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Study of Nickel–Carbon Bonding by X-ray Photoelectron Spectroscopy [1]

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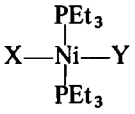
X-Ray photoelectron spectroscopy (XPS) nickel $2p_{3/2}$ *binding energies have been measured for a series of* trans *square-planar* $Ni(X)(Y)(PEt_3)_2$ *complexes and correlated with a calculated 'charge parameter' for the nickel atoms. A reasonably good correlation exists when X or Y is chloro, alkyl, vinyl, acyl, or phenyl, but not when both X and Y are acetylide. The deviation of the diacetylide complex from the correlation is attributed to a substantial π character in the nickel–carbon bonds. The agreement of the aryl, vinyl, and acyl complexes with the correlation indicates that any π character in these nickel–carbon bonds is small.*

Introduction

The possibility that strengths of carbon–metal σ-bonds could be reinforced by a π-bonding component has intrigued chemists for some time. Chatt and Shaw incorporated this concept into their classic theories of bonding and stability in square-planar complexes of nickel, palladium, and platinum having σ-bonded aryl and acetylide ligands [2, 3]. For complexes with aryl ligands, an enhanced stability of *ortho*-substituted phenyl complexes over derivatives lacking *ortho* substituents was especially noted, and two reasons were invoked for this '*ortho* effect'. First, an *ortho* substituent prevents rotation about the carbon–metal bond thus forcing the phenyl group into a conformation of maximum carbon–metal pπ–dπ overlap (π-bonding). Second, the *ortho* substituent sterically inhibits the attack of reagents at an axial site of the complex. Both arguments became widely accepted and now pervade the chemical literature [4].

The '*ortho* effect' is most evident in nickel complexes [4] making them the preferred candidates for studies of metal–carbon π-interactions. Nickel–carbon π-interactions have been previously explored using ^{19}F NMR [5], U.V. [6] and IR [7, 8] techniques. In general, the interpretations of these studies are that a π-interaction does indeed occur in nickel aryls and acetylides. However, as has been carefully emphasized in ^{19}F NMR studies of other aryl metal complexes, the actual magnitudes of the π-interactions are uncertain, possibly small, and may even be unimportant in comparison to the σ bond [9–11]. Recent tabulations of known nickel–carbon bond lengths in organonickel complexes are of little help in assessing nickel–carbon π-bond character [12, 13].

This report describes the application of X-ray photoelectron spectroscopy, XPS, to the study of nickel–carbon bonding. We have prepared a series of closely related organonickel complexes of the type



$$X-\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Ni}}-Y$$

where the metal oxidation state and coordination number, the neutral ligands, and the complex geometries were maintained constant. The range of compounds studied has been expanded from the preliminary communication to include acyl complexes, for which π-interactions have also been proposed [13, 14]. Comparing differences in core electron binding energies between complexes within this type of series minimizes the influence of secondary contributions to binding energy shifts, so that changes in XPS binding energies (*ergo* electron density) on the metal result only from the influence of bonding to the X and Y ligands [15]. Where comparisons can be made, the present binding energies are generally in good agreement with previously published values [16].

X-Ray Photoelectron Spectra

X-Ray photoelectron spectroscopy, XPS, consists of irradiating the sample with monochromatic, soft X-rays. The absorption of these X-rays results in the ejection of photoelectrons whose binding energy is given by

$$E_{binding} = h\nu_{(X\text{-}ray)} - E_{(kinetic)},$$

where $h\nu_{(X\text{-}ray)}$ is the energy of the exciting X-ray and $E_{(kinetic)}$ is the kinetic energy of the photoelectron as measured in the spectrometer. Since each element has a discrete set of core electron energy

TABLE I. q_{Ni} and XPS Parameters for $Ni(X)(Y)(PEt_3)_2$ Complexes.

