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Electron Spectroscopy for Chemical Analysis of Nickel Compounds

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ESCA data are presented for all of the elements in 46 nickel compounds containing a variety of ligands and with formal metal oxidation states of 0, +2, and +4. Included are olefin, alkyl, aryl, and π-allyl organometallic complexes. The use of line shapes and intensities in obtaining reliable spectra is indicated. Binding energies and line shapes are discussed in terms of molecular bonding and structure. Ni $2p_{3/2}$ binding energies span the following ranges (defining C 1s as 285.0 eV): Ni^0L_4, 853.6-855.2 eV; Ni(olefin), 853.7-856.0 eV; Ni(II), 854.9-857.4 eV; Ni(IV), ~861 eV.

Introduction

Since the advent of electron spectroscopy for chemical analysis (ESCA) a few years ago,[2] there has been considerable interest in the application of the technique to learning about the distribution of electrons in transition metal complexes. Papers have appeared on Mo, W, Ru, and Os,[3a] Rh and Ir,[3] Pt,[3-6a] Pd,[6b] and Ni[7] complexes. Notes have also appeared on nitrosyl[8a] and azide, dinitrogen, and nitride[8b] complexes and on a few compounds containing carbonyl[9] and cyclopentadienyl groups.[9,10]

Our interest has been directed toward nickel complexes, particularly ones involving ligands of the type involved in homogeneous catalytic reactions. We asked ourselves, "How meaningful is it to assign a 1− charge to alkyl, aryl, π-allyl, and π-cyclopentadienyl groups in organometallic complexes? What formal metal oxidation state should be assigned to olefin complexes? How much can the electron density on the metal be changed by varying the phosphine or other ligands? Do ESCA spectra depend on coordination number or geometry? Is ESCA useful for quantitative elemental analysis of compounds of this type?" We know of only one paper[11] which presents quantitative data on ESCA line intensities among different elements.

In this paper we present the detailed results of our studies on 46 nickel compounds with a variety of ligands and with formal oxidation states of 0, 2+, and 4+. A preliminary account[12] was presented earlier. We also wish to point out the pitfalls in ESCA studies of air-sensitive compounds and show how line shapes and intensities can be used as an aid in obtaining reliable spectra. Finally, we shall discuss the binding energies in terms of the molecular bonding and structure.

Experimental Section

Compounds. Most of the compounds used in this work were purchased commercially or prepared by literature procedures. References can be found in the tables.

$Ni(NH_3)_6(ZnCl_3)_2$ was prepared by analogy with the procedure of Groeneveld.[13] To 50.0 g (0.21 mol) of $NiCl_2 \cdot 6H_2O$ dispersed in 500 ml of CH_3CN was added 57.3 g (0.42 mol) of anhydrous $ZnCl_2$, giving a homogeneous blue-green solution. The precipitate which formed when anhydrous NH_3 was added was washed with acetonitrile and dried; yield 76% purple powder. *Anal.* Calcd for $H_{18}Cl_6N_6NiZn_2$: H, 3.5; Cl, 41.8; N, 16.5; Ni, 11.6; Zn, 25.5. Found: H, 3.6; Cl, 41.1; N, 16.8; Ni, 11.8; Zn, 25.1.

$Ni(3\text{-PN})_6(ZnCl_3)_2$ was prepared by adding $ZnCl_2$ to $NiCl_2 \cdot 6H_2O$ in 3-pentenenitrile (3-PN) solvent (95% trans isomer). The pale blue product precipitated in 80% yield. The 3-PN content was determined by gas chromatography after destruction of the complex with acetone. *Anal.* Calcd for $(3\text{-PN})_6Cl_6NiZn_2$: 3-PN, 54.7; Cl, 24.0; Ni, 6.6; Zn, 14.6. Found: 3-PN, 51.4; Cl, 23.8; Ni, 6.2; Zn, 14.3.

$ZnNi(CN)_4$ was precipitated by the addition of $ZnCl_2$ to an aqueous solution of $K_2Ni(CN)_4$.[14] *Anal.* Calcd for C_4N_4NiZn: C, 26.1; N, 24.6; Ni, 25.7; Zn, 28.6. Found: C, 21.2; N, 24.3; Ni, 25.5; Zn, 28.9.

$Ni(PPh_2Et)_2Br_2$ in the square-planar form was prepared by modifying the literature procedure.[15] Ether was added to a solution of the green tetrahedral isomer in dichloromethane. The resulting red solution was chilled overnight at −78° in an inert atmosphere. The brown square-planar isomer was filtered, washed with cold ether, and dried under vacuum with cooling. The sample was immediately mounted and kept cold until the spectrum was run.

$Ni[P(OMe)_3]_3(CN)_2$[16] was prepared by literature procedures.

Spectra. ESCA spectra were determined using a Varian IEE-15 spectrometer, employing both Al and Mg Kα X-rays. Samples were mounted in one of three ways: pressing into a 200-mesh stainless steel screen, crushing into lead foil with a small hammer, or rolling onto double-sided sticky tape (Permasel, New Brunswick, N. J.). In each case the support was wrapped around a small, axially bored aluminum cylinder about 1 cm in diameter and 3 cm long. The 0.005 in. thick lead foil, v.p. grade, was used as supplied by the Materials Research Corp., Orangeburg, N. Y. The surface was presumably mostly lead oxide.[17] For highly oxygen-sensitive samples the sticky tape was mounted on Al cylinders and left overnight under vacuum before the sample was added in an argon atmosphere. Otherwise the sample on the tape slowly discolored, apparently because of adsorbed oxygen.

Initially, samples were mounted in a drybox, carried to the instrument in taped vials, and lowered into the instrument under a stream of N_2. With extremely air-sensitive samples, this technique was inadequate. Partial sample oxidation was indicated by visual decoloration and by excessive O 1s line intensity, excessive width for P 2p and Ni $2p_{3/2}$ lines, and a background base line sloping up to higher binding

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[17] Cleaning the foil surface with abrasive paper reduced the intensity of C 1s and O 1s lines and caused a shift of Pb $4f_{5/2}$ and $4f_{7/2}$ lines to lower binding energy.

energy in the vicinity of Ni $2p_{3/2}$. A special sample chamber, shown schematically in Figure 1, was then constructed. The cylinder bearing the air-sensitive sample was mounted on the end of a short (~6 in.) sample rod of $^1/_2$-in. diameter. This rod was sealed into the top of the chamber with a ferrule of Teflon fluorocarbon resin (Hoke Gyrolok 316). The bottom of the chamber was then sealed by a ball valve (Apollo 316, Consolidated Brass Co.), machined out to pass the rod when in the open position. The overall assembly was short enough (~10 in. long) to pass easily through the antechamber of our Vacuum Atmospheres Inc. drybox.

After the chamber was removed from the drybox and attached to the instrument, the extension rod was screwed in place. The instrument was evacuated and the sample lowered into position using the extension rod. It is important that the assembled rods be carefully machined to a close fit so that air does not leak in when the joint is pushed past the ferrule. The optimum insertion depth was determined by measuring the F 1s line intensity of a sample of Teflon inserted to various depths.

Caution! The high-voltage X-ray beam should not be turned on until the sample is fully inserted and any exposed extension rod should be covered with insulating tape to prevent electrical shock.

ESCA spectra were run over a 20-eV range for each of the elements in the compound (except H) in addition to C and O in most cases. Lines were measured for Ni $2p_{3/2}$, P 2p, O 1s, C 1s, B 1s, N 1s, F 1s, Cl 2p, Br 3d, I $3d_{5/2}$, S 2p, K $2p_{3/2}$, and Zn $2p_{3/2}$. For samples mounted on lead foil, Pb $4f_{5/2}$ and $4f_{7/2}$ lines were also measured. Between 10 and 100 20-sec scans were averaged for each line. Binding energies, peak heights (counts/sec), and peak widths at half-height were recorded. Binding energies for Cl and Br are for the more intense $2p_{3/2}$ and $3d_{5/2}$ lines. The weaker $2p_{1/2}$ and $3d_{3/2}$ lines appeared as high-energy shoulders, giving a total line width of about 3.0 eV. Evidence for distinct $2p_{1/2}$ and $2p_{3/2}$ lines was not observed for P or S.

