I_a. It is the first time, to our knowledge, that such a mechanism (18 e $\rightleftharpoons$ 20 e $\rightleftharpoons$ 18 e) has been unambigously assigned in a d^8 low-spin Ni^{II} five-co-ordinate complex.



Scheme

This mechanism may be related to the solid state structure of the [NiBr(PMe$_3$)$_4$]$^+$ cation,[2] which consists of a distorted trigonal bipyramid with the Ni, Br, P(3)$_{eq}$, and P(4)$_{eq}$ atoms in the equatorial plane. The Ni, Br, P(1)$_{ax}$, and P(2)$_{ax}$ atoms are also co-planar, in a plane perpendicular to the equatorial one. The P(1)$_{ax}$ and P(2)$_{ax}$ atoms are symmetrically bent toward the equatorial bromine atom with short Br–P(1)$_{ax}$ and Br–P(2)$_{ax}$ contacts, which leave the cation free for *trans* nucleophilic attack by a halide ion.

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