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Photoelectron Spectroscopy of Coordination Compounds. II. Palladium Complexes

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The energies of the $3d_{3/2}$ and $3d_{5/2}$ levels have been determined for palladium and 13 of its compounds. The measured energies are related to electronegativity differences between the palladium and the ligand donor atoms except in those cases where the ligand is a π acceptor. Ligands which are π acceptors cause greater energy level shifts since they permit greater depletion of electronic charge from the palladium. The energies of the K(2s) and P(2p) levels measured for several complexes were found to be nearly constant. The energy of the Br($3p_{3/2}$) level was lowered somewhat when the bromine occupied a bridging position in $PdBr_2$. The observed shifts can be "explained" by a combination of electronegativity and π-bonding effects.

In a previous paper[1] we reported on our use of photoelectron spectra to obtain information about back-bonding in coordination compounds. In that work the observed shifts in phosphorus 2p photoelectron lines were attributed to changes in electron density resulting from the opposing effects of σ-bonding donation and π-bonding back-donation. In the present work we have enlarged our studies by examining chemical shifts in the 3d level of palladium in 13 palladium complexes and in palladium metal.

Experimental Section

The measurements were carried out as described previously.[1] The low pressure of the spectrometer is $\sim 10^{-6}$ Torr and is relatively "clean;" however, when samples are irradiated under this vacuum, they become coated with a thin deposit of pump oil. For energy calibration we have used the carbon 1s photoelectron line originating in this oil. The carbon 1s binding energy was taken to be 285.0 eV[2] and the spectrometer work function to be 3.7 eV.[3,4]

This method of calibration presents difficulties since there is evidence[5] that in some cases the oil may chemically interact with the sample so that the carbon 1s line is shifted. Also, since all our samples except palladium metal were nonconductors and were deposited on nonconducting tape, it was possible for the samples and the oil deposit to lie at different potentials. For these reasons, other means of calibration were used as a check. Some samples were mixed with graphite, sodium chloride, or palladium so that the graphite C(1s) line, the Na K-$L_{2,3}L_{2,3}(^1D_2)$ Auger line, or the palladium 3d line could be used for calibration. In some cases two different palladium complexes were intermixed so that the shift in the palladium line could be measured directly without the use of a calibration line. The results of these checks allowed us to determine a set of palladium 3d binding energies that we believe to be internally consistent to within ±0.4 eV.

For energy determinations, the peak positions were located by the following procedure. Tangents were drawn at the inflection points of the peak. Next, a line was drawn from the intersection of the tangents through the center of the peak at half-maximum. At the intersection of this line with the top of the peak a perpendicular was dropped to the base line. This point on the base line was taken as the peak position.

Preparation of Compounds.—$PdCl_2$ was obtained from D. F. Goldsmith Chemical Metal Co., Evanston, Ind. The compounds $K_2[PdCl_4]$, $K_2[PdBr_4]$, $K_2[Pd(NO_2)_4]$, $K_2[Pd(CN)_4]$, $PdBr_2$, PdI_2, $Pd(CN)_2$, and $K_2[PdCl_6]$ were prepared and characterized by standard methods.[6]

$[Pd(P(C_6H_5)_3)_2Cl_2]$.—Preparation and analysis has been previously reported.[1]

$[Pd(P(C_6H_5)_3)_2(CN)_2]$.—Palladium metal (0.18 g, 0.0017 g-atom) was dissolved in concentrated nitric acid, followed by gentle evaporation and subsequent dilution to 4 ml to eliminate excess nitric acid. This solution was then added dropwise to 100 ml of a saturated solution of triphenylphosphine in ethanol. The white, powdery product precipitated upon dropwise addition of a solution of KCN (2.0 g, 0.03 mol) in 50 ml of 25% aqueous ethanol. It was washed successively with ethanol and water several times and dried *in vacuo* at 65°; yield 1.03 g (88%). *Anal.* Calcd for $PdC_{37}H_{30}N_2P_2$: C, 66.8; H, 4.39; P, 9.08. Found: C, 67.07; H, 4.61; P, 9.20.