All raw binding energies were corrected to a hydrocarbon C 1s value of 285.0 eV.[1] This procedure appeared very reasonable in cases where the compound contained many carbons in the ligands, as in $Ni(PPh_2Et)_2Br_2$. In some cases, however, *e.g.*, K_2NiF_6, the compound contained no carbon. Spectra of K_2NiF_6 were run on both sticky tape and lead foil. Defining C 1s in the spectra as 285.0 eV gave binding energies consistently ~0.5 eV higher on lead. Spectra of tape alone, tape half covered with lead foil, and lead foil alone were run, with the results shown in Table I. The narrowness of the C 1s line in the foil-on-tape spectrum suggests that both "pump oil" on lead or carbon on sticky tape should be equally good internal standards for binding energies. Using the C 1s line as a standard does, however, give Pb binding energies differing by 0.5 eV between the half-lead and all-lead samples.

Most of the air-stable compounds were run only once. Duplicate runs on the same support indicated a reliability of binding energies of about ±0.3 eV and of line widths and relative peak heights of about ±10%. Very air-sensitive compounds were usually run a number of times, attempting to minimize the intensity of the O 1s line, the line widths of the P 2p and Ni $2p_{3/2}$ lines, and the background slope in the vicinity of Ni $2p_{3/2}$.

We were unable to obtain the spectrum of $Ni[P(OMe)_3]_3(CN)_2$[16] because an adequate vacuum could not be obtained. Apparently the compound has an appreciable dissociation vapor pressure at ambient temperature.

Results

Zerovalent Nickel Complexes. The data in Table II show that line widths less than about 2.1 eV were rarely observed. This may be taken as the typical line width in our samples for electrons coming from a given electron shell in a common environment. $Ni[P(OCH_2CCl_3)_3]_4$ was one of the few compounds which showed resolved lines for different types of carbons. The C 1s spectrum is shown in Figure 2. The two peaks of equal intensity at 289.1 and 287.5 eV are assigned to $-CCl_3$ and $-OCH_2-$ carbons, respectively. The stronger peak at 285.0 eV is assigned to "pump oil" on that portion of the lead surface which is free of sample. The assignment of the higher binding energy (BE) peaks is supported by their intensity of 1.0 relative to P 2p in the same compound and by reported values of 289.9 and 285.9 eV for $-CCl_3$ and $-CH_3$ carbons in CH_3CCl_3.[18]

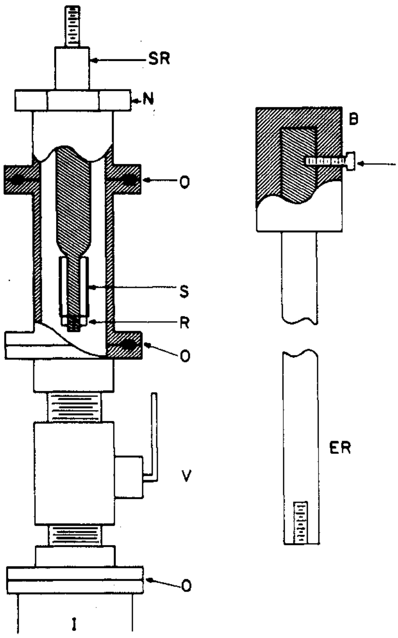

Figure 1. ESCA chamber for air-sensitive compounds: S, sample; R, retaining nut; N, nut for Teflon ferrule; V, ball valve; O, O-ring seals; I, instrument; SR, sample rod; ER, extension rod; B, Bakelite insulation; C, electrical connection.

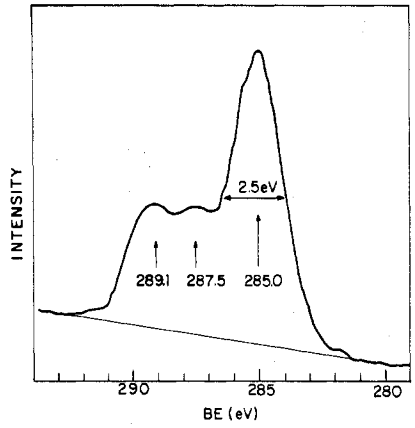

Figure 2. C 1s spectrum of $Ni[P(OCH_2CCl_3)_3]_4$. Strongest peak at 285.0 eV is due to "pump oil."

Table I. ESCA Data on Sticky Tape, Lead Foil on Tape, and Lead Foil

	δ, eV				FWHH,[b]
Element	Raw	Cor	Intens	Rel intens	eV
		Sticky Tape[a]			
C 1s	284.2	(285.0)	6700	(1.00)	1.9
O 1s	531.7	532.5	2890	0.42	1.9
		Lead Foil on Tape[c]			
C 1s	284.2	(285.0)	7350	(1.00)	1.9
O 1s	531.5	532.3	3920	0.54	2.1
Pb $4f_{5/2}$	143.3	144.1	3540	0.48	1.9
Pb $4f_{7/2}$	138.4	139.2	4610	0.63	1.9
		Lead Foil			
C 1s	284.8	(285.0)	5920	(1.00)	1.8
O 1s	531.6	531.8	4430	0.75	2.3
Pb $4f_{5/2}$	143.4	143.6	7560	1.28	1.9
Pb $4f_{7/2}$	138.5	138.7	9620	1.62	1.9

[a] A search for other elements in the tape revealed silicon with Si 2p at 101.8 eV, 8.5% of the C 1s intensity, but no detectable N 1s, P 2p or Ni $2p_{3/2}$. [b] Full width at half-height. [c] A strip of foil was run down the length of the taped aluminum cylinder so that half of the area was covered.

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Table II. ESCA Data[a] on Zerovalent Nickel Complexes

	Compd	Ni $2p_{3/2}$		P 2p		O 1s		C 1s		Other			X-Ray source	Compd prepn
1	$Ni[P(OCH_2CCl_3)_3]_4$[b]	855.2	6.6 (2.4)	133.4	1.0 (2.1)	533.0	3.7 (3.2)	289.1	1.0 (7.2)[c]	Cl 2p	201.9	1.3 (3.0)	Al	*i*
								287.5	1.0					
2	$Ni(CO)_2(PPh_3)_2$	855.2	6.2 (2.2)	131.6	1.0 (2.0)	533.6	6.9 (2.2)	285.0	1.1 (1.9)				Al	*j*
3	$Ni(dmpe)_2$	854.8 s	4.1 (3.6)	131.7	1.0 (2.5)	530.6	16.9[g] (2.3)	285.0	1.3 (2.0)				Mg	*i*
4	$Ni[P(OCH_2)_3CCH_3]_4$	854.5	9.3 (2.3)	132.5	1.0 (2.5)	533.1	2.7 (2.3)	286.0	1.0 (2.9)[d]				Al	*i*
								285.0						
5	$Ni[P(O\text{-}p\text{-tolyl})_3]_4$	854.3	7.9 (2.1)	132.3	1.0 (2.1)	532.9	2.8 (2.0)	285.0	0.7 (2.1)				Mg	*i*
6	$Ni[P(OMe)_3]_4$	854.2	8.8 (2.1)	132.2	1.0 (2.3)	532.8	6.3 (2.1)	286.0 sh	1.2[e] (2.9)[d]				Al	*i*
7	$Ni[P(OEt)_3]_4$	854.0	7.2 (2.3)	131.4	1.0 (2.1)	531.9	2.6 (1.9)	286.0	1.2 (2.8)[d]				Mg	*i*
								285.0						
8	$Ni[PPh_2OMe]_4$	854.0 m	7.8 (2.4)	131.2	1.0 (2.2)	532.8	2.6 (2.1)	285.0	0.8 (2.1)				Mg	*k*
9	$Ni(diphos)_2$[f]	854.0 m	9.6 (2.3)	131.0	1.0 (2.3)	533.6	0.3[g] (3.3)	285.0	1.0 (2.2)				Al	*l*
10	$Ni[PPh(OEt)_2]_4$	853.8	7.3 (2.2)	131.2	1.0 (2.1)	532.6	3.8 (2.0)	285.0	0.9 (2.2)				Mg	*i*
11	$Ni[t\text{-BuNC}]_4$[f]	853.6 m	17.0 (2.9)			531.7	0.4[g] (3.3)	285.0	1.0* (2.2)	N 1s	399.2	1.2 (2.7)	Al	*m*
12	$Ni[P(O\text{-}o\text{-tolyl})_3]_3$[f]	855.6 m	7.7 (2.8)	133.4	1.0 (2.7)	533.6	2.6 (2.6)	285.0	0.9 (2.6)				Al	*n*
13	$N_2[Ni(PCy_3)_2]_2$[f]	855.1 s	9.7 (3.3)	130.9[h]	1.0 (3.1)	532.5	1.0[g] (3.4)	285.0	1.2 (2.5)	N 1s	Not obsd		Al	*o*
14	$Ni(PPh_3)_3$[f]	854.4 m	8.1 (3.0)	131.3	1.0 (2.8)	533.1	1.1[g] (3.4)	285.0	1.2 (2.4)				Al	*p*
	PPh_3			130.9	1.0 (2.4)	533.4	4.8 (2.3)	285.0	1.2 (2.1)				Al	*j*