	Compound	q_{Ni}	(eV)					
			Ni $2p_{3/2}$		P $2p_{3/2}$		Cl $2p_{3/2}$	
			BE	FWHH[a]	BE	FWHH[a]	BE	FWHH[a]
I	$Ni(CH_3)$(mesityl)$(PEt_3)_2$	0.26	853.5(1)	2.3	130.7(3)	2.2		
II	Ni(2-*m*-xylyl)$_2(PEt_3)_2$	0.30	854.15(1)	2.3	131.4(0)			
III	Ni(2-*m*-xylyl)(C≡CPh)$(PEt_3)_2$	0.36	854.05(1)	2.4	131.2(1)			
IV	Ni(C≡CPh)$_2(PEt_3)_2$	0.42	854.9(1)	2.1	131.2(1)	2.0		
V	NiBr(2-*m*-xylyl)$(PEt_3)_2$	0.43	854.2(0)	2.2	131.3(0)			
VI	NiCl(mesityl)$(PEt_3)_2$	0.51	854.15(3)	2.5				
VII	NiCl(CO-1-Ad)$(PEt_3)_2$[b]	0.52	854.1(1)	2.4	131.1(1)	2.1	198.5(2)	3.0
VIII	$NiCl[C(CH{=}CH_2){=}CH_2](PEt_3)_2$	0.52	854.2(2)	2.1	131.2(2)	2.2	198.3(2)	2.8
IX	$NiCl(C_6H_5)(PEt_3)_2$	0.53	853.9(2)	2.1	131.1(0)	2.1	198.5(1)	2.3
X	$NiCl(COC_6H_5)(PEt_3)_2$	0.59	853.9(3)	2.3	131.0(1)	2.2	198.6(1)	2.9
XI	$NiBr(CCl{=}CCl_2)(PEt_3)_2$	0.59	854.6(1)	2.1	131.0(2)	2.1	200.6(2)	2.9
XII	$NiCl(CCl{=}CCl_2)(PEt_3)_2$	0.67	854.8(1)	2.2	130.9(1)	2.2	200.4(2)	3.9
XIII	$NiCl_2(PEt_3)_2$	0.72	854.9(0)	2.1	131.2(0)	2.2	198.6(1)	2.8
XIV	$NiCl(CF{=}CF_2)(PEt_3)_2$	0.88	855.0(2)	3.0	131.3(1)	2.8	198.5(0)	3.0

[a] Full width at half height of XPS peak. [b] Ad is adamantyl.

levels it is possible to obtain an elemental analysis by comparing observed and known elemental binding energies. In addition, the binding energy of the core electrons are perturbed by the electron density, and subsequent nuclear shielding, of electrons in the valence orbitals. Thus, it is possible to relate small shifts in binding energy between compounds with differences in the relative electron density (partial charge) on the element(s) being measured.

The contribution of the long range Madelung potential toward binding energy is important for ionic crystals but can generally be ignored for non-ionic molecular crystals. For the interpretation of our results, the Madelung effect has been assumed to be negligible or at least constant throughout the series.

Charge Calculations

The relative electron densities on the nickel atoms are determined by numerous factors. Most of these factors have been held constant within our series of complexes so that differences in electron density on the metal between complexes should be attributable to the interactions with the X and Y ligands. Nickel–ligand (L) interactions can, in principle, consist of both σ and π components. Based on solely the σ component, it is possible to calculate values for a 'charge parameter', q_{Ni}, for the nickel atom in each complex using eqn. 1 [17],

$$q_{Ni} = \sum_{L} I_L \qquad (1)$$

where q_{Ni} is the sum of the partial ionic characters, I_L, for the Ni–X, Ni–Y, and the two Ni–PEt_3 bonds. The partial ionic character of each bond was calculated from the Pauling equation [18]

$$I_L = 1 - e^{-0.25(x_{Ni}-x_L)^2} \qquad (2)$$

using Pauling's [18] electronegativity values for Ni, Cl, and Br and Huheey's [19, 20] group electronegativity values for the organic ligands. Huheey's calculation of electronegativity takes into account differing hybridizations and structures. Electronegativities for several of the ligands were not listed by Huheey but were calculated by his method. The contribution to q_{Ni} from each PEt_3 ligand was calculated to be 0.06 and is assumed to be constant throughout the series. The simple calculation described by eqn. 2 is based strictly on resonance theory; electron transmission through π bonds is not considered.

