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XPS Studies of Core Binding Energies in Transition Metal Complexes. 2. Ligand Group Shifts¹

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Abstract: The metal and ligand core binding energies (BE) of over 100 low-spin complexes of the transition metals iron, cobalt, nickel, copper, molybdenum, ruthenium, rhodium, palladium, tungsten, rhenium, osmium, iridium, and platinum have been measured. The complexes are derived from σ -donor ligands, including halogens, pseudohalogens, and tertiary phosphines and arsines, and from π -acceptor ligands, including the nitrosyl, aryldiazo, carbonyl, thiocarbonyl, dinitrogen, nitrile, isonitrile, and cyanide ligands. To a first approximation, the observed metal BEs can be reproduced from a single set of ligand group shifts referred to the "bare" metal atom. The metal BE increases 1 eV per unit increase in the formal oxidation state of the metal. Metal BE shifts are negative for σ -donor ligands (Cl^- , SCN^- , etc.) and positive for π -acceptor ligands (CO , NO^+ , etc.). In most cases the metal BEs calculated from the sum of the BE shifts agree with the measured BEs within the error of the experiment ($\sigma = \pm 0.2$ eV). The success of the model leads to the conclusion that relaxation effects are sensibly constant among these transition metal complexes. The empirically derived "bare" metal BEs are 2.5–4.2 eV higher than the values reported for bulk metals. The molecular charge did not affect the agreement between calculated and measured metal BEs.

One of the useful features of X-ray photoelectron spectroscopy (XPS) which has attracted many investigators is the shift in binding energy (BE) of core electrons of atoms in different chemical environments.^{3–5} The pioneering work of Siegbahn et al.³ demonstrated that these chemical shifts are associated with the effective charge on the atom from which the photoelectron originates. Excellent correlations between calculated charges and BEs have been obtained for simple molecules in the gas phase, using the point charge model,^{6–10} but calculations of effective charges for larger molecules in the solid state are seldom available, and interpretations are often qualified due to the unknown contributions of the crystal potential and relaxation effects. Consequently, alternative methods have been sought for analyzing core BEs in complicated molecules. One approach which has been successfully applied to compounds of the main-group elements assigns empirically derived values for BE shifts to the groups of atoms attached to the central atom being considered. Summation of these group shifts has been found to reproduce the BEs observed for C, N, P, As, Si, and Te compounds,^{11–15} but the group shift parameters are not transferrable from one atom to another.

Numerous XPS studies of transition-metal complexes have given considerable insight into the origins of metal BE shifts for series of closely related complexes, but no comprehensive treatment of transition-metal BEs is yet available. In view of the obvious need for a coherent interpretation of transition-metal BEs, particularly for complexes of π acceptors, the use of a single set of empirically derived group shifts for this purpose was assessed. In the following paragraphs, we will demonstrate the utility of and insights provided by the group shift method in the treatment of metal BEs for

transition-metal complexes with many of the common σ -donor and π -acceptor ligands.

Experimental Section

Data Collection. The compounds comprising this study are insulators. Consequently, sample charging¹⁶ and sample decomposition^{16–18} can be

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Table I. Partial List of Compounds^a