[a] Binding energies (eV), relative peak height, and full width at half-height (eV) in parentheses are given for each element of each compound. Peak heights are relative to P 2p or to the line denoted by an asterisk, normalized for the number of atoms in the molecule, unless noted otherwise. Abbreviations s and m refer to steep or medium backgrounded slope for Ni $2p_{3/2}$; sh indicates a shoulder. dmpe, diphos, and PCy_3 represent $Me_2PCH_2CH_2PMe_2$, $Ph_2PCH_2CH_2PPh_2$, and tricyclohexylphosphine. [b] Run on Pb foil. "Pump oil" C is defined as 285.0 eV. Pb $4f_{5/2}$ and $4f_{7/2}$ lines appeared at 143.6 and 138.7 eV, each 2.2 eV wide, intensities of 5.5 and 7.3 relative to Ni $2p_{3/2}$. [c] Total width of compound and "pump oil" C 1s. See Figure 2. [d] Two C 1s peaks obtained by deconvolution. See Figure 3. [e] High-BE C 1s shoulder taken to be 286.0 eV by analogy with C adjacent to O in $Ni[P(OEt)_3]_4$. The stronger line with intensity 2.9 is attributed to exposed tape. [f] Compound run with special sample chamber. [g] In compounds where oxygen does not appear in the molecular formula intensities of O 1s are given relative to Ni $2p_{3/2}$. [h] The P 2p line showed a shoulder to high binding energy at 132.2 eV. [i] C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2956 (1970). [j] Commercial sample. [k] C. A. Tolman, W. C. Seidel, and L. W. Gosser, submitted for publication. [l] J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 2537 (1962). [m] R. Nast, H. Schulz, and H. D. Moerler, *Chem. Ber.*, 103, 777 (1970). [n] L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, 9, 2350 (1970). [o] P. W. Jolly and K. Jonas, *Angew. Chem., Int. Ed. Engl.*, 7, 731 (1968). [p] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 94, 2669 (1972).

Table III. ESCA Data[a] on Nickel–Olefin Complexes

Compd	Ni $2p_{3/2}$		P 2p		O 1s		C 1s		Other			X-Ray source	Compd prepn
$(ACN)_2Ni$[b]	856.0 s	2.4 (4.8)			532.5	2.1[c] (2.9)	285.0	1.0* (2.6)	N 1s	399.6	0.6 (2.1)	Al	*e*
$(C_2H_4)Ni(PPh_3)_2$	855.6 m	7.8 (3.2)	131.3	1.0 (3.5)	532.8	1.2[c] (3.5)	285.0	1.1 (2.5)				Al	*f*
$(S)NiL_2$	855.4	7.9 (2.9)	133.5	1.0 (2.5)	533.6	4.6 (3.0)	285.0	1.0 (2.5)				Al	*g*
$(MA)NiL_2$	855.1 m	5.9 (2.9)	132.9	1.0 (2.6)	533.0	3.0 (2.7)	285.0	1.0 (2.6)				Mg	*g*
$(C_2H_4)Ni(PCy_3)_2$	855.0 s	6.8 (4.2)	131.1	1.0 (3.0)	532.5	1.6[c] (3.1)	285.0	1.2 (2.6)				Al	*f*
$(COD)NiL_2$	855.0	7.4 (3.0)	133.4	1.0 (2.6)	533.6	4.1 (2.7)	285.0	2.8 (2.5)				Al	*g*
$(ACN)NiL_2$	855.0	6.2 (3.0)	133.1	1.0 (2.5)	533.2	3.0 (2.8)	285.0	0.8 (2.7)	N 1s	399.7	0.4 (2.3)	Al	*g*
$(2\text{-BN})NiL_2$	854.8	8.1 (2.9)	133.6	1.0 (2.6)	533.7	3.0 (2.8)	285.0	0.9 (2.5)	N 1s	399.3	0.5 (2.4)	Al	*g*
$(C_2H_4)NiL_2$	854.7	6.7 (2.8)	132.7	1.0 (2.8)	532.7	4.7 (2.8)	285.0	1.1 (2.5)				Al	*h*
$(COD)_2Ni$	853.7 s	3.6 (5.0)[d]			531.0	3.3[c] (2.8)	285.0	1.0* (2.8)				Mg	*i*

[a] See footnote *a*, Table II. Abbreviations: ACN, acrylonitrile; S, styrene; MA, maleic anhydride; COD, 1,5-cyclooctadiene; 2-BN, 2-butenenitrile; L, $P(O\text{-}o\text{-tolyl})_3$. All compounds except $(MA)NiL_2$ were run using the special chamber. [b] Run on Pb foil. Pb $4f_{5/2}$ and $4f_{7/2}$ lines appeared at 143.6 and 138.7 eV, each 2.4 eV wide, with intensities of 0.7 and 1.0 relative to Ni $2p_{3/2}$. [c] For compounds not having oxygen in the molecular formula, intensities of O 1s are given relative to Ni $2p_{3/2}$. [d] A second peak at 855.9 eV assigned to nickel oxide contributes to the large total line width. [e] G. N. Schrauzer, *J. Amer. Chem. Soc.*, 81, 5310 (1959). [f] G. Wilke and G. Hermann, *Angew. Chem., Int. Ed. Engl.*, 1, 549 (1962). [g] Reference 24. [h] W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, 9, 2354 (1970). [i] B. Bogdanovic, M. Kroner, and G. Wilke, *Justus Liebigs Ann. Chem.*, 699, 1 (1966).

A more general situation, where chemically distinct atoms were not resolved, is shown in Figure 3 for the C 1s spectrum of $Ni[P(OCH_2CH_3)_3]_4$. Deconvolution of the broad peak into two equal intensity peaks each 2.1 eV wide, using the figures given by Siegbahn, *et al.*,[19] gives peaks centered 1.0 eV apart. The lower BE is attributed to the $-CH_3$ carbon and assigned a value of 285.0 eV for purposes of calibrating the spectrum. The 286.0-eV peak is assigned to the $-OCH_2-$ carbon, the higher binding energy resulting from the attached electronegative oxygen atom.

A common difficulty encountered in ESCA spectra is the presence of adventitious C and O. Spectra of our samples which did not contain these elements inevitably showed C 1s and O 1s lines. The carbon may be present in the support, as in the sticky tape adhesive, or on the support or sample surface in a form commonly called "pump oil," presumably some sort of hydrocarbon. Spurious oxygen may be present in the support or as oxygen chemically combined with the surface of the sample. Incomplete coverage of sticky tape by sample caused the intensity of C 1s and O 1s lines relative to P 2p to increase beyond values of 1.0 and 3.0, as with samples of $Ni(CO)_2(PPh_3)_2$ and $Ni[P(OMe)_3]_4$, both of which showed narrow Ni $2p_{3/2}$ and P 2p lines. Partial sample surface oxidation caused Ni and P peaks to broaden and shift toward higher BE and gave increased O 1s intensity. Oxidation also gave a more steeply sloping base line in the vicinity of the Ni $2p_{3/2}$ peak, caused by high-BE (low kinetic energy) "shake-up" electrons.[20] The most sensitive complexes in Table I showed these features of partial oxidation even using the special chamber, particularly $Ni(dmpe)_2$ and $N_2[Ni(PCy_3)_2]_2$. We were unable to find an N 1s line in the spectrum of the latter, presumably because the sample had decomposed in the vacuum under X-ray bombardment or by oxidation.

Among the NiL_4 complexes both Ni $2p_{3/2}$ and P 2p binding energies tend to increase as the electronegativity of the substituents attached to phosphorus increases, consistent with a reduced electron density on these atoms. This is shown in Figure 4, where the measure taken for substituent electronegativity is the A_1 carbonyl stretching frequency in compounds of the type $Ni(CO)_3L$.[21] The correlation is very good for the less air-sensitive compounds. The deviation of the most electron-rich compounds above the lines is attributable to partial sample oxidation which occurred even when the special sample chamber was used.

