A third source of evidence for π bonding comes from the bond length and vibrational frequency changes in the doublet states. The differences between these doublet states are caused by a redistribution of electron density among the (xy), (xz), and (yz) orbitals which are σ nonbonding. The change in Cr–F stretching frequency between the $^4B_{1g}$ and a^2E_g states reflects the strong π antibonding effect of the fluoride ligands. There is a *ca.* 13% change in the Cr–F force constant and a *ca.* 5% change in the Cr–F bond length. The force constant is therefore a less strong function of bond length than in NO.[20] This presumably reflects the ionic nature of the Cr–F bond. There is no significant change in the Cr–N distance or force constant between the a^2E_g and $^4B_{1g}$ states in the pyridine compound although there is a change in bond length in *trans*-Cr(en)$_2$F$_2$+. The ϵ_u(Cr–N) stretching frequency is significantly greater in the a^2E_g state than in the $^4B_{1g}$ state. There must be a mechanism which increases the Cr–N bond strength as the electron density in the (xy) orbital is increased in *trans*-Cr(py)$_4$F$_2$+ but which is inoperative in the ethylenediamine compound. This mechanism is the delocalization of the xy electron density into the pyridine rings. An analogous effect has been observed in the vibrational spectra of a series of hexacyanide complexes.

Registry No. *trans*-[Cr(py)$_4$F$_2$]NO$_3$, 27731-44-8.

References and Notes

(1) To whom correspondence should be addressed.
(2) C. D. Flint, *Chem. Phys. Lett.*, **11**, 27 (1971).
(3) J. Ferguson, H. J. Guggenheim, and D. L. Wood, *J. Chem. Phys.*, **54**, 504 (1971).
(4) C. D. Flint and P. Greenough, *J. Chem. Soc., Faraday Trans. 2*, **70**, 815 (1974).
(5) Symmetry labels are those appropriate in D_{4h} symmetry except where otherwise is indicated or obvious from context.
(6) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1307 (1974).
(7) We use the sign convention of Liehr: J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967). Other workers have used the sign convention of Ballhausen: *e.g.*, Gerlock and Slade, "Ligand-Field Parameters," Cambridge University Press, Cambridge, U.K., 1973.
(8) This argument is not restricted to D_{4h} compounds but is true for any chromophore with a holohedrized symmetry of D_{4h}.
(9) D. S. McClure in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York N.Y., 1961.
(10) J. Glerup, J. Josephsen, K. Mickelsen, E. Pedersen, and C. E. Schaffer, *Acta Chem. Scand.*, **24**, 247 (1970).
(11) C. D. Flint, *J. Sci. Instrum.*, **4**, 1064 (1971).
(12) L. Dubicki, M. Hitchman, and P. Day, *Inorg. Chem.*, **9**, 188 (1970).
(13) E. Pedersen and H. Toftlund, *Inorg. Chem.*, **13**, 1603 (1974).
(14) S. S. Mitra in "Optical Properties of Solids," S. S. Mitra and S. Nudelman, Ed., Plenum Press, New York, N.Y., 1969, Chapter 14.
(15) C. J. Ballhausen in "Spectroscopy in Inorganic Chemistry," Vol. 1, C. N. R. Rao and J. R. Ferraro, Ed., Academic Press, New York, N.Y., 1970. The Duschinsky effect (C. J. Ballhausen and Aa. E. Hansen, *Annu. Rev. Phys. Chem.*, **23**, 15 (1972)) has been neglected.
(16) R. Dingle, *Acta Chem. Scand.*, **22**, 219 (1968).
(17) O. S. Mortensen, *J. Chem. Phys.*, **47**, 4215 (1967).
(18) M. D. Sturge, H. J. Guggenheim, and M. H. L. Pryce, *Phys. Rev. B*, **2**, 2459 (1970).
(19) J. A. Ladd and W. J. Orville-Thomas, *Spectrochim. Acta*, **22**, 919 (1966).

X-Ray Photoelectron Spectroscopy of Inorganic and Organometallic Compounds of Molybdenum[1]

SAMUEL O. GRIM* and LUIS J. MATIENZO

X-Ray photoelectron spectra (XPS) of the Mo(3d$_{3/2}$) and Mo(3d$_{5/2}$) levels for about 50 compounds containing molybdenum in various oxidation states have been studied. A plot of metal binding energy *vs.* calculated charge indicates that a binding energy shift of 1 eV corresponds to a 0.3+ charge unit on molybdenum. The study of several organometallic compounds shows that strong σ-donor ligands increase the electronic density about the metal producing even lower metal binding energies than those obtained for argon-sputtered metal foil. The P(2p) binding energies of coordinated and uncoordinated phosphorus ligands are more or less constant.