$[Pd(P(C_6H_5)_3)_2Br_2]$.—Palladium metal (0.15 g, 0.0014 g-atom) was treated as described above to give a solution of palladium nitrate and triphenylphosphine in ethanol. Hydrogen bromide gas from a sodium bromide–phosphoric acid generator was bubbled through the solution until precipitation was complete. The fine, lemon yellow powder was filtered and washed successively with ethanol and water and dried *in vacuo* at 65°; yield 0.96 g (87%). *Anal.* Calcd for $PdC_{36}H_{30}P_2Br_2$: C, 54.7; H, 3.80; P, 7.84. Found: C, 54.73; H, 3.94; P, 8.01.

$[Pd(P(C_6H_5)_3)_2I_2]$.—Palladium metal (0.13 g, 0.00121 g-atom) was treated as described above to give a solution of palladium nitrate and triphenylphosphine in ethanol. A solution of HI and H_3PO_4 in ethanol was prepared by addition of solid NaI (3 g, 0.02 mol) to 50 ml of H_3PO_4, followed by dropwise addition of this solution to 50 ml of 95% ethanol. The sodium phosphate salts were precipitated and the solution was decanted. This solution was then added dropwise to the solution of $Pd(NO_3)_2$ and triphenylphosphine in ethanol. The product precipitated in the form of shiny tan platelets. It was filtered, washed successively with ethanol and water, and dried *in vacuo* at 65°; yield 0.675 g (63%). *Anal.* Calcd for $PdC_{36}H_{30}P_2I_2$: C, 48.8; H, 3.39; P, 7.02. Found: C, 49.86; H, 3.56; P, 6.51.

The stereochemistries of the compounds $[Pd(P(C_6H_5)_3)_2X_2]$ were determined through a comparison of their ir and Raman spectra in the region 600–190 cm^{-1}. Cis complexes of the type MA_2B_2 have all 9 fundamentals $(3n - 6)$ Raman active, and 8 of the 9 are ir active (from C_{2v} symmetry). *trans*-MA_2B_2 complexes, with a center of symmetry (D_{2h}), have only 3 Raman- and 6 ir-active bands, none coincidental. No coincidental lines were found for the Cl, Br, and CN complexes in the region mentioned above, where the M–ligand stretch should occur. The M–X stretch was easily identified in the Raman spectra from the isotope effect (Cl) and by being the only nonidentical facet on going from Cl to Br to CN. The I complex decomposed under the ruby laser, but the ir spectrum resembled closely those of the other three complexes. The complexes were thus determined to all be of trans symmetry. (We previously reported the Cl complex to be of cis symmetry on the basis of an earlier literature reference.[1]) Raman spectra were recorded on a Cary Model 81 recording spectrometer and the ir spectra on a Perkin-Elmer Model 621 recording spectrometer. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

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(6) P. Pascal, Ed., "Nouvean Traite de Chimie Minerale," Vol. XIX, Masson et Cie, Paris, 1958, p 577.

TABLE I

MEASURED BINDING ENERGIES OF THE $3d_{3/2}$ AND $3d_{5/2}$ LEVELS OF PALLADIUM

Compd no.	Compd	No. of recordings[a]	E_b,[b] eV		Shifts, eV	Charge on Pd, q
			$3d_{3/2}$ level	$3d_{5/2}$ level		
1	Palladium	16	340.9 ± 0.3	335.7 ± 0.3	0.0	0.00
2	$PdCl_2$	11	343.2 ± 0.4	337.9 ± 0.3	2.2	0.60
2A	Mixture of Pd and $PdCl_2$	2			2.3	. . .
3	$PdBr_2$	7	342.5 ± 0.2	337.3 ± 0.2	1.6	0.36
4	PdI_2	7	341.9 ± 0.1	336.6 ± 0.1	0.9	0.09
5	$Pd(CN)_2$	4	344.9 ± 0.2	339.6 ± 0.2	3.9	0.34
6	$K_2[PdCl_4]$	15[c]	343.7 ± 0.3	338.4 ± 0.2	2.7	0.42
7	$K_2[PdBr_4]$	7	342.8 ± 0.1	337.5 ± 0.1	1.8	0.23
8	$K_2[Pd(NO_2)_4]$	5	344.4 ± 0.4	339.2 ± 0.2	3.5	0.60
9	$K_2[Pd(CN)_4]$	4	344.4 ± 0.3	339.2 ± 0.2	3.5	0.09
10	$K_2[PdCl_6]$	6	345.6 ± 0.5	340.3 ± 0.3	4.6	0.72
11	$Pd(P(C_6H_5)_3)_2Cl_2$	6	343.1 ± 0.5	337.9 ± 0.3	2.2	0.30
12	$Pd(P(C_6H_5)_3)_2Br_2$	6	343.3 ± 0.3	338.0 ± 0.3	2.3	0.18
13	$Pd(P(C_6H_5)_3)_2I_2$	5	343.0 ± 0.4	337.7 ± 0.4	2.0	0.04
14	$Pd(P(C_6H_5)_3)_2(CN)_2$	6	343.7 ± 0.4	338.4 ± 0.4	2.7	0.05