Increasing electron density on nickel in NiL_4 complexes as one goes to the left in Figure 4 is supported by measurements of equilibrium constants for reaction 1.[22] The ratio of slopes

$$H^+ + NiL_4 \overset{K}{\rightleftharpoons} HNiL_4^+ \qquad (1)$$

of the lines for Ni $2p_{3/2}$ and P 2p in Figure 4 is about 0.5, indicating a reduced sensitivity of nickel binding energies to the effects of changing substituents on phosphorus. This is expected since the nickel atom is more remote from the substituent. The same attenuating effect is seen in the protonation data, where the slope of log K against ν_{CO} is 0.3 times as large for the NiL_4 complexes as for the free phosphines.

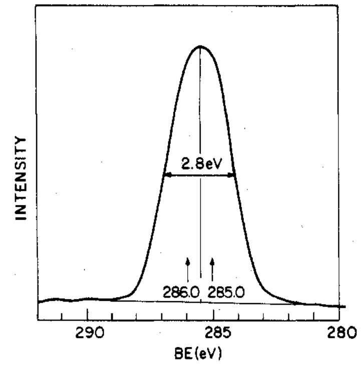

Figure 3. C 1s spectrum of $Ni[P(OCH_2CH_3)_3]_4$, showing positions of two equal-intensity components, 2.1 eV wide and separated by 1.0 eV.

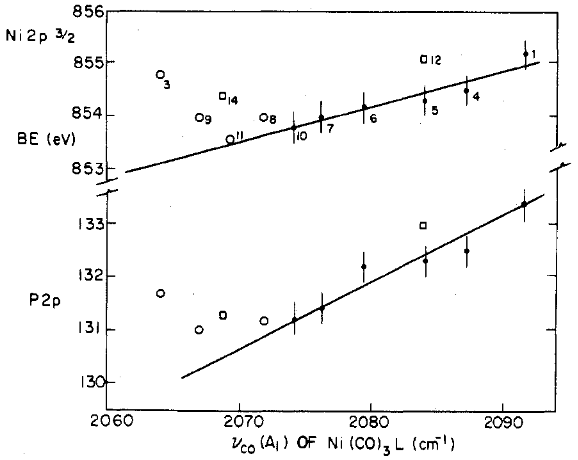

Figure 4. Ni $2p_{3/2}$ and P 2p binding energies of zerovalent nickel complexes plotted against $\nu_{CO}(A_1)$ of $Ni(CO)_3L$ from ref 21. Circles represent NiL_4 and squares NiL_3. The symbols are numbered according to Table II and left open if the spectra indicate partial reaction with O_2. Frequencies used for $Me_2PCH_2CH_2PMe_2$, $Ph_2PCH_2CH_2PPh_2$, and t-BuNC are those of PMe_3, PPh_2Me, and 2069.4 cm^{-1}, respectively. Uncertainties indicated on BE are ±0.3 eV.

Our data on Ni $2p_{3/2}$ can be compared with values of 855.4 eV reported for $Ni(CO)_4$,[10] 852.8 eV for Ni powder,[7a] 855.0 eV for $K_2Ni(CN)_4$, and 853.6 eV for $Ni(PPh_3)_2(SCN)_2$.[7c] Care must be exercised, however, because of calibration problems. We have corrected the BE's in $Ni(CO)_4$ quoted by Clark and Adams to a C 1s energy of 285.0 eV, even though the C 1s line cannot be properly regarded as coming from a saturated hydrocarbon. Data by Grim, *et al.*,[7] were referenced to vacuum-deposited gold with Au $4f_{7/2}$ defined as 83.0 eV. Grim's values for Ni $2p_{3/2}$ BE are about 1.8 eV less than ours because of the different calibration.

Nickel-Olefin Complexes. Data are given in Table III. Separate peaks for a given element in a compound were not resolved except in the case of $(COD)_2Ni$, where a second Ni $2p_{3/2}$ peak at 855.9 eV is assigned to nickel oxide. All these olefin complexes, except $(MA)Ni[P(O\text{-}o\text{-}tolyl)_3]_2$, are at least partially air sensitive. Greater average widths of Ni $2p_{3/2}$ and P 2p lines compared to those of the NiL_4 complexes in Table II suggest some oxidation, which was particularly severe with the most air-sensitive compounds $(ACN)_2Ni$, $(C_2H_4)Ni(PPh_3)_2$, $(C_2H_4)NiP(Cy_3)_2$, and $(COD)_2Ni$.[23] The expected order of decreasing binding energies $(C_2H_4)Ni[P(O\text{-}o\text{-}tolyl])_3]_2 > (C_2H_4)Ni(PPh_3)_2 > (C_2H_4)Ni(PCy_3)_2$ would pre-

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[19] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," American Elsevier, New York, N. Y., 1969, p 168.

[20] (a) T. Novakov and R. Prins, *Solid State Commun.*, 9, 1975 (1971); (b) A. Rosencwaig, G. K. Wertheim, and H. J. Guggenheim, *Phys. Rev. Lett.*, 27, 479 (1971).

[21] C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2953 (1970).

[22] C. A. Tolman, *Inorg. Chem.*, 11, 3128 (1972).

[23] Abbreviations COD, MA, ACN, and PCy_3 represent 1,5-cyclooctadiene, maleic anhydride, acrylonitrile, and tricyclohexylphosphine, respectively.

sumably be found if O_2 could be rigorously excluded. The measured Ni $2p_{3/2}$ and P 2p BE's in Table III can be taken as upper limits for the true values. Deliberate exposure of a $(C_2H_4)Ni[P(O$-*o*-tolyl$)_3]_2$ sample to air caused the yellow crystals to change to a green tar. The Ni $2p_{3/2}$ BE increased by 2.0 eV while that of 2p increased by 0.9 eV.

Reliable data were obtained for the complexes containing L = P(O-*o*-tolyl$)_3$. The increase in Ni $2p_{3/2}$ BE in the series $(C_2H_4)NiL_2 < (ACN)NiL_2 < (MA)NiL_2$ of 0.4 eV is small, just about at the limits of experimental uncertainty, but in the right direction for increasing electron withdrawal in the series of olefins. Extensive studies[24] of equilibrium 2 show

$$\text{olefin} + NiL_3 \rightleftharpoons (\text{olefin})NiL_2 + L \qquad (2)$$

that the equilibrium constant in benzene at 25° has values of 2.5×10^2, 4.0×10^4, and 4.0×10^8 for C_2H_4, ACN, and MA, respectively. Stronger bonding of acrylonitrile compared to ethylene is also indicated by the X-ray crystal structures[25] of the olefin complexes.

Compounds of Ni(II) and Ni(IV). Data for compounds conventionally regarded as Ni(II) and for one Ni(IV) compound, K_2NiF_6, are given in Table IV. The binding energies reported for K_2NiF_6 on lead are higher by ~0.5 eV than those measured on tape, calibrating in both cases to spurious C 1s at 285.0 eV. This difference appears to be general for these two modes of mounting. The Ni $2p_{3/2}$ line was short and very broad, suggesting possible surface reduction. Decomposition of K_2PdCl_6 to K_2PdCl_4 in the X-ray beam of an ESCA spectrometer has been reported by Kumar, *et al.*[6b]

Only a few of the compounds gave positive evidence of chemically distinct environments. π-$C_4H_7Ni[P(OEt)_3]_2PF_6$ contains at least four types of carbon in a 6:6:3:1 ratio, considering the carbons of the π-allyl group to be equivalent. The only distinct C 1s feature other than the peak maximum is a shoulder at 286.2 eV assigned to $-OCH_2-$ by analogy with $Ni[P(OEt)_3]_4$. The greater C 1s line width of the π-allyl complex, 3.3 eV for π-$C_4H_7NiL_2^+$ *vs.* 2.5 eV for NiL_4, suggests that the π-allyl carbon binding energies are centered below 285.0 eV, consistent with partial carbanion character. The π-$C_4H_7NiL_2PF_6$ complex gave only one P 2p peak, but it was rather broad (3.1 eV).