Results and Discussion

Fourteen complexes of the type *trans*-Ni(X)(Y)-$(PEt_3)_2$ were examined by XPS. The complexes all possess square-planar configurations and are diamagnetic. The nickel $2p_{3/2}$, phosphorus $2p_{3/2}$, and chlorine $2p_{3/2}$ binding energies, BE, are referenced to the carbon 1s line (taken to be 285.0 eV) of each sample. Replicate BE measurements were made and the averaged data are listed in Table I with the standard deviations shown in parentheses. Although high reproducibility often gave small standard deviations, the precision associated with XPS is generally thought to be ±0.2 eV. The nickel spectra are very narrow and are situated on mildly sloping baselines, consistent with earlier XPS studies of diamagnetic square-planar nickel(II) complexes [21, 22]. The samples VII, IX, X, and XIV are quite sensitive to air, and for these compounds the instrument probe was loaded in a drybox. Despite our precautions, we cannot be certain that some sample surface destruction has not occurred, so that these data may not be as reliable as those from air stable compounds. To test for the effects of complex instability, a sample of *trans*-$NiCl(C_6H_5)(PEt_3)_2$ was deliberately exposed to air for one hour and then examined by XPS. Slight broadening of the nickel $2p_{3/2}$ peak occurred, but its location did not change from that determined in the absence of air. This indicates either that some sample decomposition does not significantly affect the XPS spectrum or that sample decomposition occurred rapidly even in the absence of air. We expected to experience problems with sample surface decomposition when the acyl nickel complexes were subjected to the high vacuum in the instrument, but decomposition was not apparent. Complex II is sterically comparable to $Ni(mesityl)_2(PEt_3)_2$, which has been reported [23] to lose its PEt_3 ligands under high vacuum in the solid state. Close examination of the XPS spectra of II, or our subjecting II to 10^{-4} Torr in other apparatus failed to verify similar behavior. Because of our observations, XPS data for II are included in our analysis.

The chlorine $2p_{3/2}$ binding energies occurred in two regions. Chlorine bound to nickel was found at *ca.* 198.5 eV and chlorine bound to carbon at *ca.* 200.5 eV. This indicates that chlorine on nickel has a greater electron density than that on carbon, as anticipated, since the electronegativity of carbon is greater than that of nickel. The binding energies of chlorine on nickel were independent of the trans ligands.

The phosphorus $2p_{3/2}$ binding energies did not vary among the complexes. This observation corroborates the proposed static partial ionic character of the Ni–P bonds among the complexes.

Charge/Binding Energy Correlation

Plots of calculated 'charge parameters' *vs.* XPS binding energies show a linear correlation when complexes with similar structures are compared [24]. In Fig. 1, nickel $2p_{3/2}$ binding energies for the series of nickel complexes are plotted *vs.* the calculated 'charge parameter' for nickel in each compound. A least squares regression analysis of all the points except for complex IV produced the locus and slope shown in eqn. 3.