[a] The numbers given are the actual number of recordings for the $3d_{5/2}$ level of palladium. [b] The values quoted are the mean values and the errors are the standard deviations of the measurement. On the absolute energy scale, the error limits are larger than these deviations, as the errors in the energy of the X-ray source, errors in the energy of the calibration line, and the spectrometer work function have not been included. [c] Out of a total of 15 recordings, 6 of these were obtained from the decomposition of $K_2[PdCl_6]$ such as line 2 in Figure 2a.

Results

The palladium 3d electron spectra in our series of compounds appear as sharp lines with 2.0 eV as a typical value for the width at half-maximum intensity. Figures 1a and 1b illustrate the palladium doublet as observed from the metal and the dichloride salt. The results of a uniform mixture of Pd and $PdCl_2$ in a 1:2 ratio are shown in Figure 1c. Graphical resolution of the spectra of the mixture (Figure 1c) reveals a shift of 2.3 eV in palladium $3d_{5/2}$ level compared to a shift of 2.2 eV determined from the separate spectra of Figures 1a and 1b. The same results were obtained for a 2:1 mixture of Pd and $PdCl_2$. The agreement between these results is an example of the internal consistency of our energy calibrations.

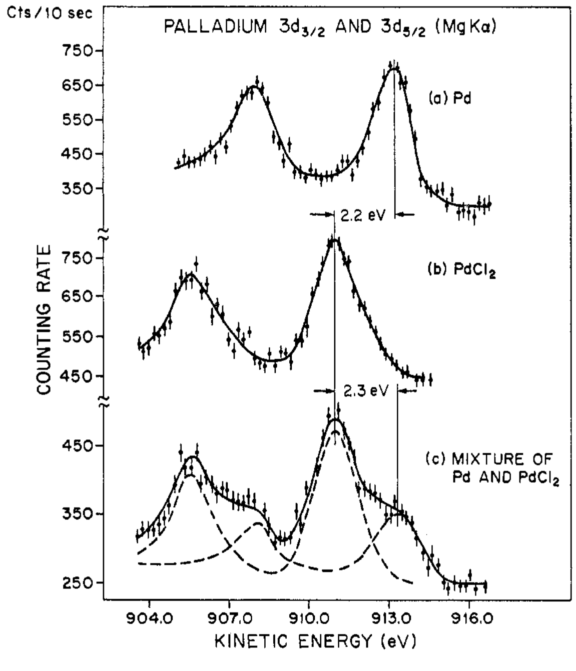

Figure 1.—Palladium 3d photoelectron spectra of (a) palladium metal, (b) palladium chloride, and (c) a 1:2 mixture of the two showing internal consistency of the calibration methods.

The Pd(3d) spectra of $K_2[PdCl_6]$ and $K_2[PdCl_4]$ are shown in Figure 2. In the $K_2[PdCl_6]$ spectrum the two "extra" peaks at binding energies of 338.4 and 343.7 eV originate in $K_2[PdCl_4]$ which is formed when the $K_2[PdCl_6]$ decomposes. With time, the heights of the "extra" peaks increase relative to the heights of the $K_2[PdCl_6]$ peaks. These observations are con-