Introduction

To date, only scattered X-ray photoelectron spectroscopy (XPS) data have been available on the molybdenum system.[2] Three reports in the literature have treated this problem very briefly. Swartz and Hercules[2b] have examined some fairly common molybdenum compounds (mainly molybdates) and have pointed out the application of XPS as an analytical technique for the determination of MoO$_2$–MoO$_3$ mixtures. Miller, *et al.*,[3] have used XPS to study MoO$_3$ catalysts supported on alumina and have been able to detect interactions between the catalyst and the support upon calcination. Clark, *et al.*,[4] have obtained data for some complexes of the type η^5-C$_5$H$_5$Mo(CO)$_2$NCR$_2$ and η^5-C$_5$H$_5$Mo(CO)$_2$R$_2$CNCR$_2$ and used them in conjunction with other spectroscopic data to discuss structure and bonding in these complexes. No systematic study on organometallic compounds of molybdenum, however, has yet been reported.[5] Results of investigations by Tolman, *et al.*,[6] on organometallic compounds of nickel indicate that possible oxidation or decomposition and difficulties with energy calibration demand careful interpretation of data obtained on very air-sensitive samples. A few other studies have obtained information on organometallic compounds of similar composition. Clark and Adams[7] have reported the study of chromium, iron, and nickel carbonyls and their π-cyclopentadienyls. Bis- and mono(arene)chromium carbonyls have been described recently,[8] and a short study on the charge localization of ionic derivatives of alkylferrocenes is also available.[9]

Results obtained from about 50 inorganic and organometallic compounds are presented. This study attempts to show the applicability of XPS to inorganic and organometallic compounds of molybdenum, particularly those containing phosphorus ligands, by combining newly obtained data with information provided by previous studies.

Experimental Section

The compounds used in this study were prepared, purified, and characterized according to published methods.[10-30] Air-sensitive compounds were handled under nitrogen and stored in Schlenk tubes. The compounds for which no preparative methods are given were reagent grade chemicals, used without further purification. The spectra were obtained from powdered samples mounted on cellophane tape using a Varian Associates IEE-15 electron spectrometer. The binding energy of molybdenum metal was obtained by argon sputtering

Table I. Binding Energies of Some Simple
Molybdenum Compounds[a]

Compd[b]	No.	Mo-$(3d_{5/2})$	Fwhm[c]	Calcd charge $(q)^d$
Mo[e]	1	227.0	1.6	0.00
$MoCl_3$	2	229.0	2.4	0.21
$MoCl_4$	3	229.6	2.4	0.76
$MoCl_5$	4	230.0	2.4	0.90
MoO_2	5	231.0	2.3	1.20
MoS_2	6	228.1	1.6	0.12
$MoSe_2$	7	227.3	1.6	~0
$MoO_2(acac)_2$	8	231.0	2.3	~1.20
MoO_3	9	231.7	2.3	1.56
$Na_2MoO_4 \cdot 2H_2O$	10	231.5	1.8	1.53
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	11	231.7	2.0	1.54

[a] Binding energies are relative to $Au(4f_{7/2})$ (BE = 83.0 eV).
[b] Commercially available materials. [c] Full width at half-maximum. [d] According to Pauling's method using electronegativity values from J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N.Y., 1972. [e] Sputtered foil under argon.

of metal foil directly in contact with the probe. The Mg $K\alpha$ X-ray line (1253.6 eV) was used for photoelectron excitation. In order to compensate for the charging of insulating samples during the photoelectron ejection process, all the spectra were referenced to the photoelectron line of $Au(4f_{7/2})$, E_b = 83.0 eV.[31] The region of interest was scanned before and after depositing gold to make sure no extraneous peaks had originated by this method of standardization. Au spectra were recorded at least in duplicate in the regions of interest and, in most cases, gave binding energies reproducible to ±0.2 eV. The reported binding energies were taken at a position corresponding to the midway point of the full peak at half-height.

Special mention is made to the fact that free phosphines are sensitive to normal depositions of gold vapor during calibration. Surface reactions of free phosphines have been observed recently when this method of standardization is employed.[32] The phosphorus P(2p) binding energies referenced to that for gold $Au(4f_{7/2})$ (83.0 eV) reported here were taken with extremely small depositions of the calibrant. As a matter of comparison, the P(2p) binding energies of these free ligands are referenced to the C(1s) signal originating mostly from the aromatic carbons and it was assigned a binding energy of 285.0 eV.

Results and Discussion

In the present investigation, the spectra covered the energy region containing the $Mo(3d_{5/2})$ and $Mo(3d_{3/2})$ levels. In some cases, the binding energies of some of the atoms of the coordinating ligands were also measured. For ligands containing nitrogen, the binding energies reported correspond to the N(1s) level; for those containing phosphorus, the energies correspond to the P(2p) level; for those containing tin, the energies correspond to the $Sn(3d_{5/2})$ level. The results obtained in this investigation are presented in tables in which the method of synthesis used to obtain a particular compound is also given.