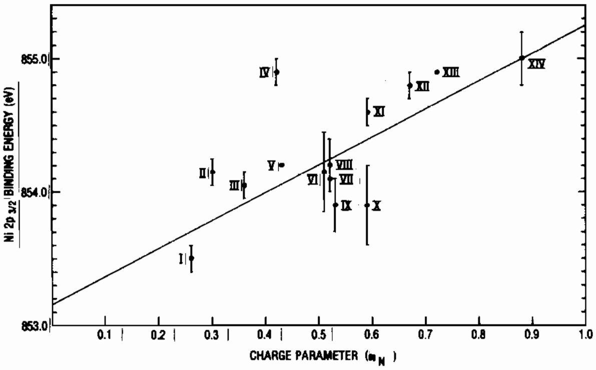


Fig. 1. Correlation of nickel $2p_{3/2}$ binding energies with the calculated q_{Ni} for $Ni(X)(Y)(PEt_3)_2$ complexes.

$$BE = (853.16 \pm 0.25) + (2.09 \pm 0.45)q_{NI} \qquad (3)$$

A correlation coefficient of 0.81 indicates the plot is statistically meaningful. The coefficient would undoubtedly be improved if 'weighting factors' for each point were included in the correlation relating to the reliability (*vide supra*) of the binding energies. Inclusion of a point for elemental nickel at a BE of 853.0 eV and q_{Ni} of 0, as was done in the communication [1], markedly improved the correlation coefficient without significantly affecting eqn. 3. However, we cannot justify why the BE (local environment) for elemental nickel can be assumed equal to that of *trans*-$Ni(X)(Y)(PEt_3)_2$, where X and Y are σ bonded ligands having the same electronegativity as nickel.

For the complex bearing two acetylide ligands, substantial deviation from the correlation occurs in the direction of higher binding energy. This is exactly what is expected if electron drift from metal to the acetylide ligands occurs through π bonds. Like behavior has been previously documented for complexes with cyano ligands, which are powerful π acceptors, where the core electron binding energies were higher than those predicted from the charge correlation [24]. For the remaining complexes, deviations from the correlation are small and may not be statistically significant. Not unexpected, no large deviations from the plot to lower BE's were observed. Such a result would be caused by a ligand to metal electron drift through π bonds.

Based on the XPS data, a π interaction is discernable only for the diacetylide complex. For aryl, vinyl, and acyl nickel complexes, where $p\pi$–$d\pi$ bonding is also possible, the interaction must be much smaller. For these latter complexes, the Ni–C σ bond seems to dominate the ground state electronic distribution.

Experimental

Literature procedures were used to prepare *trans*-NiCl(mesityl)(PEt$_3$)$_2$ [3], *trans*-NiCl(C$_6$H$_5$)(PEt$_3$)$_2$ [25], *trans*-NiCl(COC$_6$H$_5$)(PEt$_3$)$_2$ [25], *trans*-NiCl(CO-1-adamantyl)(PEt$_3$)$_2$ [25], *trans*-NiBr(CCl=CCl$_2$)(PEt$_3$)$_2$ [26], and *trans*-NiCl(CCl=CCl$_2$)-(PEt$_3$)$_2$ [27] The *trans*-Ni(C≡CC$_6$H$_5$)$_2$(PEt$_3$)$_2$ complex was obtained from a mixture of NiCl$_2$(PEt$_3$)$_2$, PhC≡CH, and NaOCH$_3$ in methanol Air sensitive compounds were handled under nitrogen or argon atmospheres Melting points were determined in capillary tubes open to air

trans-*Methyl(mesityl)bis(triethylphosphine)nickel(II), I*

To a stirred mixture of *trans*-chloro(mesityl)bis-(triethylphosphine)nickel(II) (0 22 g, 0 50 mmol) in 25 ml of ether at –78 °C was added 1.0 ml of 1 5 *N* LiCH$_3$ (1 5 mmol) in ether The mixture was slowly warmed to 25 °C over several hours At 25 °C, the solution slightly darkened, and it was recooled to –20 °C After 6 weeks, the cold solution was suction filtered affording 2–3 mg of yellow crystals, m.p 115–116 °C dec The filtrate was quickly washed with 20 ml of H$_2$O and then recooled to –20 °C After 3 days, 28 7 mg of pale yellow crystals of I had formed and were collected by suction filtration, m p 115–116 °C dec The filtrate was diluted with CH$_3$OH, cooled, and then refiltered to collect an additional 73 0 mg of I, m p 114–116 °C dec The total yield was 47 5% The XPS measurements were performed on the first crystals isolated without delay Elemental analyses were run on the sample after storage for 7 months at –20 °C The aged sample had a very noticeable odor of PEt$_3$