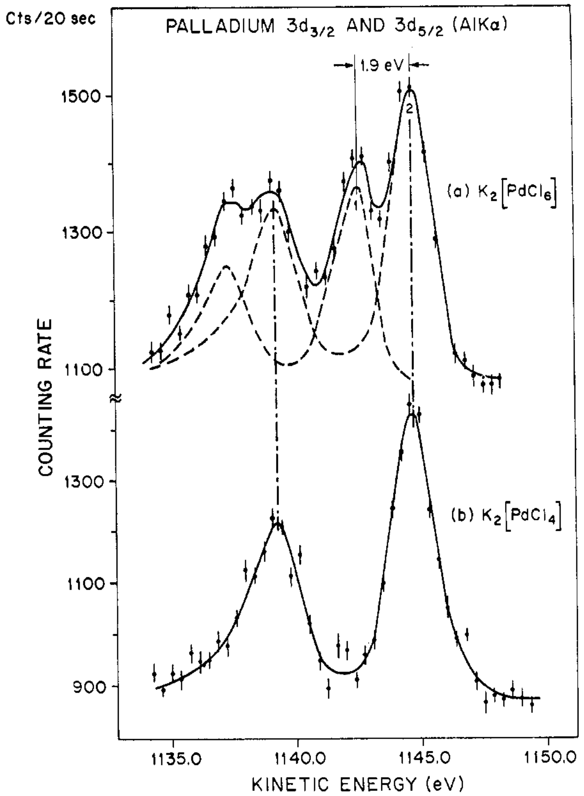

Figure 2.—Photoelectron spectra of (a) $K_2[PdCl_6]$ and (b) $K_2[PdCl_4]$. Part (a) shows the effect of the X-ray beam in decomposing $K_2[PdCl_6]$ to form $K_2[PdCl_4]$.

sistent with the known instability of $K_2[PdCl_6]$ and its demonstrated transformation into $K_2[PdCl_4]$ and Cl_2.[7]

These results give us an unexpected check on the Pd(3d) binding energy difference between $K_2[PdCl_6]$ and $K_2[PdCl_4]$. Since no color change occurred, the result of the partial decomposition of a sample of $K_2[PdCl_6]$ is most likely a surface that is an intimate mixture of $K_2[PdCl_6]$ and $K_2[PdCl_4]$, with a homogeneity that could not be easily obtained by mechanically mixing the two compounds. One can hope, therefore, that for these data, differences arising from solid state and/or surface effects are negligible. It is extremely difficult to obtain experimental data regarding shifts in photoelectron lines due to solid state or surface phenomena; however, such information is of great importance since photoelectron shift data are usually interpreted in terms of molecular models under the assumptions that the solid state and surface effects are small and approximately the same in the various compounds studied. In the present work, these assumptions are supported by our observation that the $K_2[PdCl_6]$–$K_2[PdCl_4]$ shift is independent of whether the $K_2[PdCl_4]$ sample is pure or intimately mixed with $K_2[PdCl_6]$.

Some of the compounds studied contain carbon; however, in only one case ($Pd(CN)_2$) did we observe an increase in the width of the carbon calibration line, indicating a difference between the C(1s) binding energy of the pump oil and of the sample. Because of this interference, the $Pd(CN)_2$ data were calibrated in reference to the K-$L_{2,3}L_{2,3}(^1D_2)$ Auger line of sodium in NaCl[8] and, independently, in reference to the Pd(3d) lines of palladium metal. The results were consistent. We used the same methods to calibrate data for a carbon-containing compound whose C(1s) line was not broadened, namely, $K_2[Pd(CN)_4]$. The result was the same as that obtained when the data were calibrated against the C(1s) line.

Table I lists the 3d binding energy values for the palladium compounds studied. The recorded errors are the standard deviations of the measurements and do not include errors in the calibration line or errors in the energy of the X-ray photon. The shifts listed are a weighted average of the shifts determined from the $3d_{3/2}$ data and from the $3d_{5/2}$ data. In all cases greater weight was given to the $3d_{5/2}$ data, which we consider to be more reliable. Also presented in Table I are estimated charges for the palladium atoms. These are discussed below.

Discussion

In Table I we have listed not only the measured binding energies of the palladium 3d levels for the various compounds studied but also the differences between these values and the 3d binding energies of pure palladium metal. These differences, which we call chemical shifts, can be discussed in an approximate way in terms of a simple, charged-sphere model.[9] Under this model an atom is considered to be a sphere with a surface represented by the valence electrons. Changes in core-level binding energies that are produced by changes in chemical bonding are interpreted as changes in the electrostatic potential inside the sphere due to changes in the charge on the surface of the sphere. A net removal of charge results in an increase in the inner-shell binding energies. The fact that the measured shifts listed in Table I are all positive indicates that upon coordination there is a net withdrawal of electrons from the palladium atom.