(2) [Fe(CH ₃ CN)Cl(das) ₂][BPh ₄] ^b	(59) [MoOCl(das) ₂][PF ₆]	(80) RhCl ₂ (NO)(PPh ₃) ₂
(4) [Fe(CO)Cl(das) ₂][BPh ₄]	(64) Ru(CO) ₃ (PPh ₃) ₃	(81) Rh(N ₂ - <i>p</i> -C ₆ H ₄ F)Cl ₂ (PPh ₃) ₂
(5) [FeCl(NO)(das) ₂][BPh ₄]	(65) [Ru(CO) ₂ (NO)(PPh ₃) ₂][PF ₆]	(84) PdCl ₂ (PPh ₃) ₂
(6) [Fe(NO)(das) ₂][ClO ₄] ₂	(66) [Ru(N ₂ - <i>p</i> -C ₆ H ₄ F)(CO) ₂ (PPh ₃) ₂][BF ₄]	(85) W(N ₂) ₂ (dppe) ₂ ^d
(9) [FeI(NO)(das) ₂]I	(67) RuCl ₃ (NO)(PEt ₂ Ph) ₂	(86) W(CO) ₂ (dppe) ₂
(10) [FeCl(NO)(das) ₂][BF ₄] ₂	(68) Ru(N ₂ - <i>p</i> -C ₆ H ₄ CH ₃)Cl ₃ (PPh ₃) ₂	(88) W(NN(CH ₂) ₂ Ph)Br(dppe) ₂
(16) Fe(CO) ₃ (PPh ₃) ₂ ^c	(69) RuCl ₂ (das) ₂	(95) ReCl ₃ (PMe ₂ Ph) ₃
(17) [Fe(CO) ₂ (NO)(PPh ₃) ₂][PF ₆]	(70) RuCl(NO ₂)(das) ₂	(96) ReOCl ₃ (PPh ₃) ₂
(18) [Fe(N ₂ - <i>p</i> -C ₆ H ₄ CH ₃)(CO) ₂ (PPh ₃) ₂][PF ₆]	(71) [RuCl(N ₂)(das) ₂][SbF ₆]	(97) OsBr ₃ (NO)(PPh ₃) ₂
(29) [Co(NO)(das) ₂][ClO ₄] ₂	(72) [Ru(CO)Cl(das) ₂][BPh ₄]	(98) Os(N ₂ - <i>p</i> -C ₆ H ₄ F)Br ₂ (PPh ₃) ₂
(30) [CoCl(NO)(das) ₂][ClO ₄]	(73) [RuCl(NO)(das) ₂]Cl ₂	(104) Ir(NHNC ₆ H ₅)Cl ₃ (PPh ₃) ₂
(31) [CoBr(NO)(das) ₂][ClO ₄]	(75) Ru(NO) ₂ (PPh ₃) ₂	(105) IrCl ₃ (PMe ₂ Ph) ₃
(38) Co(NO)(PPh ₃) ₃	(77) RhCl(PPh ₃) ₃	(106) Ir(CO)Cl(PPh ₃) ₂
(41) [Ni(das) ₂][ClO ₄] ₂	(78) Rh(CO)Cl(PPh ₃) ₂	(110) PtClH(PEt ₃) ₂
(42) [Ni(NO ₂)(das) ₂][ClO ₄]	(79) RhCl(CS)(PPh ₃) ₂	(111) PtCl ₂ (PEt ₃) ₂
(43) [NiCl(das) ₂][ClO ₄]		

^a A complete listing of compounds and their binding energies is available as supplementary material. ^b das is *o*-phenylenebis(dimethylarsine). ^c PPh₃ is triphenylphosphine. ^d dppe is 1,2-bis(diphenylphosphino)ethane.

significant. Since both factors can vary with the spectrometer and with experimental conditions, significant large discrepancies in reported BEs are common.¹⁹ The data base for the present report is of course subject to these same difficulties. The data reported in Table I were obtained using two McPherson ESCA-36 photoelectron spectrometers that were calibrated and standardized by the same method.²⁰ All BEs are referenced to a C 1s BE of 285.0 eV except for the dithiocarbamate complexes (285.3 eV) and tetraphenylborate salts. The C 1s BE for tetraphenylborate salts was taken as the weighted average of C 1s for the cation (285.0 eV) and the C 1s value for tetraphenylborate anion (284.5 eV).¹ Spectrometer operating conditions have been described in detail elsewhere.^{1,21} The BEs reported in Table I are the result of 2–5 separate measurements and were generally reproducible within ± 0.2 eV, with line widths typically 1.2–2.5 eV. When unexpected multiple peaks were found and/or obvious decomposition was noted visually, the spectrum was remeasured using a low-temperature probe. The BEs for several samples (59, 67, 84, 85, 96) have been measured on two or three different spectrometers. No systematic differences were noted among the values obtained from different spectrometers. A more detailed discussion of the BE data for several of the complexes examined in this study can be found elsewhere.^{1,21–25}

The BEs of several of the complexes in Table I have been reported by others. References to these will be found in Table I. The BEs reported in the literature of compounds 29, 67, 68, 71, 75, 80, 81, 95, 96, 105, 106, 110, and 111 are in substantial agreement with the present values. One compound, Rh(NO)Cl₂(PPh₃)₂ (80), has an N 1s BE 2.0 eV lower than that reported by Su and Faller,²⁶ but the value reported by Su and Faller was shown to be that for the oxidation product, Rh(NO₂)Cl₂(PPh₃)₂. The BEs for eight compounds, 67, 68, 75, 80, 81, 97, 98, and 104, have also been reported by Clark et al.²⁷ Approximately half of the data for these five compounds are in agreement, but the other values differ by more than 2 σ . The large number of common data points provides a basis for determining whether the discrepancies are random or are due to systematic errors. The observed differences between the BEs reported from the two different instruments are plotted vs. the electron kinetic energy in Figure 1. Although large differences in the "absolute" BEs are evident, the relative BEs agree. Thus, discrepancies in BEs for these five compounds are likely due to differences in calibration procedures. Figure 1 vividly demonstrates the difficulties in comparing the "absolute" BEs reported using different spectrometers, but also shows that the