Nickel acetylacetonate gave a C 1s spectrum with a shoulder at 286.4 eV assigned to the two carbonyl carbons. The more intense peak due to the three other carbons was assigned a value of 285.0 eV for calibration purposes. Broad C 1s lines for $(\pi$-$C_5H_5)_2Ni$ (2.8 eV), $Ni[CH_3C(CH_2PPh_2)_3$-$(NO)]BPh_4$ (2.7 eV), Me_2Ni(dipy) 2.7 eV), $ZnNi(CN)_4$ (3.1 eV), and $PhNi(PEt_3)_2(CN)$ (2.7 eV) presumably arise from an unresolved superposition of lines of different BE from the compound or from the compound and sticky tape. The broad $(\pi$-$C_5H_5)_2Ni$ C1s line is consistent with electrons from both tape and electron-rich cyclopentadienyl rings. Extensive electron transfer from Ni to π-allyl or π-cyclopentadienyl groups is also suggested by the Ni $2p_{3/2}$ energies, which are similar to those of $Ni(NO_3)_2$ or $NiCl_2$.

The occurrence of a strongly sloping background in the vicinity of the Ni $2p_{3/2}$ line and shake-up electrons[20] at slightly higher BE was taken to indicate partial sample oxidation in Ni(0) or olefin complexes. Paramagnetic Ni(II) complexes characteristically show this behavior, as can be seen in Table IV.[26] Ni $2p_{3/2}$ lines for paramagnetic Ni(II) compounds tend to be less intense (relative to P 2p) and broader and to be located on a steeper background. The effect is strikingly seen in Figure 5 for $Ni(PPh_2Et)_2Br_2$, which can be isolated as either the paramagnetic tetrahedral isomer or the diamagnetic square-planar one.[15] Trace c shows that a spectrum identical with that of the isolated tetrahedral isomer was obtained after the square-planar isomer was warmed on the probe. The same effect has been observed by Matienzo, Swartz, and Grim.[7b,c] The Ni $2p_{3/2}$ BE is reproducibly higher by about 0.7 eV for the tetrahedral isomer, apparently reflecting a higher electron density on nickel in the square-planar complex.

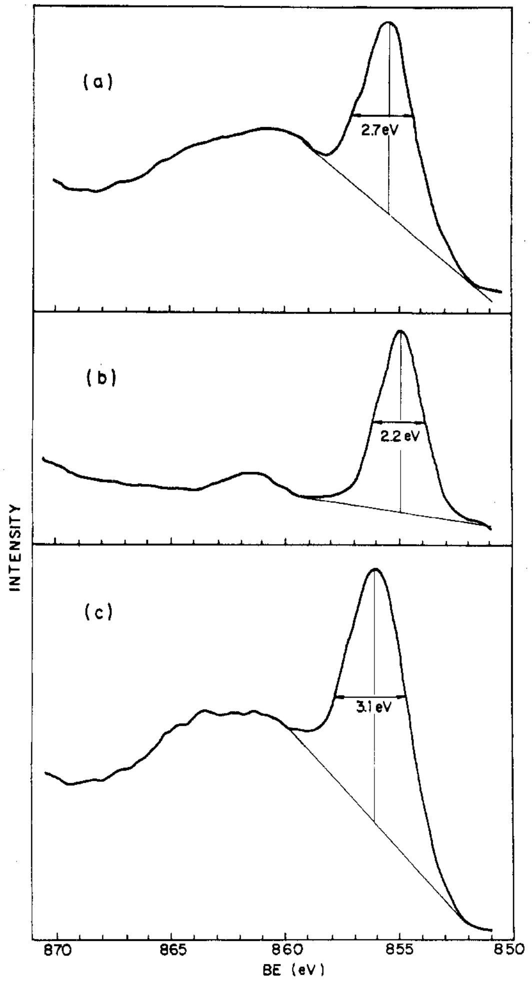

Figure 5. Ni $2p_{3/2}$ spectra of $Ni(PPh_2Et)Br_2$: (a) tetrahedral isomer; (b) square-planar isomer at −196°; (c) square-planar isomer after heating to +80°. The method used to measure peak heights and widths is also indicated.

The complex $Ni(PPh_2Et)_2Cl_2$, reportedly only isolated as the diamagnetic square-planar isomer,[15] showed a Ni $2p_{3/2}$ line very similar in appearance and position to the tetrahedral $Ni(PPh_2Et)I_2$ and $Ni(PPh_2Et)_2Br_2$ complexes. Although our sample was prepared by the same method and had the same melting point as that reported by Hayter and Humiec,[15] the magnetic moment was determined to be 1.29 ± 0.04 BM[27] indicating that part of the dichloride was in the tetrahedral form.

Discussion

Binding energies for Ni $2p_{3/2}$ electrons generally increase with increasing formal oxidation state but do span a range of

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[24] C. A. Tolman and W. C. Seidel, to be submitted for publication.

[25] L. J. Guggenberger, *Inorg. Chem.* 12, 499 (1973).

[26] The diamagnetic complexes which show steep base lines are air sensitive and the effect may be due to partial oxidation.

[27] We are indebted to Dr. J. F. Weiher for determination of the magnetic moment.

Table IV. ESCA Data[a] on Ni(IV) and Ni(II) Complexes

Compd	Ni $2p_{3/2}$		P 2p		O 1s		N 1s		C 1s		Other			X-Ray source	Compd prepn
K_2NiF_6[b]	861.2	1.2 (4.3)			533.2	1.1[c] (3.6)			285.0	1.1[c] (3.0)	F 1s	687.8	3.0 (2.3)	Al	*i*
											K 2p	294.4	2.4* (2.3)		
π-$C_4H_7Ni[P(OEt)_3]_2PF_6$	857.4 s	5.3 (3.7)	133.9	1.0 (3.1)	532.8	3.7 (2.8)			286.2 sh	1.2 (3.3)	F 1s	687.2	2.0 (3.3)	Al	*j*
									285.0	0.9					
$Ni(NO_3)_2$	857.3 s	2.3 (2.7)			533.5	2.1 (2.6)	407.2	1.0* (1.9)	285.0	5.4[c] (2.1)				Al	*k*
$Ni(3\text{-}PN)_6(ZnCl_3)_2$	857.2 s	3.4 (2.5)			532.9	3.7[c] (2.2)	401.1	0.4 (2.3)	285.0	1.0* (2.2)	Cl 2p	199.4	1.7 (3.1)	Al	*l*
											Zn $2p_{3/2}$	1022.7	1.2 (3.4)		
$Ni(NH_3)_6(ZnCl_3)_2$	857.0 s	6.0 (2.6)			532.9	0.8[c] (2.7)	401.0	1.0* (2.4)	285.0	1.8[c] (2.6)	Cl 2p	199.4	1.5 (3.1)	Al	*l*
											Zn $2p_{3/2}$	1023.2	8.8 (2.4)		
$NiCl_2$[e]	856.8 s	2.9 (2.5)							285.0	0.8[c] (2.6)	Cl 2p	199.5	1.5* (3.0)	Al	*k*
$(\pi$-$C_5H_5)_2Ni$	856.8 s[d]	2.2 (3.4)			532.9	3.8[c] (3.0)			285.0	1.0* (2.8)				Al	*i*
$K_2Ni(CN)_4$[e]	856.5	5.5 (2.1)					399.0	1.0* (1.9)	285.0	1.6 (2.5)	K $2p_{3/2}$	293.4	2.4 (2.2)	Al	*m*
$Ni[CH_3C(CH_2PPh_2)_3(NO)]BPh_4$	856.4	7.7 (2.5)	131.4	1.0 (2.4)	532.2	5.2 (3.2)	401.7	1.2 (1.4)	285.0	0.8 (2.7)	B 1s	189.4	1.9 (3.3)	Mg	*n*
$[Ni(acac)_2]_3$	856.1 s	3.7 (2.5)			532.0	2.2 (2.3)			286.4 sh	1.0 (3.7)				Al	*i*
									285.0	1.0* (3.7)					
$Me_2Ni(dipy)$	856.1 s	5.5 (2.8)			531.6	1.8[c] (3.0)	400.4	1.3 (2.1)	285.0	1.0* (2.7)				Al	*o*
$ZnNi(CN)_4$	856.0	7.1 (2.6)			532.2	0.2[c] (3.0)	399.3	1.1 (2.6)	285.0	1.0* (3.1)	Zn $2p_{3/2}$	1022.2	12.7 (2.7)	Al	*l*
$Ni[PPh(OEt)_2]_3(CN)_2$	856.0	19.5 (2.4)	132.3	1.0 (2.2)	532.7	3.5 (2.4)	398.7	2.9 (2.4)	285.0	1.2 (2.2)				Mg	*p*
$Ni(PPh_2Et)_2Cl_2$[f]	856.0 s	4.4 (2.8)	131.5	1.0 (2.1)					285.0	1.2 (1.9)	Cl 2p	198.6	1.4 (2.9)	Al	*q*
$Ni(PPh_2Et)_2I_2$[g]	855.9 s	3.8 (2.4)	131.8	1.0 (2.1)					285.0	1.0 (1.9)	I $3d_{5/2}$	620.3	20.7 (2.0)	Al	*q*
$Ni(PPh_3)_2(SCN)_2$	855.7	9.9 (2.4)	131.6	1.0 (2.4)			398.9	0.8 (2.1)	285.0	0.9 (2.1)	S 2p	163.0	1.3 (2.4)	Al	*r*
$Ni(PPh_2Et)_2Br_2$[g]	855.6 s	4.5 (2.7)	131.4	1.0 (2.1)					285.0	1.0 (1.8)	Br 3d	68.8	2.0 (2.5)	Al	*q*
$Me_2Ni(diphos)$	855.2 s	4.7 (3.4)	131.9	1.0 (3.4)	532.6	1.7[c] (3.2)			285.0	1.2 (2.4)				Al	*s*
π-$C_3H_5Ni(PPh_3)Br$	855.2 s	6.9 (3.5)	131.7	1.0 (3.0)	532.8	0.8[c] (2.7)			285.0	1.7 (2.1)	Br 3d	68.6	3.4 (2.9)	Al	*t*
$PhNi(PEt_3)_2CN$	855.0	12.4 (2.8)	130.4	1.0 (2.3)	531.9	0.3[c] (3.6)	398.3	1.8 (2.3)	285.0	1.3 (2.7)				Mg	*u*
$Ni(PPh_2Et)_2Br_2$[h]	854.9	9.4 (2.2)	131.6	1.0 (2.3)					285.0	1.0 (2.0)	Br 3d	69.1	2.0 (2.6)	Al	*l, q*

