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X-Ray Photoelectron Spectra of Aryl-nickel Complexes

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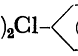
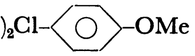
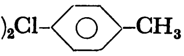
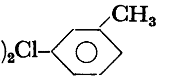
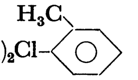
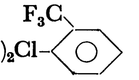
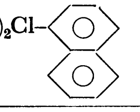
The nature of bondings in aryl–nickel complexes has been clarified by means of X-ray photoelectron spectroscopy (XPS). Pi bonding between nickel and aryl ligand seem to be of little importance. Ni–Cl bondings are of partially ionic character. A correlation between stereochemical structure and satellites has been discussed. It is suggested that the aryl-nickel complexes examined have diamagnetic square-planar structures. Measurements of solid-state susceptibilities support this view.

TABLE 1. Ni $2p_{3/2}$, Cl 2p, AND P 2s BINDING ENERGIES ON NICKEL COMPLEXES

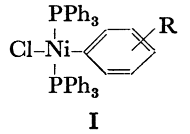
		Ni $2p_{3/2}$	Cl 2p	P 2s
1	$NiCl_2$	857.3	199.5	—
2	$Ni(PPh_3)_2Cl_2$	856.2	198.4	189.0
3	$Ni[P(n\text{-}C_4H_9)_3]_2Cl_2$	854.3	198.3	189.5
4	$Ni(PPh_3)_2Cl$- 	854.6	198.4	188.4
5	$Ni(PPh_3)_2Cl$- 	855.0	200.4 198.5	189.3
6	$Ni(PPh_3)_2Cl$- 	854.4	198.9	189.5
7	$Ni(PPh_3)_2Cl$- 	854.4	198.3	188.9
8	$Ni(PPh_3)_2Cl$- 	855.3	199.0	189.5
9	$Ni(PPh_3)_2Cl$- 	854.8	198.5	189.4
10	$Ni(PPh_3)_2Cl$- 	854.7	198.8	188.7
11	$Ni(PPh_3)_2Cl$- 	854.1	199.0	188.9

The stability of the aryl-nickel complexes is extremely high in contrast to the instability of transition metal-alkyl complexes. The increasing stability is probably ascribed to either or both of the following two factors; the substitution of β hydrogen atoms to the metal atom, and the stabilization by π acceptor ligands. Pi bonding between the transition metal and the aryl-ligand has been discussed in various aspects since the work by Chatt and Shaw.[1] It could be said that the stability of the complex is related with the energy difference (ΔE) between the highest occupied d orbital and the lowest unoccupied orbital. Since π bonding between the metal d orbital and the aryl-ligand reduces the energy of the d orbital and increases ΔE, the stability of the complex increases. Experimental evidence for this interaction is still ambiguous.

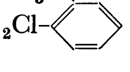
Recent studies on coordination complexes by X-ray photoelectron spectroscopy (XPS) revealed its usefulness, and we have applied this method to examination of a series of aryl-organometallic complexes.[2] Through measurements of the binding energies, we obtained some information on the nature of metal-ligand bondings. We also found the satellites associated with the 2p photoelectron lines of the nickel compounds. These satellites seem to originate from the shake-up process related to the paramagnetism.[2,3] A detailed discussion is given on the stereochemical structure on which the magnetic state depends.

Results and Discussion

The Nature of Nickel-Ligand Bondings. The observed values of Ni 2p, Cl 2p, and P 2s binding energies are summarized in Table 1. The structures of aryl-nickel complexes are shown in I.



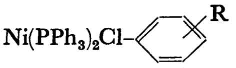
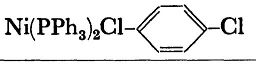
I

Ni 2p binding energies of aryl-nickel compounds are lower than those of $NiCl_2$ (**1**) and $Ni(PPh_3)_2Cl_2$ (**2**). It could be pointed out from these results that the positive charge less than that of (**1**) or (**2**) is assigned to Ni atom in aryl-nickel complexes, and the coordinated aryl group donates considerably more electron density to nickel atom than the chlorine ligand. Hence, the nickel-aryl π bonding or back-donation seems to be of little importance in the aryl-nickel complexes. If metal-aryl π bonding does exist, it would be the most important in square-planar *ortho*-substituted aryl-nickel complexes where the ligands locate to form a conformation ensuring a maximum pπ-dπ overlap by steric constraints. However, for even *ortho*-substituted aryl-nickel complexes $Ni(PPh_3)_2Cl$-  (**9**) and Ni-$(PPh_3)_2Cl$-  (**10**), a high binding energy could not be observed. Similar results have been obtained by Fahey and Baldwin.[4]