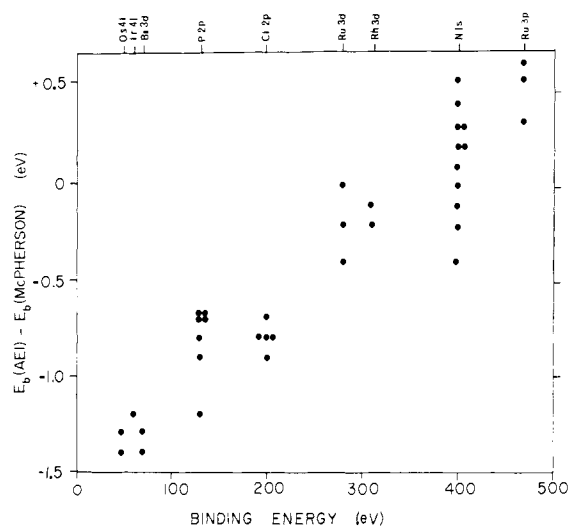


Figure 1. A comparison of the core level BEs recorded for the same complexes (67, 68, 75, 80, 81, 97, 98, and 104 in Table I) on two different commercial spectrometers. The data recorded using an AEI instrument are taken from ref 27.

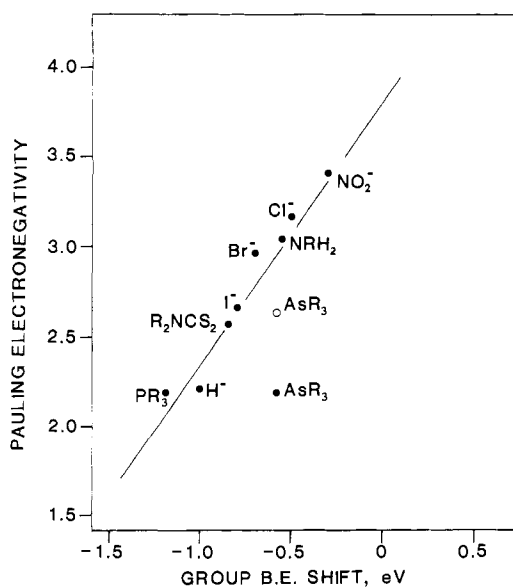


Figure 2. Linear relationship between the ligand group shifts and the corresponding ligand Pauling electronegativities⁴¹ (●). Only the point for AsR₃ deviates markedly from the fit. The point for AsR₃ is closer to the line if its electronegativity is calculated using the Sanderson electronegativity scale⁴¹ (○).

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Table II. Ligand Contributions to Core Binding Energies of Transition Metals

ligand	metal BE shift, eV	ligand	metal BE shift, eV
H ⁺ (3) ^a	-1.0	PR ₃ (46)	-1.2
Cl ⁻ (51)	-0.5	(C ₆ H ₅) ₂ P(CH ₂) ₂ P(C ₆ H ₅) ₂ (16)	-2.3
Br ⁻ (16)	-0.6	o-[As(CH ₃) ₂] ₂ C ₆ H ₄ (36)	-1.2
I ⁻ (8)	-0.8	NH ₂ (CH ₂) ₂ NH ₂ (5)	-1.1
NCS ^{-b} (3)	-0.5	CS (1)	0.2
N ₃ ⁻ (1)	-0.7	N ₂ (5)	0.3
R ₂ NCS ₂ ⁻ (11)	-1.9	CO (23)	0.6
NO ₂ ⁻ (4)	-0.3	ArN ₂ ⁺ (12)	1.6
CH ₃ NC (3)	-0.4	NO ⁺ (37)	1.8
CH ₃ CN (1)	-0.5	±1 (formal oxidation state)	±1.0
HNNPh (3)	-0.6		

^a In each case the number in parentheses is the number of complexes from the present data set in which the ligand is found.

^b Either -N or -S bonded.

relative BEs (BE shifts) are in agreement. The BEs for several compounds and standards have been measured on the HP5950A at Purdue University, the McPherson ESCA36 at the Naval Research Laboratory, and the McPherson ESCA36 at the University of Arizona.²⁸ These results show that the three instruments give the same values of BEs (±0.2 eV) when comparable calibration procedures are used. Consequently, the data reported by Walton and co-workers can be compared directly with the BEs in Table I.