Several simple compounds containing molybdenum in known oxidation states have been studied, and their $Mo(3d_{5/2})$ binding energies measured. As expected, an increase in oxidation state provides an increase in metal binding energy. In order to obtain an approximate variation of charge density with binding energy, simple compounds were chosen to establish this ratio. The method employed was based on an approximate calculation of charge using Pauling's method.[33] Since the oxidation state of molybdenum varies among the compounds under consideration, electronegativity values on Pauling's scale for individual oxidation states[34a] were used instead of the original Pauling value (χ_{Mo} = 1.8).[34b] Since the electronegativity of the acetylacetonato group (acac) is not known, an indirect method was used for its evaluation. Larsson, *et al.*,[35] have recently estimated the charge on $V(acac)_3$ from XPS studies. By using their results, the electronegativity of the acetylacetonato group is calculated as $\chi_{acac} \approx 2.4$.
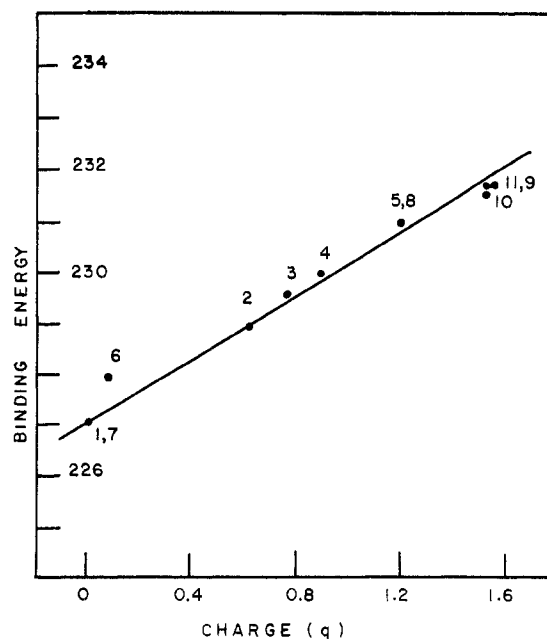

Figure 1. Plot of $Mo(3d_{5/2})$ binding energy (in eV) *vs.* calculated charge. Data points shown are those given in Table I.

Table I summarizes the data obtained for simple compounds of molybdenum, as well as the calculated charges. If these results are plotted (Figure 1), a fairly linear correlation is obtained. The slope of this curve indicates that a binding energy shift of 1 eV produces a variation of charge of roughly 0.3 unit.[36] Since the electronegativities of the ligands may not be the same in all of the compounds and since the correlations due to Madelung potentials are not known, this is only an approximate method of calculation. Studies on chromium[37] and tungsten[38] compounds indicate similar changes in binding energy with charge.

The variation of binding energy with a constancy of oxidation state is observed in the series of molybdenum(IV) compounds—*i.e.*, oxide, sulfide, and selenide. This is just a reflection of the change of ionic character of the metal–ligand bond expected on the basis of electronegativity changes.

$MoO_2(acac)_2$, according to usual assignments, contains molybdenum in the oxidation state of +VI. However, on the basis of studies on correlations between oxidation state and binding energy, it was suggested[2b] that the metal exists in this compound in the +IV oxidation state and that the complex contains two neutral acetylacetone molecules coordinated to the metal. These results may be interpreted in a different manner. The substitution of one oxygen atom in MoO_3 by two acetylacetonato ligands will produce an appreciable decrease of charge around molybdenum since the electronegativity of the acetylacetonato group is considerably less than that of oxygen, roughly 2.4 compared to 3.44. Because the charge on Mo in $MoO_2(acac)_2$ is comparable to that in MoO_2, binding energies of these two compounds are expected to be the same although their metal atoms exist in different oxidation states.

The $Mo(3d_{5/2})$ binding energy for molybdenum metal was measured on a sample made of commercially available metal foil. Figure 2, spectrum A, shows the type of signals obtained for this sample when directly placed on the probe. As it may be noticed, an $Mo(3d_{5/2})$ binding energy of about 231 eV is obtained for this signal after corrections for charging effects are applied. Argon sputtering,[39] a fairly reliable technique for cleaning metallic surfaces and reducing oxides, was used to clean the surface of the foil. Figure 2 also shows the spectra of the metal foil after 15 and 30 min of argon sputtering, B and C, respectively. It has previously been shown that the

Table II. Binding Energies of Organometallic Compounds of Molybdenum[a]