P 2s binding energies of nickel complexes remain constant for all the series of compounds. A small or no change is expected in P 2s binding energies on coordination of phosphine to a metal atom. From a comparison of Ni 2p binding energy of $NiCl_2$ (857.3 eV) with that of $Ni(PPh_3)_2Cl_2$ (856.2 eV), it is suggested that a net electron transfer from phosphines to a nickel atom might occur.

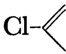
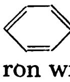
Cl 2p binding energies of some compounds containing

Table 2. Cl 2p binding energies of related compounds

	Cl 2p
$NiCl_2$	199.5
NH_4Cl	196.9[a]
Cl_3CCONH_2	200.2
$Cl_2CHCONH_2$	199.1
$ClCH_2CONH_2$	198.6
2,3-Dichloro-1,4-naphthoquinone	200.3
Chloranil	200.1
	198.3—199.0
	198.5, 200.4

a) J. Escard, G. Mavel, J.E. Guerchais, and R. Kergoat, *Inorg. Chem.*, **13**, 695 (1974).

chlorine are summarized in Table 2. Cl 2p binding energies vary considerably in the series of related compounds. We see that Cl 2p binding energy takes a maximum value in chlorine combining to aryl group and a minimum in NH_4Cl (Tables 1 and 2). Cl 2p binding energies in aryl-nickel complexes (198.3—199.0 eV) are lower than that of $NiCl_2$ (199.5 eV), but higher than that of NH_4Cl (196.9 eV). This shows that, although Cl 2p binding energies are highly affected through a Madelung contribution in these ionic structures, the electron density on Cl in aryl-nickel complexes increases by coordination of PPh_3 or aryl group and nickel-chlorine bond has partially ionic character. On the other hand, it is revealed from measurements of a series of chloroacetamides that, when the chlorine combines to the atom with higher electron density, the electron density on chlorine should increase and the Cl 2p binding energies in aryl-nickel complexes have about the same value of Cl 2p binding energy in α-chloroacetamide. This suggests that the chlorine in aryl-nickel complexes withdraws the electron on nickel atom to which the electron is supplied from the ligand.

As for complex Cl--$Ni(PPh_3)_2Cl$ (**5**), the Cl peak corresponding to binding energy of 198.5 eV is assigned to Cl coordinated directly to central Ni atom and the peak of binding energy of 200.4 eV to Cl bonded to aryl group. The large difference in energy shows that the two bonds differ largely from each other in nature. Cl 2p binding energies do not change among chlorine atoms bonded to aryl group in the compounds such as chloranil, 2,3-dichloro-1,4-naphthoquinone, and Cl–-$Ni(PPh_3)_2Cl$. The results indicate that the electron withdrawing from Ni to the aryl substituent in the complex (5) is not probable and, therefore, back-donation is of minor importance.

Stereochemical Structure and Satellites. We have observed photoelectron satellites accompanied by the Ni 2p line. Generally, the satellites associated with the 2p photoelectron lines of Ni compounds are interpreted to be due to promotion of a nickel 3d electron into an unoccupied level, this being called a shake-up phenomenon.[3] Matienzo *et al.* reported the selection rule ($\Delta L_v=0$, $\Delta S_v=0$) for the monopole shake-up transitions and discussed the correlation between paramagnetism and shake-up satellites. They suggested that, for the same ligand under different stereochemical geometries, the 2p binding energies of the nickel ion increase in the order, planar < tetrahedral < octahedral.[5] However, experimental evidence is insufficient for confirming the suggestion. For the sake of clarification, we have measured Ni 2p binding energies of $Ni(AcO)_2 4H_2O$ (**12**) (octahedral), $Ni(PPh_3)_2Cl_2$ (**2**) (tetrahedral), and $Ni[P(n\text{-}C_4H_9)_3]_2Cl_2$ (**3**) (square-planar). The results are shown in Fig. 1. It was found for paramagnetic nickel compounds **2** and **12** that parent lines are broad and large shake-up satellites appear, whereas for diamagnetic nickel compound(**3**) narrow parent lines and a small satellite only for $3p_{3/2}$ peak appear. The result for paramagnetic nickel compounds is consistent with that of previous studies, but not for diamagnetic compounds; no satellites were observed in the XPS spectra of diamagnetic nickel compounds reported previously.[2,5] Thus, the cause of the appearance of the small satellite for **3** is uncertain in the present state. A possibility is as follows; A paramagnetic substance is partially formed in the surface region of complex **3** on X-ray irradiation. Two satellites for Ni $2p_{3/2}$ of complex **2** would be assigned