Materials. Most samples were expressly prepared for this study according to literature methods. The materials were identified by elemental analyses (C, H, X, N),²⁹ IR spectroscopy, color, melting point, and where appropriate, by Faraday method magnetic susceptibility measurements.³⁰ Dr. Barry L. Haymore generously provided samples of [Ir(NHNPh)(CO)Cl₂(PPh₃)₂][PF₆], Ir(NHNPh)Cl₃(PPh₃)₂, and [Ir(N₂Ph)Cl(PPh₃)₂][PF₆], while Ir(CO)Cl(PPh₃)₂ was purchased from Strem Chemical. References to synthesis and characterization of the complexes are given in Table I.

Results and Discussion

The relationships among formal oxidation state, ligand effects, and the chemical shifts of core BEs of transition metals have been investigated by several authors.^{1,21,23,31-38} These studies have shown that the metal BEs generally increase with the oxidation state of the metal and with the electron-withdrawing power of the ligand. For example, Cook et al.³¹ demonstrated that the Pt 4f_{7/2} BE increases with L in the order PPh₃ < PhC₂Ph ~ C₂H₄ < CS₂ < TCNE < O₂ < Cl₂ for Pt(PPh₃)₂L. With these results in mind, we wished to assess the relative electron-withdrawing power of the important π-acceptor ligands: CO, NO⁺, (N₂R)⁺, CS, and N₂. Our initial efforts^{1,23,25} and the work of others^{34,38} demonstrated that the assessment of the relationship between metal BEs and the electron-withdrawing power of these ligands was often complicated by changes in the other ligands attached to the metal and by changes in molecular charge. Nonetheless, some trends in the relative electron-withdrawing ability of some of these ligands were discernable from measurements of metal BEs of isostructural and isoelectronic complexes^{1,25} (Table I: 2, 4, 10; 16, 17, 18; 64, 65, 66; 69, 70; 71, 72, 73; 78, 79; 85, 86, for example). However, isostructural and isoelectronic complexes are not always available for these diverse ligands, and some of the BE differences are only marginally larger than the errors of individual experiments. Consequently, additional methods for assessing these BE shifts were needed. Our initial results and those of others³¹⁻³⁹ suggested

(28) Metal and ligand core binding energies for the following complexes have been reproduced within experimental error (±0.2 eV) on two or all of the spectrometers: MoCl₂(dppf)₂, [MoOCl(das)₂][PF₆], Ru(NO)Cl₃(PEt₂Ph)₂, [Pd(CNCH₃)₄][PF₆]₂, W(N₂)₂(dppf)₂, ReOCl₃(PPh₃)₂, and [Pt(CNCH₃)₄][PF₆]₂.

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Table III. Standard XPS Core Binding Energies for "Bare" Metal(0) Species in the Solid State

metal	core level	derived BE, eV ("bare" metal)	obsd BE, eV (pure bulk metal)	difference, eV (derived - obsd)
Fe	2p _{3/2}	709.7	706.7 ^a	3.0
Co	2p _{3/2}	781.4	778.0 ^a	3.4
Ni	2p _{3/2}	855.4	852.4 ^a	3.0
Cu	2p _{3/2}	935.6	932.2 ^b	3.4
Mo	3d _{5/2}	231.9	227.7 ^c	4.2
Ru	3d _{5/2}	282.4	279.9 ^b	2.5
Rh	3d _{5/2}	310.6	307.0 ^c	3.6
Pd	3d _{5/2}	339.0	335.1 ^b	3.9
W	4f _{7/2}	34.6	31.2 ^e	3.4
Re	4f _{7/2}	44.1	40.1 ^d	4.0
Os	4f _{7/2}	53.9	50.6 ^d	3.3
Ir	4f _{7/2}	63.8	60.6 ^d	3.2
Pt	4f _{7/2}	74.5	71.1 ^b	3.4

^a Ewing, C. T.; Brant, P., unpublished results. ^b Johansson, G.; Hedman, J.; Berndtsson, A.; Klasson, M.; Nilsson, R. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 295. ^c "PHI Handbook of X-ray Photoelectron Spectroscopy", Muilenberg, G. E., Ed.; Perkin-Elmer Corp., Physical Electronics Division: Eden Prairie, MN, 1979. ^d Folkesson, B. *Acta Chem. Scand.* **1973**, *27*, 287. ^e Colton, R. J.; Rabalais, W. *Inorg. Chem.* **1976**, *15*, 236.