[a] See footnote *a*, Table II. Abbreviations: 3-PN, 3-pentenenitrile; acac, acetylacetonate; dipy, dipyridyl; diphos, $Ph_2PCH_2CH_2PPh_2$. [b] Run on lead foil. Pb $4f_{5/2}$ and $4f_{7/2}$ lines, each 1.9 eV wide, appeared at 144.0 and 139.1 eV with intensities of 4.5 and 5.8 relative to Ni $2p_{3/2}$. [c] Intensity relative to Ni $2p_{3/2}$. [d] A shoulder at 857.9 eV is assigned to nickel oxide. [e] Run on stainless steel screen. [f] Apparently a mixture of tetrahedral and square-planar forms; $\mu = 1.3$ BM. [g] Tetrahedral form. [h] Square-planar form. [i] Purchased commercially. [j] C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 6777 (1970). [k] Commercial samples of the hexahydrates dried over H_2SO_4 for 5 days. [l] See Experimental Section. [m] Reference 14. [n] D. Burglund and D. W. Meek, *Inorg. Chem.*, 11, 1493 (1972). [o] T. Yamamoto. A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 93, 3350 (1971). [p] B. B. Chastain, E. A. Rick, R. L. Preutt, and H. B. Gray, *ibid.*, 90, 3994 (1968). [q] Reference 15. [r] L. M. Venanzi, *J. Chem. Soc.*, 719 (1958); F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, 83, 344 (1961). [s] M. L. H. Green and M. J. Smith, *J. Chem. Soc. A*, 639 (1971). [t] G. Wilke, *et al.*, *Angew Chem., Int. Ed. Engl.*, 5, 151 (1966). [u] D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 93, 3543 (1971).

values within an oxidation state, depending on the ligands. Ranges found were 853.6-855.2 eV for NiL_4, 854.9-857.4 eV for Ni(II), and ~861 eV for the Ni(IV) complex K_2NiF_6. Note the overlap between Ni(0) and Ni(II) classes. There is a general relationship between Ni BE and air stability. The Ni(0) complex, $Ni[P(OCH_2CCl_3)_3]_4$ (855.2 eV), is more stable in air than the formally Ni(II) compound $PhNi(PEt_3)_2CN$ (854.9 eV). The nickel-olefin complexes with Ni $2p_{3/2}$ BE of 853.7-856.0 eV span the overlapping region between Ni(0) and Ni(II). Comparing BE's for Ni[O-*p*-tolyl)$_3$]$_4$ (854.3 eV) and (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$ (854.7 eV) certainly suggests that the ethylene complex might best be regarded as a Ni(0) complex, with C_2H_4 in the complex having an electronegativity comparable to that of a phosphite. The ethylene complex is also extremely air sensitive. It should be pointed out that the olefinic C-C bond length of 1.46 Å[25] in (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$ is the longest reported for a transition metal-ethylene complex and is close to the 1.472-Å C-C bond in ethylene oxide.[28] Though the nickel must contribute heavily to the ethylene π^* orbital, the bonding is best regarded as substantially covalent (as in cyclopropane) rather than as a dicarbanion complex of Ni(II). Similar conclusions from ESCA studies have been reached by others.[3b,5] An excellent discussion of the bonding of acetylene to transition metals, which is also applicable to olefin complexes, has been given by Greaves, Lock, and Maitlis.[29] Ni $2p_{3/2}$ binding energies in (COD)Ni[P(O-*o*-tolyl)$_3$]$_2$, with both double bonds of the 1,5-cyclooctadiene coordinated,[23,24] and in $(COD)_2Ni$, with four double bonds coordinated, are clearly not in accord with regarding these complexes as Ni(IV) and Ni(VIII) as one would in the metallocyclopropane view of metal-olefin bonding.

Among the formally Ni(II) compounds the highest Ni $2p_{3/2}$ BE's are found where the nickel is in a cation or surrounded by hard ligands like NO_3^-, NH_3, or Cl^-. Lower binding energies are found for nickel in anions or neutral molecules, especially those containing nickel-carbon bonds or phosphines.

Increases in metal binding energies of ~2 eV for each increase in formal oxidation state by 2+ have been reported for Pt[3-6a] and Pd.[6b] We found about the same change on going from Ni(0) to Ni(II). Going from Ni(II) to Ni(IV), however, increases the Ni $2p_{3/2}$ BE by ~5 eV. This is consistent with the ordinary chemical experience that it is about as easy to oxidize Pt(II) to Pt(IV) as Pt(0) to Pt(II), but much more difficult to oxidize Ni(II) to Ni(IV).

Binding energies of P 2p electrons for a wide variety of phosphorus-containing compounds have been reported by Jolly, *et al.*[30] We have seen (Figure 4) that substituents on phosphorus have a significant effect on P 2p BE's in NiL_4 complexes. There is also a dependence on metal oxidation state, as seen in the following examples: 131.2 eV in $Ni[PPh(OEt)_2]_4$ *vs.* 132.3 eV in $Ni[PPh(OEt)_2]_3(CN)_2$; 131.0 eV in Ni(diphos)$_2$ *vs.* 131.9 eV in Me_2Ni(diphos). For L = PPh_3, values of 130.9, 131.3, 131.6, and 131.7 eV were found in free L, NiL_3, $Ni(CO)_2L_2$, and π-C_3H_5NiLBr. We conclude that little or no change in P 2p BE is expected on coordination of a phosphine to a metal atom but that small but significant increases in BE will occur as other, more electron-withdrawing ligands are attached or as the formal oxidation state of the metal is increased. This is in accord with the findings of Jolly,[30] who reported P 2p BE's of 130.6 eV for PPh_3 and 131.6 eV for *trans*-Rh(CO)Cl$(PPh_3)_2$.