Compd	No.	Mo(3d$_{5/2}$)[b]	P(2p)[c]	N(1s)	Sn(3d$_{5/2}$)	Syn ref
[(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$	12	226.4 (2.2)				10
Mo(η^5-C$_5$H$_5$)(CO)$_3$Cl	13	227.8 (2.1)				11
(CH$_3$)$_3$SnMo(CO)$_3$(η^5-C$_5$H$_5$)	14	227.5 (2.0)			484.3 (2.8)	12
Cl(CH$_3$)$_2$SnMo(CO)$_3$(η^5-C$_5$H$_5$)	15	227.0 (1.9)			484.3 (2.1)	12
Cl$_3$SnMo(CO)$_3$(η^5-C$_5$H$_5$)	16	227.7 (2.0)			485.2 (2.0)	13
(C$_7$H$_8$)Mo(CO)$_3$	17	227.4 (2.2)				14
[(C$_7$H$_7$)Mo(CO)$_3$$^+$][BF$_4$$^-$]	18	228.1 (2.5)				15
(Mes)Mo(CO)$_3$[d]	19	227.0 (2.0)				16
[(o-CH$_3$C$_6$H$_4$)$_3$P]Mo(CO)$_3$	20	226.0 (2.4)	128.9 (3.8)			17
(tmen)Mo(CO)$_4$[e]	21	226.2 (2.2)		398.3 (2.0)		18
(phen)Mo(CO)$_4$[f]	22	226.2 (2.3)		397.8 (2.4)		18
(dipy)Mo(CO)$_4$[g]	23	225.3 (2.1)		397.0 (2.0)		19
(dipy)Mo(CO)$_3$[P(OPh)$_3$]	24	225.2 (2.4)	130.4 (2.5)	397.2 (2.2)		20
(dipy)Mo(CO)$_3$[P(O(n-Bu))$_3$]	25	225.4 (2.2)	130.6 (2.3)	397.5 (2.3)		20
fac-[(PhO)$_3$P]$_3$Mo(CO)$_3$	26	225.8 (2.0)	131.3 (2.6)			21
[Ph$_2$PCH$_2$OPPh$_2$]Mo(CO)$_4$	27	226.3 (1.9)	130.0 (2.5)			22
[Ph$_2$P(CH$_2$)$_2$OPPh$_2$]Mo(CO)$_4$	28	226.4 (1.9)	130.1 (2.6)			22
[Ph$_2$PCH$_2$PPh$_2$]Mo(CO)$_4$	29	226.3 (2.1)	129.5 (2.4)			23
[Ph$_2$P(CH$_2$)$_2$PPh$_2$]Mo(CO)$_4$	30	225.9 (2.2)	129.1 (2.4)			23
[Ph$_2$P(CH$_2$)$_3$PPh$_2$]Mo(CO)$_4$	31	226.6 (1.8)	129.8 (2.3)			18
[Ph$_2$P(CH)$_2$PPh$_2$]Mo(CO)$_4$	32	226.0 (1.7)	129.3 (2.5)			24
[Ph$_2$P(CH$_2$)$_2$PPh$_2$]Mo(CO)$_3$P(O(n-Bu))$_3$	33	226.2 (2.5)	130.2 (3.5)			21
[Ph$_2$P(CH$_2$)$_2$PPh(CH$_3$)]Mo(CO)$_4$	34	226.3 (2.0)	129.6 (2.4)			25
[Ph$_2$P(CH$_2$)$_2$PPh(C$_2$H$_5$)]Mo(CO)$_4$	35	226.2 (1.9)	129.6 (2.2)			25
[Ph$_2$P(CH$_2$)$_2$PPh(i-C$_3$H$_7$)]Mo(CO)$_4$	36	226.5 (2.2)	130.1 (2.4)			25
[Ph$_2$P(S)CH$_2$PPh$_2$]Mo(CO)$_4$	37	225.8 (2.4)	129.9 (3.0)			26
LLMo(CO)$_4$[h]	38	227.0 (2.0)	129.0 (2.4)	397.2 (2.4)		27
trans-[(n-Bu)$_3$P]$_2$Mo(CO)$_4$	39	226.4 (1.8)	129.7 (2.0)			28
cis-(Ph$_2$(n-Bu)P)$_2$Mo(CO)$_4$	40	226.9 (2.0)	129.9 (2.2)			28
trans-(Ph$_2$(n-Bu)P)$_2$Mo(CO)$_4$	41	226.9 (1.8)	130.1 (2.2)			28
[Mo(CO)$_5$]$_2$[Ph$_2$P(CH$_2$)$_2$PPh(CH$_3$)]	42	226.8 (2.2)	129.7 (2.4)			25
[(C$_2$H$_5$)$_4$N$^+$][Mo(CO)$_5$Cl$^-$]	43	226.8 (1.9)				29
[(CH$_3$)$_2$N]$_3$PMo(CO)$_5$	44	226.6 (2.6)				30
[p-ClC$_6$H$_4$]$_3$PMo(CO)$_5$	45	226.5 (2.0)	130.0 (2.2)			30
[p-CH$_3$C$_6$H$_4$]$_3$PMo(CO)$_5$	46	226.9 (2.0)	129.9 (2.3)			30
[m-CH$_3$C$_6$H$_4$]$_3$PMo(CO)$_5$	47	226.9 (2.3)	130.0 (2.3)			30
[m-CF$_3$C$_6$H$_4$]$_3$PMo(CO)$_5$	48	226.2 (2.0)	129.6 (2.2)			30