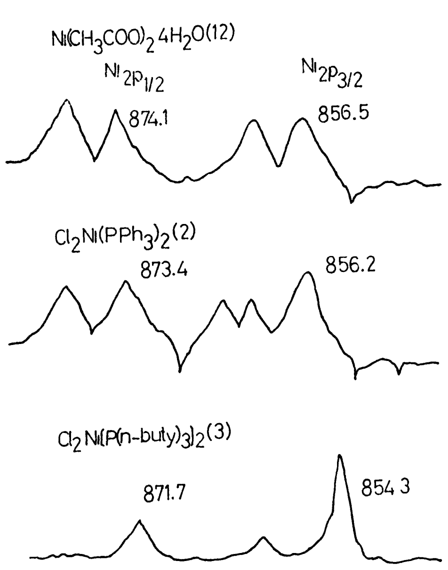


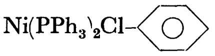
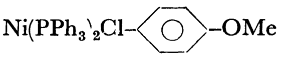
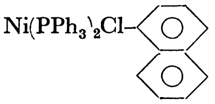
Fig. 1. Ni 2p XPS spectra of octahedral (**12**), tetrahedral (**2**), and square-planar (**3**) compounds of nickel.

Table 3. Ni 2p binding energies of nickel complexes

Compound	Ni $2p_{3/2}$	Sat.	Ni $2p_{1/2}$	Sat.
1	857.3	862.6	874.5	878.8
2	856.2	862.1, 865.3	873.4	879.8
3	854.3	861.8	871.7	—
4	854.6	861.3	871.8	880.7
5	855.0	861.8	871.8	880.3
6	854.4	861.8	871.0	881.8
7	854.4	861.3	871.7	881.1
8	855.3	861.8	871.7	880.3
9	854.8	862.3	872.0	—
10	854.7	862.8	872.2	—
11	854.1	861.6	871.6	—

to two type transitions, probably 3d→4s and 3d→ligand transitions. The possibility of development of a satellite due to the 3d→ligand transition is discussed by Frost *et al.*[3] Figure 1 also indicates that a definite correlation exists between the binding energy and stereochemistry of complexes. Hence, it is confirmed that information on the stereochemistry can be obtained through the measurements of the binding energy and satellites.

TABLE 4. MOLAR MAGNETIC SUSCEPTIBILITIES OF NICKEL COMPLEXES

	Compound	Molar magnetic susceptibilities (emu/mol)
2	Ni(PPh$_3$)$_2$Cl$_2$	$+4.86\times10^{-3}$
4		-2.70×10^{-4}
6		-1.16×10^{-4}
11		-2.97×10^{-4}

The main peak (Ni 2p) and satellites in the aryl-nickel complexes are summarized in Table 3. For all the aryl-nickel complexes, small satellites are observed on core level of nickel. In the case of aryl-nickel complexes **4**, **5**, **6**, **7** and **8**, there is a satellite for each parent peak, while in the case of aryl-nickel complexes **9**, **10** and **11**, there is a satellite only for $2p_{3/2}$. We have no good explanation for these satellites, but it is to be noted that the satellites observed in the complexes **9**, **10** and **11** are as sharp and weak as those in the diamagnetic complex **3** as shown in Fig 2. It is not clear whether the weak satellites associated with Ni $2p_{1/2}$ peak in the complexes **4**—**8** are of intrinsic origin or are due to the partial decomposition by X-ray irradiation. However, these satellites are very weak and the parent lines are narrow and sharp as compared with those observed for typical paramagnetic complexes like **12** and **2**. The binding energies of the Ni 2p peaks in these complexes are lower than those observed for complexes **12** and **2**. The difference between complexes **4**—**8** and complexes **9**—**11** is considered to be due to the stabilization of the latter complexes by the *ortho*-substitution of ligand.[1] It could be deduced from these considerations that all the aryl-nickel complexes examined have the diamagnetic square-planar nickel.