Table IV. Statistical Analysis of the Agreement between Calculated and Measured Metal Core Level Binding Energies

	% of BE(calcd) - BE(exptl) within 2σ (±0.4 eV)
all complexes (109) ^a	72
complexes with no π-acceptor ligands (36)	93
complexes with one π-acceptor ligand (46)	72
complexes with two or more π-acceptor ligands (27)	60
charged complexes (45)	75
uncharged complexes (64)	68

^a Values in parentheses are the number of complexes in each category.

that a single set of empirical values for group shifts of the common σ-donor ligands could be derived. For example, a one-electron oxidation of a metal complex has often been observed^{1,24,25,36,38} to result in a metal BE shift of approximately 1 eV, irrespective of the particular metal involved, and plots of ΔBEM vs. ΔBEM', for isoelectronic, isostructural complexes of different transition metals, yield lines with a slope of unity.⁴⁰ The metal BEs of several pairs of complexes of the type [MX₂L₂]^{0,+} (X = Cl, CO; L = o-phenylenebis(dimethylarsine) or 1,2-bis(diphenylphosphino)ethane) were obtained. The observed metal binding energy increased by 1.0, 1.3, and 1.0 eV respectively for M = Fe, Ru, and Mo. Since the cationic charge has no discernable effect

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on the ligand or metal BEs (vide infra), a BE shift of 1.0 eV was assigned to a unit increase in the formal oxidation state of the metal (Table II).

Approximate values for ligand group shifts were obtained from several sets of compounds in which the oxidation state of the central metal is constant, but the coordination sphere differs by one ligand (5, 6, 9; 29, 30, 31; and 41, 42, 43, for example). These complexes provided the initial, approximate values for the group shifts of the ligands. With use of these values for the ligand group shifts and metal oxidation state shift, values for the uncharged, unligated "bare" metal atom were then obtained.

Application of iterative techniques to the entire data base resulted in the final group shift and oxidation state parameters (Table II), and the "bare" metal(0) BEs (Table III). By using Tables II and III the metal BE in any complex in Table I can be calculated from eq 1, where the first term is the summation

$$MBE(\text{eV}) = \sum_{\text{ligand}} \Delta M + N + M'(0) \quad (1)$$

over all ligand group shifts, N is the metal oxidation state, and $M'(0)$ is the "bare" metal BE. In contrast with the nontransferability of group shifts for main group elements, the single set of ligand group shifts reproduces the experimental BEs for the transition-metal complexes reported in Table I.

The differences between BE(calcd) and BE(obsd) for several classes of complexes have been examined statistically (Table IV). The agreement between calculated and observed BEs for complexes containing only σ -donor ligands is within 2σ (± 0.4 eV) for 93% of the compounds in the Table I, which is nearly that expected on a purely random basis (98%). Comparison of the calculated and observed metal BEs for complexes in which only a single π -acceptor ligand is attached to the metal shows a statistically poorer agreement (72%). However, careful examination of the errors reveals no systematic trends (i.e., no correlation with metal, oxidation state, ν_{XY} , etc.). Moreover, BE(calcd) - BE(obsd) differs by more than 3σ for only three of these compounds (38, 67, 88). The fact that the sample is small (47 compounds) and the compounds are generally reactive may well account for the enhanced discrepancy factor ($\sigma' = 0.26$ eV) for these compounds with one π -acceptor ligand. Significant differences between BE(calcd) and BE(obsd) are encountered for complexes when more than one π -acceptor ligand is attached to the central metal atom. Not only do nearly half of the calculated BEs differ from the observed BEs by more than 3σ , but the average difference is large ($\sigma'' = 0.63$ eV). In an attempt to improve the agreement between BE(calcd) and BE(obsd), average values for the group shifts were obtained for $L_nM(XY)_2$ complexes (0.4 for CO; 1.2 for NO^+ , and 0.2 for N_2). However, calculations of metal BEs using these lower values of group shifts do not improve the statistical fit of the data.

Collectively, the agreement between calculated and observed metal BEs is rather poor for the molybdenum compounds. The origin of these discrepancies is unknown. However, it should be noted that as a group, these molybdenum complexes are very reactive and easily oxidized, and several of the ligands are easily lost from the coordination sphere. Yet, no direct evidence for decomposition of these compounds during data collection could be found, and therefore they have been included in Table I.

The empirically derived values for the ligand group shifts in Table II fall into two categories: negative values for σ -donor ligands, and positive shifts for π -acceptor ligands. Except for three compounds ($\text{Co}(\text{dmdtc})_3$, $\text{PdCl}_2(\text{PPh}_3)_2$, and $\text{IrCl}_3(\text{PMe}_2\text{Ph})_3$) the group shifts of σ -donor ligands reproduce the observed metal BEs within the errors of the experiment. The agreement between calculated and observed metal BEs is independent of the central metal, its oxidation state, and the molecular charge. The lack of dependence of ligand group shift on the central atom is in direct contrast with results of studies of BEs of main-group elements. Although studies of the main-group elements C, N, P, As, Si, and Te have demonstrated that BEs of the central atom can be faithfully reproduced using empirically derived values for ligand group shifts, both the magnitudes and signs of these shifts vary with the central atom. Thus, the group shift for H attached to

N is -0.34 eV, but when attached to P it is $+0.47$ eV!

