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Preliminary communication

ABSENCE OF NICKEL—CARBON π-BONDING IN NICKEL ARYLS

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Summary

When nickel core electron binding energies in *trans*-$Ni(X)(Y)(PEt_3)_2$ complexes (X, Y = alkyl, alkenyl, alkynyl, aryl, halide) are compared with calculated nickel charges, nickel—aryl π-bonding is concluded to be unimportant.

The possibility of transition-metal—aryl π-bonding has frequently been mentioned in the chemical literature since 1959 [1]. Experimental evidence confirming such an interaction remains equivocal and controversial. For example, some authors [2] claim metal—aryl bond lengths are shortened by π-bonding, while others [3, 4] say these bond lengths are normal. Interpretations concerning the extent of metal—carbon π-bonding from ^{19}F NMR studies of fluoroaryl metal complexes are equally controversial [5, 6]. If it does exist, metal—aryl π-bonding would likely be most important in square-planar *ortho*-substituted arylnickel complexes where steric constraints orient the ligands in a conformation of maximum p_π—d_π overlap [7, 8]. To assess the extent of π-bonding in arylnickels, we have measured the nickel $2p_{1/2}$ and $2p_{3/2}$ binding energies in a series of organonickel complexes and, by comparison with calculated charges, have concluded that nickel—aryl π-bonding is of little importance.

X-Ray photoelectron binding energies were recorded on a Varian IEE-15 electron spectrometer and were referenced to the carbon 1*s* line (taken to be 285.0 eV) of each sample. For elemental nickel, the reference was the carbon 1*s* line of "pump oil". The values shown in Fig. 1 are the average of three or more measurements with the confidence limits taken as the standard deviations. In Fig. 1, the nickel $2p_{3/2}$ binding energies for elemental nickel and several *trans* square-planar $Ni(X)(Y)(PEt_3)_2$ complexes are plotted vs. a calculated nickel "charge parameter" [9], q_{Ni}, which is based on pure σ-bonding. A similar plot (not shown) was obtained with nickel $2p_{1/2}$ binding energies. The ligands X and Y are alkyl, alkenyl, alkynyl, aryl, and halide groups. The q_{Ni} is the sum of the

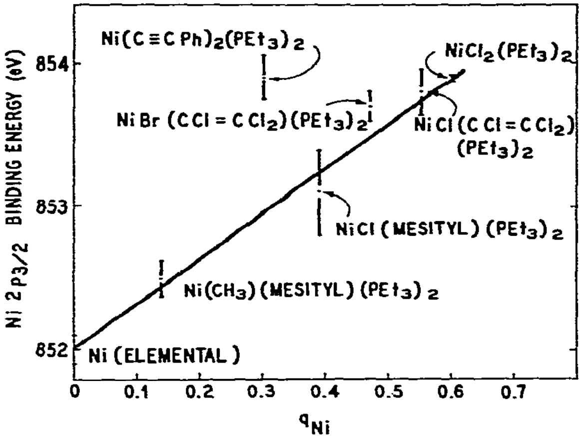

Fig. 1. Correlation of nickel $2p_{3/2}$ binding energies with the sum of the partial ionic characters of the nickel—ligand bonds, q_{Ni}.

partial ionic characters for all nickel—ligand bonds. The partial ionic character of each bond was calculated using Pauling's equation [10]. The electronegativities for nickel and the halogens were Pauling's [10], while Huheey's [11] electronegativities, χ_P, were used for the carbon ligands. The χ_P for the $CCl{=}CCl_2$ group was calculated by Huheey's method. The ionic character of the Ni—PEt_3 bonds are assumed to be very small and to remain constant for all the organonickel compounds, so they have been neglected. The negligible effect of the PEt_3 ligand on q_{Ni} is corroborated by comparing the Ni $2p_{3/2}$ binding energy of elemental nickel (853.0 eV) with that predicted for $Ni(PEt_3)_4$ (852.9 eV)*.

A straight line connects the two compounds in Fig. 1 for which Ni to X or Y π-bonding should be least important, i.e., elemental nickel and $NiCl_2(PEt_3)_2$. This line represents the relationship between nickel binding energy and q_{Ni} for complexes with pure σ nickel—carbon bonds**. The correlation of nickel binding energies with q_{Ni} is remarkably good for all compounds except $Ni(C{\equiv}CPh)_2(PEt_3)_2$. The high binding energy observed for this alkynyl complex is caused by nickel donating its electrons through π bonds to the alkynyl ligand which induces an increased positive charge on nickel relative to that predicted by pure σ-bonding. The small deviation of the point for $NiBr(CCl{=}CCl_2)(PEt_3)_2$ from the line remains unexplained. The correlation in Fig. 1 leads us to conclude that nickel—carbon π-bonding is of little importance in alkyl-, alkenyl-, and aryl-nickel compounds, while π-bonding is important in the alkynyl complex. Nickel—alkynyl π-bonding is also strongly suggested by infrared [14] and ultraviolet [15] spectral studies.

The greater stability of *ortho*-substituted arylnickel complexes compared to those without *ortho* substituents [4, 7, 8] must now be attributed primarily to

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*This prediction is derived from the linear relationship of nickel binding energies in air-stable $Ni(PR_3)_4$ complexes with $\nu(CO)$ (A_1) in $Ni(CO)_3PR_3$ complexes [12]. For $Ni(CO)_3PEt_3$, $\nu(CO)$ (A_1) occurs at 2061.7 cm^{-1} [13] and corresponds to a Ni $2p_{3/2}$ binding energy of 852.9 eV for $Ni(PEt_3)_4$.

**The binding energy for elemental nickel is assumed to be equal to that of $NiZ_2(PEt_3)_2$, where Z is a σ-bonded ligand having the same electronegativity as nickel.

steric factors. The observed trend in binding energies can also explain the relatively high reactivities of methyl nickel complexes toward protonic reagents [4, 16, 17] when compared to aryl and alkynyl complexes, since the electron density, or basicity, on nickel is greater in the methyl nickel complexes. A similar sensitivity to nickel basicity has been demonstrated in the protonation of nickel(0) complexes [18].

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