Blackburn, *et al.*,[31] reported P 2p binding energies of 131.9 eV for free PPh_3 and 131.6 eV for $Ni(PPh_3)_2Cl_2$ and concluded that the electron density on phosphorus remained the same or *increased* on coordination to Ni(II). Their value for the Ni(II) complex is very close to ours of 131.7 eV in π-$C_3H_5Ni(PPh_3)$Br but their number for free PPh_3 is high, possibly because their sample was contaminated with phosphine oxide. This possibility illustrates why line widths and relative heights should be given along with binding energies in reporting ESCA data. A P 2p BE of 131.2 eV in PPh_3, a value close to ours, has been reported by another group.[32] The BE increases to 133.2 eV when the quaternary phosphonium ion $MePPh_3^+$ is formed.[32]

Increases in binding energies on coordination were also found for N 1s electrons of nitrogen-bonded ligands. The N 1s BE of 401.0 eV in $Ni(NH_3)_6(ZnCl_3)_2$ can be compared with 400.7 eV for amine nitrogen in $Rh(NH_3)_6(NO_3)_3$ and 398.8 eV in solid NH_3 reported by Hendrickson, *et al.*,[33] who have reported N 1s binding energies for a wide variety of nitrogen-containing compounds. Our N 1s energy in Me_2Ni(dipy) of 400.4 eV is also higher than the free pyridine value of 398.0 eV.[2] Our values for coordinated cyanide (398.3-399.3 eV), isothiocyanate (398.9 eV), and nitrate (407.2 eV) are in good agreement with those in other compounds.[33]

The N 1s energy of 401.7 eV in the one nitrosyl complex $Ni[CH_3C(CH_2PPh_2)_3(NO)]BPh_4$ is about in the middle of the range (399.6-403.3 eV) of values reported by Finn and Jolly[8a] for a variety of transition metal nitrosyl complexes. The N-O stretching frequency of ~1760 cm^{-1} [34] also lies in the middle of the frequency range (1505-1939 cm^{-1}). Both N 1s BE and ν_{NO} are higher than the 399.8 eV and 1735 cm^{-1} of $NiCl(NO)(PPh_3)_2$,[8a] indicating less back-donation from nickel to nitrosyl in the cationic complex. This and the position of the Ni $2p_{3/2}$ BE in Table IV indicate that the electron density on nickel is more nearly in accord with regarding the metal in the complex as Ni(II), contrary to the conclusion of Berglund and Meek.[34]

Cl $2p_{3/2}$ energies in ionic compounds were found in the narrow range of 198.6-199.5 eV. The higher value of 199.9 eV in $Ni[P(OCH_2CCl_3)_3]_4$ is attributable to the presence of three chlorines on one carbon. Zn $2p_{3/2}$ BE's occurred in the range 1022.2-1023.2 eV. Little systematic can be said about the O 1s binding energies because of spurious oxygen.

The results of relative peak intensity measurements are summarized in Table V as observed average peak height relative to that of P 2p electrons and compared with the data of Wagner,[11] who used a similar instrument and a variety of inorganic compounds. The two sets of results differ considerably.

Also compared in this table are observed relative intensities and calculated emissivity ratios (see the Appendix for calculation details). Our observed ratios are all less than calculated except for B, C, and O. High intensities for C and O are attributable, at least in part, to surface contamination. The low average N 1s intensity is partly attributable to decom-

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Table V. Comparison of Mean Peak Heights with Calculated X-Ray Absorption Coefficients

Z	Electron	Approx BE, eV	Intens			
			Found[a]	Calcd	Found/calcd	Found by Wagner[c]
5	B 1s	190	1.9 (1)	0.36	5.3	0.36
6	C 1s	285	1.1 ± 0.2[b] (36)	0.67	1.64	0.61
7	N 1s	400	1.0 ± 0.6 (12)	1.20	0.83	1.05
8	O 1s	532	3.3 ± 0.7[b] (18)	1.98	1.67	1.56
9	F 1s	688	2.5 ± 0.5 (2)	3.25	0.77	2.56
15	P 2p	132	(1.0)	(1.00)	(1.00)	(1.00)
16	S 2p	163	1.3 (1)	1.44	0.90	1.26
17	Cl 2p	200	1.5 ± 0.1 (4)	1.99	0.75	1.77
19	K $2p_{3/2}$	295	2.4 (1)	2.85	0.84	2.17
28	Ni $2p_{3/2}$	855	6.9 ± 2.4 (45)	15.66	0.44	9.38
30	Zn $2p_{3/2}$	1023	7.6 ± 4.2 (3)	21.13	0.36	10.86
35	Br 3d	69	2.5 ± 0.6 (3)			1.35
53	I $3d_{5/2}$	620	20.7 (1)			12.8

[a] Mean peak heights relative to P 2p based on the number of measurements shown in parentheses. [b] Values more than twice the mean are not included in the average. [c] Reference 11.

position of some samples with loss of nitrogen, *e.g.*, $N_2[Ni(PCy_3)_2]_2$. Weak nitrogen lines for the olefin complexes containing acrylonitrile or 2-butenenitrile (Table III) suggest that these compounds also suffered partial decomposition. The lower values of the other intensity ratios may be due to neglect of the $F(E_j)$ term in the Appendix, to nonlinearity of K_j with $1/E_j$, or to surface contamination.

Hydrocarbon surface contamination can affect the relative intensities of other elements by a preferential attenuation of low kinetic energy (high BE) electrons, which have a small escape depth. This factor should cause the ratios of observed to calculated intensities to decrease systematically as binding energy increases and can be seen in Table V in the L series from Cl to Zn. Changing sources from Al Kα (1486.6 eV) to Mg Kα (1253.6 eV) is also expected to affect relative intensities because of the dependence of escape depth on kinetic energy. There is evidence for greater Ni $2p_{3/2}$ intensities with the Al source in Tables II and III, but the differences are not large compared to values for different compounds with the same source.

Intensity variability for a given source was substantial. The greater relative Ni $2p_{3/2}$ peak heights in diamagnetic nickel complexes was mentioned earlier. Notably high values were found for Ni[*t*-BuNC]$_4$ (17.0) and $Ni[PPh(OEt)_2]_3(CN)_2$ (19.5). Zn $2p_{3/2}$ intensities varied considerably in the three compounds $ZnNi(CN)_4$ (12.7), $Ni(NH_3)_6(ZnCl_3)_2$ (8.8), and $Ni(3\text{-}PN)_6(ZnCl_3)_2$ (1.2).

Conclusion

ESCA of organometallic compounds can give useful information about electron distribution. Spectra must be interpreted carefully because of possible oxidation or decomposition and difficulties in energy calibration. Alkyl, aryl, π-allyl, and π-cyclopentadienyl groups can be usefully regarded as uninegative ions in assigning formal oxidation states, but they are less electronegative than Cl^- or NO_3^-. Ethylene complexes of nickel are properly regarded as Ni(0) complexes,[35] but the metal BE can be systematically increased by substituting highly electron-withdrawing groups on the double bond. Changing the substituents on phosphorus in NiL_4 complexes can change the Ni $2p_{3/2}$ BE to an extent comparable to oxidation from Ni(0) to Ni(II). Ni $2p_{3/2}$ spectra of nickel complexes depend markedly on whether the complex is diamagnetic or paramagnetic.

ESCA is not yet reliable for quantitative elemental analysis. Peak intensities (and line widths) do, however, give useful information in assigning spectra, detecting impurities, and noticing the occurrence of decomposition or oxidation and should be reported along with binding energies.

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Appendix. Estimation of Emissivity from X-Ray Mass Absorption Coefficients

For a given set of operating conditions and instrument geometry, the observed intensity I_j of a particular photoelectron j should be proportional to an instrument response function K_j, the emissivity per atom for constant X-ray flux A_j, and the atom concentration N_j and should be inversely proportional to the electron-scattering cross section of the matrix through which the electron must escape, S_j; *i.e*

$$I_j = K_j A_j N_j / S_j \tag{3}$$

According to Helmer and Weichert[36] K_j should be inversely proportional to electron kinetic energy E_j. The scattering cross section S_j is mainly dependent on electron-plasmon interactions of the form $(1/E_j) \cdot F(E_j)$,[37] where the term $F(E_j)$ changes slowly with E_j in the range of interest. Therefore, K_j and S_j in eq 3 will tend to cancel each other to give

$$I_j \propto A_j N_j \tag{4}$$

Because X-ray scattering is negligible at the long wavelengths of Al and Mg Kα radiation (8.34 and 9.89 Å), emissivity will be directly proportional to X-ray absorption. We have calculated A_j, for elements 1-30, from published[38] mass absorption coefficients by setting A_j equal to the net atomic absorption coefficient for a particular electron. This net absorption coefficient was estimated by subtracting a power law extrapolation of the absorption coefficient for the next shell from the total coefficient. For the K shell this gives A_j directly; for the L shell it yields the summation of A_j for the three levels. The individual A_j values were estimated by distributing them according to the L_I/L_{II+III} values reported by Siegbahn.[2] Where resolvable, the L_{II} and L_{III} peaks were apportioned according to electron distribution.

The results have been normalized to constant X-ray flux by expressing A_j relative to a common photoelectron, A_j for P 2p electrons.