The derived group shifts for the σ -donor ligands in Table II have been examined to determine their possible relationship with other ligand properties such as ligand-field strength, covalent/ionic radii, and electronegativity. Of these factors only electronegativity correlates well with the derived group shifts (Figure 1). The group shifts found for main-group elements were also found to correlate with ligand electronegativity. The source of the variation in group shift with the central atom for N, P, and As was ascribed by Lindberg and Hedman¹³ to the differing electronegativities of these central atoms. The transferability of ligand group shifts among the transition metals comprising the present study is consistent with their explanation of variable values for group shifts of the main-group elements. In contrast with the large variation in the electronegativity of N, P, and As (3.0, 2.1, and 2.0, respectively), the transition metals represented in Table I have a narrow range of electronegativities (1.9–2.2).⁴¹ These electronegativity values are also presumed to have small increases with increasing oxidation state of the central metal.⁴¹ If the ligand group shifts are dependent on the electronegativity of the central transition metal, the present empirical fit of the data might be improved by including an appropriate term to reflect the electronegativity of the metal. However in view of the limited number of data presently available and the rather large experimental uncertainties in the observed BEs, inclusion of effects of changes in electronegativity of the central metal atom was not believed to be warranted at the present time. The possible dependence of ligand group shift on electronegativity of the central metal also suggests that the values in Table II may not accurately reproduce metal BEs for the early transition metals which have significantly lower electronegativities (1.3–1.6).

In order to calculate the BE of a particular complex using the ligand-group shifts in Table II, a reference BE was needed for each metal. Initially, values for each metal in its zero oxidation state with no attached ligands were chosen as a matter of convenience.⁴² Once these reference BEs were obtained, it was noted that they have values 2.5–4.2 eV greater than those of the bulk metal (Table III). If the values for the group shifts accurately account for effects of ligand and oxidation state, then the reference BEs correspond to an unligated, uncharged, low-spin, metal atom imbedded in an inert nonconducting host matrix. The core BE for such a metal atom would be expected to be higher than the core BE obtained from measurements on the bulk metal due to additional relaxation effects in the metallic state which have been estimated to be 2.9–3.5 eV.⁴³

The group shifts obtained for the π -acceptor ligands are positive and range from $+0.2$ eV for CS to 1.8 eV for NO^+ in the order: $\text{CS} < \text{N}_2 < \text{CO} < \text{RN}_2^+ < \text{NO}^+$. This ordering corresponds to that found using other techniques such as IR spectroscopy and Mössbauer spectroscopy.^{44–46} The presence of π -acceptor ligands in the complex generally leads to poorer agreement between BE(obsd) and BE(calcd) (Table IV). At present, the origin of this larger discrepancy is unknown.

The data for complexes with π -acceptor ligands suggest that the group shift decreases when more than one π -acceptor ligand is present,⁴⁷ and decreases with increasing oxidation state of the central metal.⁴⁸ These apparent trends are intriguing since they

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(42) Once the shift per unit oxidation state (1 eV) and ligand group shifts in Table II are in hand, then the reference BE of the "bare" metal atom can be calculated. Adjustment of this reference BE to achieve a "best fit" of the entire set of data for the metal can then be made.

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(47) Average values of group shifts in complexes with (a) one π -acceptor ligand (CO, 0.8; NO^+ , 1.8; N_2 , 0.4 eV), (b) two π -acceptor ligands (CO, 0.4; NO^+ , 1.2; N_2 , 0.2 eV), and (c) three π -acceptor ligands (CO, 0.4 eV).

are consistent with the accepted π -bonding model for M–XY complexes, and with IR spectra of polysubstituted metal carbonyls.⁴⁹ However, we must re-emphasize that these trends are only apparent and are not statistically significant within the context of the present experimental errors. Moreover, including separate values for group shifts for mono-, di-, and triligated complexes does not improve the agreement between BE(calcd) and BE(obsd). Consequently, a more detailed assessment of the effects of π -acceptor ligands on metal BEs must await larger numbers of more accurate BE data.