[a] Binding energies relative to Au(4f$_{7/2}$) (BE = 83.0 eV). [b] Numbers in parentheses indicate the width of the band measured at half-maximum (fwhm). [c] In the case of compounds containing more than one unequivalent phosphorus atom, the center of the P(2p) signal is reported. [d] Mes = 1,3,5-trimethylbenzene. [e] tmen = N,N,N',N'-tetramethylethylenediamine. [f] phen = o-phenanthroline. [g] dipy = α,α'-dipyridyl. [h] LL = N,N'-dimethyl-N,N'-bis(diphenylphosphinomethyl)ethylenediamine.
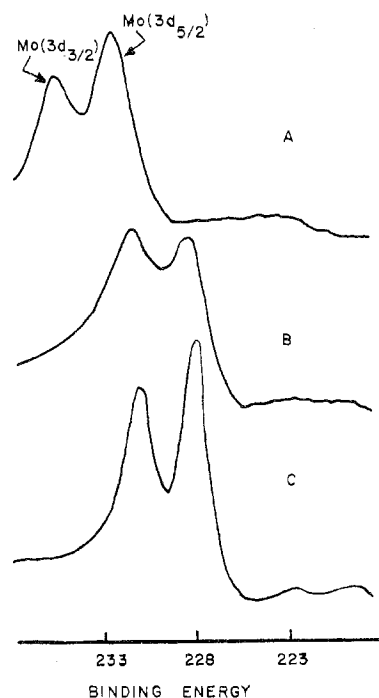

Figure 2. XPS spectra of the Mo(3d$_{5/2}$), Mo(3d$_{3/2}$) doublet of molybdenum foil: (A) before argon sputtering; (B) after 15 min of argon sputtering; (C) after 30 min of argon sputtering. Charging corrections have been omitted in this figure.

existent species on the surface of molybdenum foil is MoO$_2$.[2b] Therefore, as cleaning proceeds, a shift of roughly 4 eV, as well as a sharpening of the peaks is observed for the Mo(3d$_{5/2}$) and Mo(3d$_{3/2}$) signals.

Table II presents the data obtained for 36 organometallic compounds of molybdenum. The reported binding energies are the averages of at least two measurements, and their uncertainties are ± 0.2 eV. The Mo(3d$_{5/2}$) binding energies range from 225.2 to 228.1 eV. As observed before in nickel compounds, for example, if only compounds of the Ni(II) ion are considered, the range of binding energies is about 5.3 eV.[40] This variation has been attributed to interaction of the different ligands with the metal, among other factors. In the present case, the nature of the ligands around the central atom changes, but the geometry of the molecule remains essentially octahedral.

In compounds of (η^5-C$_5$H$_5$)Mo(CO)$_3$X, where X could be, for example, another (η^5-C$_5$H$_5$)Mo(CO$_3$) unit,[41] a halide, or any other group, the electronic density around the molybdenum atom would depend on X. If [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ and (η^5-C$_5$H$_5$)Mo(CO)$_3$Cl (compounds 12 and 13 in Table II) are compared, it is expected and observed that the greater electronegativity of the chlorine removes charge from molybdenum and thus increases its binding energy. In compounds 14–16, X becomes (CH$_3$)$_{3-n}$SnCl$_n$, where $n = 0$, 1, 3. These groups are expected to have lower electronegativities than that of chlorine, thus increasing negative density on the molybdenum atom. The group electronegativities for –SnCl$_3$ and –Sn(CH$_3$)$_3$ are available from calculations made by Huheey.[42]

These are 2.73 and 2.30, respectively. However, the trichlorotin group is also thought to be a good π acceptor[43] (and a weak σ donor), which would simultaneously decrease the electronic charge on molybdenum. Overall, the decrease in binding energy of Mo in η^5-$C_5H_5Mo(CO)_3X$ upon replacing Cl by $SnCl_3$, $(CH_3)_2SnCl$, or $(CH_3)_3Sn$ is not large. The Mo and Sn binding energies are both largest in the $SnCl_3$ compound as expected.

(Cycloheptatriene)tricarbonylmolybdenum, **17**, is known to form the tropyllium ion when treated with trityl fluoroborate.[15] The XPS results obtained for these compounds show a net increase of about 0.7 eV when this process takes place. From the results obtained for simple molybdenum compounds, it has been roughly established that a binding energy shift of 1 eV corresponds to about 0.3+ unit of charge on molybdenum. For compound **18**, $[(C_7H_7)Mo(CO)_3^+][BF_4^-]$, the estimated percentage of the positive charge residing on the molybdenum atom is about 28% which suggests that, in this particular case, the cycloheptatrienyl ring still preserves a large portion of the positive charge. The drift of electronic density toward the metal atom by substitution of three carbonyl groups from $Mo(CO)_6$ by an arene molecule is observed in the case of compound **19** which contains a mesitylene ring π bonded to the metal. Pignataro, Foffani, and Distefano[44] have reported some XPS data for organometallic compounds of chromium. In this case, the replacement of three carbonyl groups from $Cr(CO)_6$ by benzene to form $(C_6H_6)Cr(CO)_6$ produces a decrease of about 0.6 eV in the binding energy of the metal atom.