Anal Calcd for C$_{22}$H$_{44}$P$_2$Ni C, 61 56, H, 10 33 Calcd for C$_{22}$H$_{44}$NiO$_{0\,5}$ C, 60 57, H, 10 17 Found C, 60 56, H, 10 06

trans-*bis(2,6-Dimethylphenyl)bis(triethylphosphine)-nickel(II) II, and* trans-*bromo(2,6-dimethylphenyl)-bis(triethylphosphine)nickel(II), V*

A solution of 2,6-dimethylphenyllithium, prepared from 0 15 g (22 mg atom) of lithium pieces and 1 85 g (10 mmol) of 2,6-dimethyl-1-bromobenzene in 20 ml of ether and 10 ml of hexane, was added dropwise to a stirred solution of 1 8 g (4 9 mmol) of *trans*-NiCl$_2$(PEt$_3$)$_2$ in 10 ml of hexane The mixture was diluted with ether, washed with H$_2$O, filtered, and the solvent was removed under vacuum Treating the residue with ether caused pale yellow crystals to separate Filtration gave 0 14 g (6%) of II m p 151–152 °C dec Found C, 66 20, H, 9 49 C$_{28}$H$_{48}$-NiP$_2$ calcd C, 66 56, H, 9 57% The NMR (C$_6$D$_6$) exhibits the aryl methyl group resonances as a singlet at δ 2 99 and the PEt$_3$ methyl resonances as a pseudo quintet at δ 0 68 ppm

On cooling, the filtrate precipitated a brown solid which was filtered to yield 1 62 g (69%) of V m.p 108 5–109 5 °C (lit [27] m p 112 °C)

trans-*(Phenylethynyl)(2,6-dimethylphenyl)bis(triethylphosphine)nickel(II), III*

0 87 g (1 8 mmol) of V and 0 22 g (2 0 mmol) of LiC≡CPh were combined in 8 ml of ether and left over the weekend at –78 °C The solution was washed with H$_2$O, filtered, and the solvent was removed under vacuum The residue was taken up in hexane and on storage at –78 °C, a yellow solid formed Filtration of this material yielded 0 23 g (26%) of impure product The filtrate was concentrated and recooled Pale yellow crystals formed that were filtered to yield 0 38 g (42%) of III m p 94–95 °C (Found C, 67 07, H, 8 80 C$_{28}$H$_{44}$NiP$_2$ calcd C, 67 08, H, 8 85%) The NMR (C$_6$D$_6$) exhibits the aryl methyl group resonance as a singlet at δ 2 77 and the PEt$_3$ methyl group resonances as a pseudo quintet at δ 1 00 ppm The IR spectrum (Nujol) contains $\nu_{(C\equiv C)}$ at 2075 s cm^{-1}

XPS Measurements

All XPS data were obtained with a Varian 15 IEE spectrometer using Mg Kα X-rays [h$\nu_{(X\text{-ray})}$ = 1253 6 eV) Energy resolution was approximately 0 1 eV with a nominal reproducibility of ±0 2 eV Temperature and pressure during XPS analyses were typically 42 °C and 3 × 10^{-7} Torr, respectively Binding energy spectra were obtained by repeated sequential scanning over the desired energy regions to enhance the signal-to-noise ratio All binding energies were corrected for sample charging by referencing the carbon (1s) binding energy to 285 0 eV

Samples for analysis were crushed and dusted onto Scotch adhesive tape just prior to insertion and examination in the spectrometer Air sensitive samples were prepared for examination and loaded in the sample probe under nitrogen or argon XPS spectra of the adhesive tape showed carbon, oxygen, and some silicon, but no bands which would interfere with the spectra of the nickel complexes

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