Conclusions

It has been shown that a single set of group shifts for common σ -donor ligands can be derived which will reproduce the metal binding energies of iron, cobalt, nickel, copper, molybdenum, ruthenium, rhodium, palladium, tungsten, rhenium, osmium, iridium, and platinum complexes. These empirically derived values of the group shifts have a linear correlation with ligand electro-negativity. The BEs of complexes of these metals with π -acceptor ligands can also be fit albeit with somewhat less accuracy to the group shift model. The σ -donor ligands have negative values of group shifts, while the π -acceptor ligands have positive values of group shifts and fall in the order: $\text{CS} < \text{N}_2 < \text{CO} < \text{RN}_2^+ < \text{NO}^+$. The reference state for each of the metals is taken as the "bare" unligated low-spin metal(0) atom and has values which are 2.5–4.2 eV greater than those of the bulk metal. Furthermore, from the reproducibility of metal BEs using single-valued ligand-group shift and bare metal(0) BEs, it is concluded that relaxation effects^{52–54} in this series of complexes are largely constant.

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Registry No. $\text{FeCl}_2(\text{das})_2$, 14127-26-5; $[\text{Fe}(\text{CH}_3\text{CN})\text{Cl}(\text{das})_2][\text{BPh}_4]$, 53966-14-6; $[\text{FeCl}_2(\text{das})_2][\text{BF}_4]$, 37817-55-3; $[\text{Fe}(\text{CO})\text{Cl}(\text{das})_2][\text{BPh}_4]$,

(48) Values of NO^+ group shift vs. metal oxidation state: M(-), 2.7; M(0), 2.4; M(+), 1.7; M(2+), 1.8 eV.

(49) In the series of isostructural and isoelectronic metal carbonyls $\text{Ni}(\text{C}^-\text{O})_4$, $\text{Co}(\text{CO})_4^-$, and $\text{Fe}(\text{CO})_4^{2-}$, ν_{CO} decreases with decreasing formal oxidation state of the metal.⁵⁰ This phenomenon is usually taken to indicate increased donation from the metal into the antibonding orbitals of the CO ligands. For the series of complexes $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{CO})_3\text{L}$, $\text{Ni}(\text{CO})_2\text{L}_2$, and $\text{Ni}(\text{CO})\text{L}_3$, ν_{CO} decreases with increasing substitution⁵¹ which is taken to indicate that the nickel atom will donate a given total amount of electron density to the CO ligands which results in increasing electron density on individual CO ligands as their numbers decrease.