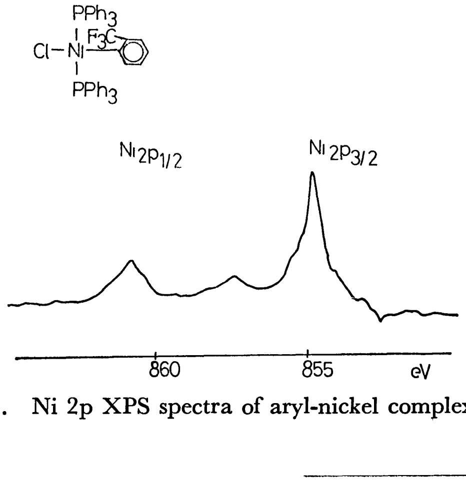


Fig. 2. Ni 2p XPS spectra of aryl-nickel complex (**10**).

For the sake of confirmation, we have measured solid-state magnetic susceptibilities. The result shows that the aryl-nickel complexes are diamagnetic (Table 4). The conclusion from XPS measurements is thus supported.

Experimental

Aryl-nickel complexes were prepared as described in a previous report.[6]

Photoelectron spectra were taken with a JASCO ESCA-1 electron spectrometer. The Mg*K*α X-ray line (1253.6 eV) was used as a photoelectron excitation source. The samples were used as fine powder dusted onto aluminum foil or Scotch tape which was mounted on a copper sample holder. The recorded binding energies were recorded in triplicate, accuracy being within ±0.25 eV in most cases. All raw binding energies were corrected to C 1s value of 284 eV. The procedure appeared very reasonable in the case where the compound contained many carbons. The binding energy of NiCl$_2$ were calibrated by using 1s line of the impurity carbon. An attempt was made to refer the spectra to the Au($4f_{7/2}$) photoelectron line. The photoelectron line of Au($4f_{7/2}$) deposited *in vacuo* onto the samples were defined as 83 eV. The results from the two methods agreed with each other.

Solid-state magnetic susceptibilities were measured with a Faraday balance at room temperature.**

References

1) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1959**, 705.

2) J. Escard, G. Mavel, J. E. Guerchais, and R. Kergoat, *Inorg. Chem.*, **13**, 695 (1974); S. O. Grim, L. J. Matienzo, and W. E. Swartz, Jr. *ibid.*, **13**, 447 (1974); L. O. Pont, A. R. Siedle, M. S. Lazarus, and W. L. Jolly, *ibid.*, **13**, 483 (1974); C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *ibid.*, **12**, 2770 (1973).

3) D. C. Frost, A. Ishitani, and C. A. McDowell, *Mol. Phys.*, **24**, 861 (1972); K. S. Kim, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 217 (1974); W. L. Jolly, in D. A. Shirley (editor), "Electron Spectroscopy," North-Holland, Publ. Co., Amsterdam (1972); T. Novakov, *Phys. Rev. B*, **3**, 2693 (1971); T. Novakov and P. Prins, *Solid State Commun.*, **9**, 1975 (1972); A. Rosencwaig, G. K. Wertheim, and H. J. Guggenheim, *Phys. Rev. Lett.*, **27**, 479 (1971).

4) D. R. Fahey and B. A. Baldwin, *J. Organometal. Chem.*, **70**, C11, (1974).

5) L. Yin, I. Adler, T. Tsang, L. T. Matienzo, and S. O. Grim, *Chem. Phys. Lett.*, **24**, 81 (1974); L. J. Matienzo, L. Yin, S. O. Grim, and W. E. Swartz, Jr. *Inorg. Chem.*, **12**, 2762 (1973).

6) M. Hidai, T. Kashiwagi, T. Ikeuchi, and Y. Uchida, *J. Organometal. Chem.*, **30**, 279 (1971).

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