During the present studies, the volatility of $Mo(CO)_6$ has discouraged measurement of its binding energy, but available data show that the free metal has a lower binding energy than the hexacarbonyl by about 0.5 eV.[2b]

Compound **20**, $[(o-CH_3C_6H_4)_3P]Mo(CO)_3$, very unusual in structure, is believed to contain one of the rings of tris-(o-tolylphosphine) acting as a π-bonded ring.[17] XPS data show no conclusive evidence about the nature of the phosphorus atom since the compound has a P(2p) binding energy of 128.0 eV, lower than that found in the uncoordinated ligand (129.6 eV). The breadth of the P(2p) signal for compound **20** furthermore indicates possible decomposition.

The remainder of the compounds (**21–48**) in Table II, with the exception of $[Et_4N][Mo(CO)_5Cl]$, **43**, are zerovalent molybdenum carbonyl derivatives of the type $LMo(CO)_5$, $L_2Mo(CO)_4$, and $L_3Mo(CO)_3$. Although there is a scatter of $Mo(3d_{5/2})$ binding energies among these compounds, several trends are observable. First, as L (L = phosphorus or nitrogen donor) is substituted for CO, the average binding energy of the group of compounds decreases in the series $LMo(CO)_5$ (226.7 eV for six compounds), $L_2Mo(CO)_4$ (226.3 eV for seventeen compounds), and $L_3Mo(CO)_3$ (225.7 eV for four compounds). This indicates a higher electron density on Mo with increasing substitution for CO by better σ donors and poorer π acceptors than CO. This is the expected behavior but it had not been observed previously by XPS. In a somewhat related situation Tolman[6] has observed that the binding energy of Ni(2p) in $Ni(PZ_3)_4$ compounds increases with the electronegativity of Z, but a study of Ni binding energy with n in $Ni(PZ_3)_n(CO)_{4-n}$ was not performed.

Further, within a given series, $L_2Mo(CO)_4$ or $L_3Mo(CO)_3$, compounds with nitrogen ligands have lower binding energies than those with phosphorus ligands. For example, the average Mo binding energy of thirteen $P_2Mo(CO)_4$ compounds is 226.4 eV and the average of three $N_2Mo(CO)_4$ compounds is 225.9 eV. The two $P_3Mo(CO)_3$ compounds average 226.0 eV whereas the two $N_2PMo(CO)_3$ compounds average 225.3 eV. The lower molybdenum binding energy with nitrogen ligands compared to phosphorus ligands indicates a higher electron density on molybdenum caused by nitrogen being a better σ donor and/or a poorer π acceptor than phosphorus.

The phosphorus 2p binding energies are also presented in Table II. The range of energies is only 1.1 eV which is not surprising in view of the results obtained by Pelavin, *et al.*, for phosphorus compounds.[45] These authors observed a range of only 4.5 eV although the oxidation states of phosphorus varied from 0 to +V. Introduction of fluorine increased the range to 7.5 eV. Van Wazer, *et al.*,[46] have shown that, when comparing similar species of phosphorus compounds, such as $(C_6H_5)_3P$ and $(C_6H_5)_3PZ$ (where Z = O, S, Se), the change in oxidation state produces an increase of roughly 1.6 eV.

Several reports in the literature have tried to use XPS of triphenylphosphine and its metal complexes to study the direction of electronic drift on this ligand upon coordination. Blackburn, *et al.*,[47] 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 either remained the same or increased on coordination to Ni(II). Jolly, *et al.*,[45] found that an increase in the P(2p) binding energy occurred when *trans*-Rh(CO)-Cl(PPh_3)_2 was compared with the free ligand. Van Wazer *et al.*,[46] reported the P(2p) binding energies of Ph_3P and $[Ph_3P]_2HgI_2$, for which there was essentially no change in the binding energy of the phosphorus 2p electrons. Under these circumstances, these authors indicated that a balance of interactions was causing a constancy of the P(2p) binding energy of the coordinated phosphine. More recent[6] reports have shown that little or no increase occurs upon coordination of the phosphine to a metal atom and that small but significant increases in binding energy occur with increases in oxidation state of the metal atom and through the use of more electronegative ligands. New measurements on triphenylphosphine[6] have indicated that the higher value obtained by Blackburn, *et al.*,[47] was perhaps the result of some phosphine oxidation. We find that the P(2p) binding energies of the phosphines used in this study increase very slightly (and perhaps insignificantly based on experimental error) upon coordination, ranging from +0.1 to +0.5 eV.