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$\text{Fe}(\text{NO})(\text{SCN})(\text{dmdtc})_2$, 62637-75-6; $\text{Fe}(\text{CO})_2(\text{dedtc})_2$, 36309-90-7; $[\text{Fe}(\text{NO})(\text{CNCH}_3)(\text{dedtc})_2][\text{BF}_4]$, 80010-18-0; $[\text{CoCl}_2(\text{das})_2][\text{ClO}_4]$, 17083-97-5; $[\text{Co}(\text{N}_3)_2(\text{das})_2][\text{ClO}_4]$, 37386-58-6; $[\text{Co}(\text{NO})_2\text{Br}(\text{das})_2][\text{Br}]$, 73891-35-7; $[\text{Co}(\text{H})_2(\text{das})_2][\text{ClO}_4]$, 54548-84-4; $[\text{Co}(\text{NO})\text{Cl}(\text{das})_2][\text{ClO}_4]_2$, 67684-44-0; $\text{CoBr}_2(\text{das})_2$, 60536-79-0; $[\text{Co}(\text{NO})(\text{das})_2][\text{ClO}_4]_2$, 53495-87-7; $[\text{Co}(\text{NO})\text{Cl}(\text{das})_2][\text{ClO}_4]$, 67684-46-2; $[\text{Co}(\text{NO})\text{Br}(\text{das})_2][\text{ClO}_4]$, 66777-80-8; $[\text{CoCl}_2(\text{en})_2][\text{Cl}]$, 13408-72-5; $[\text{Co}(\text{NO})(\text{en})_2\text{ClO}_4][\text{ClO}_4]$, 39721-22-7; $[\text{Co}(\text{NO})\text{Br}(\text{en})_2][\text{ClO}_4]$, 14637-97-9; $\text{Co}(\text{NO})(\text{dmdtc})_2$, 36434-42-1; $\text{Co}(\text{NO})(\text{dedtc})_2$, 80010-19-1; $\text{Co}(\text{dmdtc})_3$, 23677-76-1; $\text{Co}(\text{NO})(\text{PPh}_3)_3$, 18712-92-0; $[\text{Co}(\text{NO})_2(\text{dppe})][\text{BPh}_4]$, 24533-59-3; $\text{Co}(\text{NO})\text{Cl}_2(\text{PMe}_2\text{Ph})_2$, 38402-83-4; $[\text{Ni}(\text{das})_2][\text{ClO}_4]_2$, 80010-20-4; $[\text{Ni}(\text{NO})_2(\text{das})_2][\text{ClO}_4]$, 80010-22-6; $[\text{NiCl}(\text{das})_2][\text{ClO}_4]$, 31363-31-2; $\text{NiCl}_2(\text{dppe})$, 38754-20-0; $\text{NiBr}_2(\text{dppe})$, 14647-21-3; $\text{NiI}_2(\text{dppe})$, 47671-01-2; $\text{Ni}(\text{N}_2\text{CH}_3)_2(\text{dppe})$, 71604-08-5; $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$, 13007-90-4; $\text{Ni}(\text{CO})_2(\text{dppe})$, 15793-01-8; $\text{Ni}(\text{NO})\text{Cl}(\text{PPh}_3)_2$, 18898-45-8; $\text{CuCl}(\text{PPh}_3)_3$, 15709-76-9; $\text{Cu}(\text{BH}_4)(\text{PPh}_3)_2$, 16903-61-0; $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$, 25145-64-6; $\text{Mo}(\text{N}_2)\text{Cl}(\text{dppe})_2$, 32073-70-4; $\text{Mo}(\text{N}_2)\text{Br}(\text{dppe})_2$, 56398-30-2; $\text{Mo}(\text{N}_2\text{CH}_3)_2(\text{dppe})_2$, 56398-29-9; $\text{MoCl}_2(\text{dppe})_2$, 31096-73-8; $[\text{Mo}(\text{CO})_2(\text{dppe})_2][\text{ClO}_4]$, 31453-78-8; $[\text{MoOCl}(\text{das})_2][\text{PF}_6]$, 63984-95-2; $[\text{MoOCl}(\text{dppe})_2][\text{PF}_6]$, 80010-23-7; $\text{Mo}(\text{NO})_2(\text{das})_2$, 36236-94-9; $\text{Mo}(\text{NO})(\text{dedtc})_3$, 20960-03-6; $\text{Mo}(\text{NO})_2(\text{dedtc})_2$, 39797-80-3; $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, 14741-36-7; $[\text{Ru}(\text{NO})(\text{CO})_2(\text{PPh}_3)_2][\text{PF}_6]$, 40464-69-5; $[\text{Ru}(\text{N}_2\text{-p-C}_6\text{H}_4\text{F})(\text{CO})_2(\text{PPh}_3)_2][\text{BF}_4]$, 54733-53-8; $\text{Ru}(\text{NO})\text{Cl}_3(\text{PET}_3\text{Ph})_2$, 15389-58-9; $\text{Ru}(\text{N}_2\text{-p-C}_6\text{H}_4\text{CH}_3)\text{Cl}_3(\text{PPh}_3)_2$, 34110-14-0; $\text{RuCl}_2(\text{das})_2$, 14170-32-2; 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$[\text{W}(\text{CO})_2(\text{dppe})_2][\text{PF}_6]$, 80010-25-9; $[\text{W}(\text{NN}(\text{CH}_2)_2\text{Ph})\text{Br}(\text{dppe})_2]$, 80028-16-6; $[\text{W}(\text{CO})_2\text{Br}(\text{dppe})_2]\text{Br}$, 80010-26-0; $[\text{W}(\text{CO})_2\text{Br}_2(\text{PPh}_3)_2]$, 18973-51-8; $[\text{W}(\text{CO})_3\text{Br}_2(\text{PPh}_3)_2]$, 18130-07-9; $[\text{W}(\text{OBr}_2)(\text{PMe}_2\text{Ph})_3]$, 80010-27-1; $[\text{WBr}_4(\text{PMe}_2\text{Ph})_2]$, 80041-04-9; $[\text{Re}(\text{N}_2\text{C}_6\text{H}_5)_2\text{Cl}_2(\text{PMe}_2\text{Ph})_2(\text{NH}_3)]$, 80041-05-0; $[\text{ReCl}_3(\text{PMe}_2\text{Ph})_3]$, 15613-32-8; $[\text{ReOCl}_3(\text{PPh}_3)_2]$, 17442-18-1; $[\text{Os}(\text{NO})\text{Br}_3(\text{PPh}_3)_2]$, 29292-11-3; $[\text{Os}(\text{N}_2\text{-p-C}_6\text{H}_4\text{F})\text{Br}_3(\text{PPh}_3)_2]$, 62287-71-2; $[\text{OsBr}_2(\text{PPh}_3)_3]$, 36543-21-2; $[\text{OsH}(\text{CO})\text{Br}(\text{PPh}_3)_3]$, 16971-32-7; $[\text{Os}(\text{CO})_2\text{Br}_2(\text{PPh}_3)_2]$, 17456-72-3; 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Supplementary Material Available: Table I contains the metal, nitrogen, and ligand binding energies reported in ref 1, along with references to their preparation (14 pages). Ordering information is given on any current masthead page.