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XPS Photoelectron Study (ESCA) of Some Nickel(II) Phosphine Complexes with Catalytic Activity in Cyclotrimerization Reactions of Acetylenes

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Complexes of transition metals containing tertiary phosphine ligands have been widely investigated by XPS photoelectron spectroscopy (ESCA), the larger amounts of data being reported for palladium(II) and platinum(II) complexes [1–5]. ESCA data depend significantly on the oxidation state of the central metal [2, 4], but are much less dependent on other structural effects. Thus, the 2p binding energies of P tend to be remarkably constant, a fact which has been explained by invoking a balance between heteropolar σ, and π bonding mechanisms between metal and phosphorus, leading to a redistribution of electronic charge and resulting ultimately in an approximate constancy of the atomic charge on the P donor atoms [1–5].

No ESCA data are reported instead in the literature for Ni(II) phosphine complexes, apart from $(Ph_3P)_2NiCl_2$ measured by J. R. Blackburn [1]. We undertook therefore a systematic investigation of the ESCA spectra of several complexes of L_2NiX_2 type (L = tertiary phosphine, X = Cl, Br, I, NCS, $RC{\equiv}C^-$), which offer a variety of structural effects, including various stereochemical arrangements (tetrahedral and planar, the latter in *trans* or *cis* configuration), substituent effects in the phosphine ligands, and the varying σ- and π-donor abilities of the X ligands, and have furthermore acquired recently particular interest in the field of catalytic polymerization because of their ability in promoting stereoselective oligomerization of acetylenic monomers [6–9].

The series of investigated compounds were prepared and characterized by methods reported previously [6–9].

XPS spectra were run on a VG ESCA 3 photoelectron spectrometer using $AlK\alpha_{1,2}$ radiation (E = 1486.6 eV). Samples were dusted as thin film onto a gold plate to minimize charging effects.

The samples proved sufficiently stable to X-rays under experimental conditions adopted and showed no signs of damage or charging effects.

The b.e. reported are measured at the half width of the half maximum of the band.

Measurements represent averages of no fewer than three independent values on differently deposited samples and at least three successive runs for each deposition to compensate errors due to charging effects. The uncertainty corresponds to one standard deviation of ∓ 0.2 eV.

The binding energies of Ni(II) 2p 3/2 and P 2p of the complexes examined are reported in the Table.

TABLE. Ni 2p 3/2 and P 2p Binding Energies (eV) for Ni(II) Phosphine Complexes.

Compound	Structure	Ni 2p 3/2	P 2p
$(Ph_3P)_2NiI_2$	tetragonal	855.1	131.9
$(Bu_3P)_2NiI_2$	*trans*-planar	855.3	132.0
$(Ph_2PC_2H_4PPh_2)NiI_2$	*cis*-planar	855.2	132.2
$(Ph_3P)_2NiBr_2$	tetragonal	855.2	131.8
$(Ph_3P)_2NiCl_2$	tetragonal	855.3	131.9
$(Ph_3P)_2Ni(NCS)_2$	*trans*-planar	854.3	131.0
$(Ph_3P)_2Ni(C{\equiv}CPh)(NCS)$	*trans*-planar	854.0	131.1
$(Ph_3P)_2Ni(C{\equiv}CPh)_2$	*trans*-planar	854.9	131.9
$(Bu_3P)_2Ni(C{\equiv}CPh)_2$	*trans*-planar	855.0	132.0

From the b.e. data of Ni 2p 3/2 and P 2p, it is clearly evident that no major change in b.e. is accompanied to changes in spin state and coordination geometry of these Ni(II) complexes, *e.g.* the b.e. differences are confined within the limits of experimental error in the series L_2NiI_2 with L = triphenylphosphine (high-spin, pseudo-tetrahedral), L = tri-n-butylphosphine (low-spin, *trans*-planar), and L_2 = bis(diphenylphosphino)ethane (low-spin, *cis*-planar). This is in line with other previous reports and measurements of negligible differences in b.e. with varying coordination geometry, *e.g.* in triphenylphosphine complexes of different steric structure [1], and in tetragonal and planar Ni(II) complexes with dithiocarbazate ligands [11, 12] and points to a mechanism which assures near constancy of atomic charge distributions in tetrahedral and planar nickel complexes with the same or with similar ligands. As suggested previously, this situation is probably related to the occurrence of strong π-backdonation effects Ni → P, and to the availability of metal π-donor orbitals in both types of structures [1], furthermore the presence of large organic substituent groups at the P atom undoubtedly helps dispersing atomic charge differences among several atoms besides phosphorus, as noted by Clark [3], and thus contributes to minimize b.e. differences on P 2p both between planar and tetrahedral and between *trans* and *cis* planar structures [3], as well as between complexes with phosphines of different basicity. This substantial similarity of chemical environment around the nickel atom is in agreement with the observed lack of major changes in Ni binding energies between *cis* and *trans* planar forms.

Also the effect of anionic ligands in L_2NiX_2 complexes is negligible on the P and Ni binding energies, as long as X is a halogen or an acetylide ion; the obvious implication is that atomic charge distribution among the chromophore atoms is in any case governed primarily by the donor–acceptor σ and π interactions between nickel and phosphorus atoms. That difference in polarity of metal–X bonds does not result in significant b.e. changes of metal core orbitals has already been observed by Blackburn [1], and explained as a compensation between σ and π donor effects; small changes in the series L_2PtX_2 (X = Cl, I) [3] seemed to imply a greater positive charge on the metal for X = I, and give therefore evidence for a higher overall donation ability of chlorine, but the observed effect is really too small, and in the present case we observe small differences in Ni 2p 3/2 b.e., *e.g.* between L_2NiCl_2 and L_2NiI_2, (~ 0.2 eV), but in the reverse order as observed by Clark (hence rather in line with a larger polarity of metal–Cl bond), and anyway not sufficiently significant if compared with the experimental uncertainty which is about ∓ 0.2 eV. For a possible, smaller difference in the behaviour of acetylide complexes see below.

Thiocyanate is the only anionic ligand in the investigated series to exert a marked difference on the core orbital b.e. of the remaining atoms, both the Ni 2p 3/2 and P 2p b.e. being lower by *ca.* 1 eV with respect to complexes with halides or acetylides. Phenomenologically, this small decrease of Ni and P binding energies gives evidence for a stronger overall donor ability of the NCS^- ligand towards the L_2Ni moiety, and of metal–ligand donor–acceptor interactions which become now of comparable importance to those occurring between metal and phosphorus. A small effect in the same sense is possibly exhibited also by the acetylide ligand, which appears to shift the Ni 2p 3/2 b.e. by some 0.4 eV to lower values (compare 854.9 eV in $(Ph_3P)_2Ni(C{\equiv}CPh)_2$ against 855.3 in $(Ph_3P)_2NiCl_2$), although the effect is still comparable to the experimental uncertainty.

The experimental data obtained from ESCA measurements do not follow the trend for the catalytic activity and selectivity exhibited by the investigated nickel phosphine complexes in the aromatic oligomerization of acetylenic monomers [6–9]. However, correlations can be drawn with some particular aspects of the stability and catalytic activity of the present nickel phosphine complexes. Thus, the thiocyanate ligands produce the situation of strongest covalent bonding to nickel, as revealed through the increase of negative metal charge, which leads to slower and more difficult replacement of anion ligands. In fact, thiocyanate complexes are slow catalysts, and replacement of NCS^- through acetylide ions can be stopped to the mixed $L_2Ni(NCS)(C{\equiv}CPh)$ species, itself an active intermediate in the catalytic trimerization of acetylenes [13].

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