Compounds **40** and **41**, *cis*- and *trans*-[Ph_2(*n*-Bu)P]_2Mo-(CO)_4, illustrate the fact that XPS is unable to differentiate between cis and trans complexes containing phosphines. Similar findings for facial and meridional phosphine complexes of heavy transition metals recently have been reported by Leigh and Bremser.[48]

Compound **38**, $[Ph_2PCH_2N(CH_3)CH_2]_2Mo(CO)_4$, shows the same P(2p) and N(1s) binding energies for the coordinated and uncoordinated ligands. In general, coordination shifts of nitrogen ligands[6] are appreciably greater than P(2p) shifts. Thus, if the metal in compound **38** were coordinated to the nitrogen atoms of the ligand, an increase in the N(1s) binding energy should be expected. Ir and nmr data (^{31}P and ^1H nmr), in agreement with XPS results (see ref 27), indicate that the compound contains a ligand coordinated through its phosphorus atoms.

The results of this study can be summarized as follows. (a) A good correlation is obtained for simple molybdenum compounds and their calculated Pauling charges. From these results, an increment in binding energy of 1 eV (relative to Mo metal) produces 0.3 unit of charge on the metal. (b) Organometallic compounds of molybdenum, some of which display a fairly high concentration of negative charge on the metal, have a rather narrow range of binding energy dependent upon the nature of the ligand. The molybdenum $3d_{5/2}$ binding energy in molybdenum carbonyl derivatives decreases with increasing substitution of tertiary phosphines and amines for CO.

9, 1313-27-5; **10**, 10102-40-6; **11**, 12054-85-2; **12**, 12091-64-4; **13**, 12128-23-3; **14**, 12214-92-5; **15**, 12083-78-2; **16**, 12294-73-4; **17**, 12125-77-8; **18**, 41650-47-9; **19**, 12089-15-5; **20**, 36346-24-4; **21**, 14971-45-0; **22**, 15740-78-0; **23**, 15668-64-1; **24**, 15492-88-3; **25**, 15492-87-2; **26**, 41174-20-3; **27**, 50860-45-8; **28**, 50860-48-5; **29**, 26743-81-7; **30**, 15444-66-3; **31**, 15553-68-1; **32**, 21034-85-5; **33**, 54340-51-1; **34**, 43210-24-6; **35**, 43213-00-9; **36**, 49564-07-0; **37**, 54340-52-2; **38**, 54340-53-3; **39**, 17652-79-8; **40**, 24508-50-7; **41**, 25966-10-3; **42**, 43210-23-7; **43**, 14780-96-2; **44**, 14971-43-8; **45**, 54340-54-4; **46**, 36491-12-0; **47**, 36491-11-9; **48**, 54340-55-5.

References and Notes

(1) (a) Taken in part from the Ph.D. dissertation of L. J. Matienzo, University of Maryland, 1973. (b) Reported at the 6th Central Regional Meeting of the American Chemical Society, Detroit, Mich., April 1974. (c) Supported by the National Science Foundation under Grant No. GP 30703.

(2) (a) W. Dremser, *Fortschr. Chem. Forsch.*, **36**, 1 (1973); (b) W. E. Swartz, Jr., and D. M. Hercules, *Anal. Chem.*, **43**, 1774 (1971).

(3) A. W. Miller, W. Atkinson, M. Barber, and P. Swift, *J. Catal.*, **22**, 140 (1971).

(4) D. Briggs, D. T. Clark, H. R. Keable, and M. Kilner, *J. Chem. Soc., Dalton Trans.*, 2143 (1973).

(5) After submission of this article, another publication, W. B. Hughes and B. A. Baldwin, *Inorg. Chem.*, **13**, 1531 (1974), appeared which complements the essential findings of this report.

(6) C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *Inorg. Chem.*, **12**, 2770 (1973).

(7) D. T. Clark and D. B. Adams, *Chem. Commun.*, 740 (1971).

(8) H. Binder and Ch. Elschenbroich, *Angew. Chem., Int. Ed. Engl.*, **12**, 659 (1973).

(9) R. Gleiter, R. Seeger, H. Binder, E. Fluck, and M. Cais, *Angew. Chem., Int. Ed. Engl.*, **11**, 1028 (1972).

(10) R. B. King, "Organometallic Synthesis," Vol. I, Academic Press, New York, N.Y., 1965.

(11) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(12) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966).

(13) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 179 (1964).

(14) E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

(15) H. J. Dauben, Jr., and L. R. Honnen, *J. Amer. Chem. Soc.*, **80**, 5570 (1958).

(16) E. O. Fisher and K. Öfele, *Chem. Ber.*, **90**, 2532 (1957).

(17) J. A. Bowden and R. Colton, *Aust. J. Chem.*, **24**, 2471 (1971).

(18) G. R. Dobson and R. A. Brown, *J. Inorg. Nucl. Chem.*, **34**, 2785 (1972).

(19) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).

(20) L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966).

(21) P. M. McAllister, Ph.D. Dissertation, University of Maryland, 1968.

(22) W. L. Briggs, M.S. Thesis, University of Maryland, 1972.

(23) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).