Registry No. $Ni[P(OCH_2CCl_3)_3]_4$, 28799-98-6; $Ni(CO)_2(PPh_3)_2$, 13007-90-4; Ni(dmpe)$_2$, 15628-25-8; $Ni[P(OCH_2)_3CCH_3]_4$, 14730-03-1; Ni[P(O-*p*-tolyl)$_3$]$_4$, 36700-08-0; $Ni[P(OMe)_3]_4$, 14881-35-7; $Ni[P(OEt)_3]_4$, 14839-39-5; $Ni[PPh_2OMe]_4$, 41685-57-8; Ni(diphos)$_2$, 15628-25-8; $Ni[PPh(OEt)_2]_4$, 22655-01-2; Ni[*t*-BuNC]$_4$, 19068-11-2;

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(35) Cook, *et al.*,[5] have concluded from ESCA studies, that the platinum in $(C_2H_4)Pt(PPh_3)_2$ is better regarded as Pt(0) than as Pt(II). Certainly their data indicate that C_2H_4 is much less electron withdrawing than O_2 or Cl_2.

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Ni[P(O-*o*-tolyl)$_3$]$_3$, 41716-77-2; N$_2$[Ni(PCy$_3$)$_2$]$_2$, 21729-50-0; Ni(PPh$_3$)$_3$, 25136-46-3; (ACN)$_2$Ni, 12266-58-9; (C$_2$H$_4$)Ni(PPh$_3$)$_2$, 23777-40-4; (S)NiL$_2$, 41685-58-9; (MA)NiL$_2$, 41813-01-8; (C$_2$H$_4$)Ni(PCy$_3$)$_2$, 41685-59-0; (COD)NiL$_2$, 41685-51-2; (ACN)NiL$_2$, 31666-48-5; (2-BN)NiL$_2$, 41685-61-4; (C$_2$H$_4$)NiL$_2$, 31666-47-4; (COD)$_2$Ni, 1295-35-8; K$_2$NiF$_6$, 17218-47-2; π-C$_4$H$_7$Ni[P(OEt)$_3$]$_2$PF$_6$, 32678-25-4; Ni(NO$_3$)$_2$, 13138-45-9; Ni(3-PN)$_6$(ZnCl$_3$)$_2$, 41685-63-6; Ni(NH$_3$)$_6$(ZnCl$_3$)$_2$, 41685-64-7; NiCl$_2$, 7718-54-9; (π-C$_5$H$_5$)$_2$Ni, 1271-28-9; K$_2$Ni(CN)$_4$, 14220-17-8; Ni[CH$_3$C(CH$_2$PPh$_2$)$_3$(NO)]BPh$_4$, 33789-62-7; [Ni(acac)$_2$]$_3$, 29090-30-0; Me$_2$Ni(dipy), 32370-42-6; ZnNi(CN)$_4$, 41685-66-9; Ni[PPh(OEt)$_2$]$_3$(CN)$_2$, 24419-45-2; Ni(PPh$_2$Et)$_2$Cl$_2$, 15633-29-1; Ni(PPh$_2$Et)$_2$I$_2$, 41685-69-2; Ni(PPh$_3$)$_2$(SCN)$_2$, 15709-62-3; Ni(PPh$_2$Et)$_2$Br$_2$, 41716-78-3; Me$_2$Ni(diphos), 31387-22-1; π-C$_3$H$_5$Ni(PPh$_3$)Br, 12336-45-7; PhNi(PEt$_3$)$_2$CN, 41685-72-7; Ni(PPh$_2$Et)$_2$Br$_2$, 15633-28-0; B, 7440-42-8; C, 7440-44-0; N, 7727-37-9; O, 7782-44-7; F, 7782-41-4; P, 7723-14-0; S, 7704-34-9; Cl, 7782-50-5; K, 7440-09-7; Ni, 7440-02-0; Zn, 7440-66-6; Br, 7726-95-6; I, 7553-56-2.

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Hindered Ligand Systems. VII. Crystal Field Spectrum of *cis,cis*-1,3,5-Tris(pyridine-2-carboxaldimino)cyclohexanenickel(II)

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The assignment of the spectrum of the titled compound, based on conventional crystal field calculations and averaged angular coordinates from X-ray structural data ($\phi = 32°$, $\theta_1 = 51°$, and $\theta_2 = 57°$), has not been successful. The criteria for failure include the necessity of choosing a value of Dq in large excess of those normally found for tris(α-diimine) complexes of Ni(II). A series of solutions which approximate the observed spectrum has been obtained with $\phi > 32°$ and θ(average) = 57 ± 1°. The solutions require Dq values which are only slightly larger than the normal range. A possible explanation for the increased value of ϕ is explored.

The existence and approximate formation criteria of a group of complexes whose stereochemistries range between trigonal prismatic and octahedral have been established and discussed in some detail.[1] Each complex can be classified according to its twist angle, ϕ, the angle which describes the rotation of one triangular face of donor atoms with respect to the other.[2] Sexadentate ligands which contain the pyridine-2-carboxaldimino group comprise a series of these complexes wherein equilibrium values of ϕ occur throughout the range between 0 and 60°. Complexes of one of these ligands, *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane ((py)$_3$tach) have been investigated in this laboratory.[3] The structure of the Zn(II) complex is known[4] to have an average twist angle of about 4°, while the Mn(II) and Co(II) complexes are isomorphous and presumably isostructural.[3,4] The average twist angle in the Ni(II) complex has been shown[5] to be about 32°.

An interpretation of the spectrum of the Co(II) complex, assuming $\phi = 0°$, was seemingly straightforward,[3] but the spectrum of the Ni(II) complex, which was first recorded[6] in 1968, has not yet been interpreted with certainty. The purpose of this publication is to outline some of the problems associated with the interpretation according to crystal field theory.

Crystal Field Theory

The crystal field potential which was used for all calculations is

$$V = 7eq\pi^{1/2}\{3(1/5)^{1/2}(BY)_2{}^0(r^2/R^3) + ((3/4)(BY)_4{}^0 - 35(1/140)^{1/2}[(BY)_4{}^3 - (BY)_4{}^{-3}])(r^4/R^5)\}$$

with $(BY)_l{}^m = B_l{}^m(\theta_1,\theta_2)Y_l{}^m$ and

$$B_2{}^0(\theta_1,\theta_2) = (1/7)(3[\cos^2\theta_1 + \cos^2(\pi-\theta_2)] - 2)$$

$$B_4{}^0(\theta_1,\theta_2) = (1/7)((35/3)[\cos^4\theta_1 + \cos^4(\pi-\theta_2)] - 10[\cos^2\theta_1 + \cos^2(\pi-\theta_2)] + 2)$$

$$B_4{}^{\pm 3}(\theta_1,\theta_2) = (1/7)(\sin^3\theta_1\cos\theta_1 + \sin^3(\pi-\theta_2)\cos(\pi-\theta_2)e^{\mp i3\phi})$$

where θ_1 and θ_2 are polar angles and ϕ is the twist angle.[7] This potential is appropriate to D_{3h} ($\phi = 0°$) and D_3 ($0° < \phi < 60°$) symmetries if $\theta_1 = \theta_2$ and O_h ($\phi = 60°$) symmetry if $\theta_1 = \theta_2 = \cos^{-1}(1/3)^{1/2}$. It is also appropriate to C_{3v} ($\phi = 0°$) and C_3 ($0° < \phi < 60°$) symmetries if $\theta_1 \neq \theta_2$. The one-electron matrix elements are $\langle d_{\pm2}|V|d_{\pm2}\rangle = -3B_0{}^2\rho_2 + (3/8)B_4{}^0\rho_4$, $\langle d_{\pm1}|V|d_{\pm1}\rangle = (3/2)B_2{}^0\rho_2 - (3/2)B_4{}^0\rho_4$, $\langle d_0|V|d_0\rangle = 3B_2{}^0\rho_2 + (9/4)B_4{}^0\rho_4$, and $\langle d_{\pm2}|V|d_{\mp1}\rangle = \pm(35/4)B^{\pm3}\rho_4$, where $\rho_n = eq\langle r^n/R^{n+1}\rangle$ and $B_l{}^m(\theta_1,\theta_2)$ is further abbreviated to $B_l{}^m$.

It is possible to express $B_l{}^0(\theta_1,\theta_2)$ in terms of its value at $\theta_1 = \theta_2 = \cos^{-1}(1/3)^{1/2}$ (the octahedral value) and a complicated, but easily derived, set of trigonometric functions of β_1 and β_2, the latter being the respective differences between the observed (or effective) polar angles and the octahedral

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