(24) R. B. King and C. A. Eggers, *Inorg. Chim. Acta*, **2**, 33 (1968).

(25) S. O. Grim, J. Del Gaudio, C. A. Tolman, and J. P. Jesson, *Inorg. Nucl. Chem. Lett.*, **9**, 1083 (1973).

(26) S. O. Grim and J. D. Mitchell, *Syn. Reactiv. Inorg. Metal-Org. Chem.*, **4**, 221 (1974).

(27) L. J. Matienzo, Ph.D. Dissertation, University of Maryland, 1973.

(28) S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).

(29) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc. A*, 2068 (1969).

(30) R. M. Singer, Ph.D. Dissertation, University of Maryland, 1969.

(31) D. J. Hnatowich, J. Judis, M. L. Perlman, and R. C. Ragaini, *J. Appl. Phys.*, **42**, 4883 (1971).

(32) L. J. Matienzo and S. O. Grim, *Anal. Chem.*, **46**, 2052 (1974).

(33) K. Siegbahn, *et al.*, "ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, Sweden, 1967.

(34) (a) J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N.Y., 1972; (b) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.

(35) R. Larsson, B. Folkesson, and G. Schön, *Chem. Scr.*, **3**, 88 (1973).

(36) The slope of the line in Figure 1 of ref 5 gives approximately the same result.

(37) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **9**, 612 (1970).

(38) G. E. McGuire, G. K. Schweitzer, and T. A. Carlson, *Inorg. Chem.*, **12**, 2450 (1973).

(39) L. Yin, S. Ghose, and I. Adler, *Appl. Spectrosc.*, **26**, 355 (1970).

(40) L. J. Matienzo, L. I. Yin, S. O. Grim, and W. E. Swartz, Jr., *Inorg. Chem.*, **12**, 2762 (1973).

(41) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(42) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).

(43) G. W. Parshall, *J. Amer. Chem. Soc.*, **88**, 704 (1966).

(44) S. Pignataro, A. Foffani, and G. Distefano, *Chem. Phys. Lett.*, **20**, 350 (1973).

(45) M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

(46) W. E. Morgan. W. J. Stec, R. G. Albridge, and J. R. Van Wazer, *Inorg. Chem.*, **10**, 926 (1971).

(47) J. R. Blackburn, R. Nordberg, F. Stever, R. G. Albridge, and M. M. Jones, *Inorg. Chem.*, **9**, 2374 (1970).

(48) G. J. Leigh and W. Bremser, *J. Chem. Soc., Dalton Trans.*, 1216 (1972).

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602

Transition Metal Cyanocarbon Derivatives. III. Novel Chelates and Dicyanoketeneimmonium Derivatives from Hydrolyses, Alcoholyses, and Aminolyses of 1-Chloro-2,2-dicyanovinyl and Tricyanovinyl Derivatives of Molybdenum and Tungsten[1,2]

R. B. KING* and MOHAN SINGH SARAN[3]

Hydrolyses of $(NC)_2C{=}C(CN)M(CO)_3C_5H_5$ (M = Mo and W) in the presence of alumina or triethylamine give orange $C_3(CN)_2NH_2M(CO)_2C_5H_5$ (M = Mo and W). Similar hydrolyses of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) give red $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ (M = Mo and W). The NH and OH but not the CH hydrogens in these two types of complexes can be deuterated with D_2O in tetrahydrofuran at room temperature. Alcoholyses of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) in the presence of sodium hydroxide or sodium alkoxide give the red esters $C_3(CO_2R)(CN)(OR)NHM(CO)_2C_5H_5$ (M = Mo or W, R = CH_3 or C_2H_5). Aminolyses of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) with the secondary amines $(CH_3)_2NH$ and piperidine give the bright yellow dicyanoketeneimmonium derivatives $[R_2NCC(CN)_2]M(CO)_2C_5H_5$ (M = Mo or W; R = CH_3 or 2R = $-(CH_2)_5-$). Infrared, proton, and carbon-13 nmr spectroscopies have been used to elucidate the structures of these new types of complexes. A reaction scheme for the formation of $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ and $C_3(CO_2R)(CN)(OR)NHM(CO)_2C_5H_5$ derivatives from $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ through terminal dicyanovinylidene intermediates of the type $RM(CO)_2[C{=}C(CN)_2](C_5H_5)$ (R = H or CO_2R) is proposed and discussed.

Introduction

The first paper of this series[4] described the preparation of an extensive series of polycyanovinyl transition metal derivatives by the nucleophilic displacement of chloride in polycyanovinyl chlorides with metal carbonyl anions. An example of a reaction of this type was the formation of the tricyanovinyltungsten derivative $(NC)_2C{=}C(CN)W(CO)_3C_5H_5$ (I, M = W) from tricyanovinyl chloride and $NaW(CO)_3C_5H_5$. This tricyanovinyltungsten derivative could be isolated as a yellow crystalline solid by chromatography of the reaction