The formation of a coordinate ligand–palladium σ bond can be viewed as the donation of an electron lone pair from the ligand into an empty metal orbital. The metal and ligand atom will compete for this electron pair and the resulting distribution of the electron density will depend upon their relative electron-attracting powers. Therefore, the observed binding energy shifts are related to the differences between the metal and ligand electronegativities. If in addition the ligand atom has accessible empty π-type bonding orbitals (*i.e.*, if it is an acceptor ligand), the electron density distribution will be affected also by the nature of any π bonds that are formed. (Palladium has 4d electrons available for donation to ligand π orbitals of the proper symmetry.) For example, the large difference between the shifts for $Pd(CN)_2$ (3.9 eV) and $PdCl_2$ (2.2 eV) may be attributed in part to the fact that CN is a π-acceptor ligand, whereas Cl is a σ- and π-donor ligand but cannot act as a π donor *in these complexes*.

In order to make these considerations more quantitative, we have plotted in Figure 3 the measured $3d_{5/2}$ binding energies against the estimated charge on the palladium atom. The charge was estimated by means of Pauling's principles of electronegativity[10] and under the assumptions that only nearest neighbors and that only σ bonds contribute to the palladium charge.

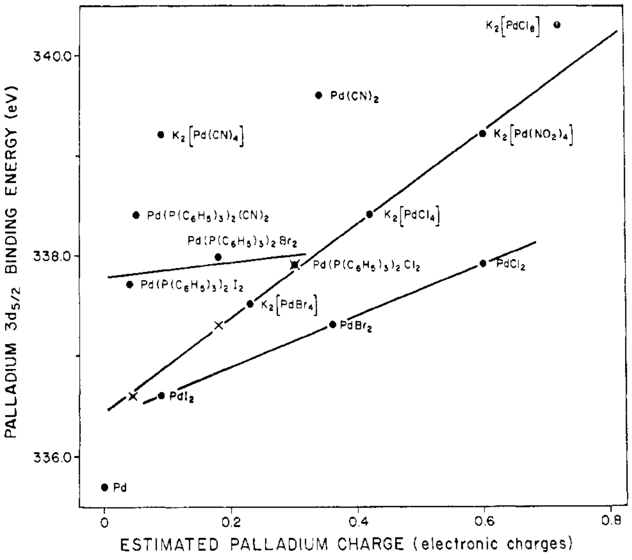

Figure 3.—Palladium $3d_{5/2}$ binding energies plotted against the estimated palladium electronic charge. The X's represent the charge calculated for the dihalides assuming the effective electronegativity of a bridging halide to be half that of a nonbridging halide.

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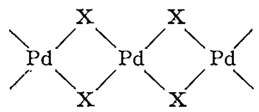
[7] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford, the Clarendon Press, 1950, p 1576.

[8] The K-$L_{2,3}L_{2,3}(^1D_2)$ Auger line of sodium was calibrated against the C(1s) line of pump oil and was found to have a kinetic energy of 984.0 eV.

[9] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Upsal.*, [4] **20,** 79 (1967); "ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967.

[10] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 97–102.

Compounds of the type PdX_2 were assumed to have polymeric structures with two bridging X atoms for each PdX_2 unit



In these cases all bonds were considered to be the same and the palladium was assumed to have four equivalent nearest neighbors. This structure is not proven for $PdBr_2$ and PdI_2 but is highly probable in light of the marked tendency of palladium(II) to form square-planar complexes. For ions of the type PdX_4^{2-} it was assumed that the 2− charge is equally distributed among the four X atoms, and the electronegativities of these atoms were adjusted accordingly.

In Figure 3 straight lines are drawn through points representing compounds of similar structure. The compounds PdI_2, $PdBr_2$, and $PdCl_2$ form one such group; $K_2[PdBr_4]$, $K_2[Pd(NO_2)_4]$, and $K_2[PdCl_4]$ another group; and $[Pd(P(C_6H_5)_3)I_2]$, $[Pd(P(C_6H_5)_3)Br_2]$, and $[Pd(P(C_6H_5)_3)Cl_2]$ still another. That the lines through these groups do not coincide may be due in part to the arbitrariness of the charge calculations. Although such calculations might be expected to give reasonable estimates of relative charges for a common element in a series of similar compounds, it is not obvious that one can treat these charges as absolute quantities and compare them among compounds of different structures.

The differences between the binding energies for the PdX_4^{2-} and PdX_2 groups are probably due in part to the lower effective electronegativity of the bridging halides in PdX_2.

The data for the group of compounds $[Pd(P(C_6H_5)_3)_2X_2]$ are distinguished by the fact that it is possible to draw through the points a line of almost zero slope. For these compounds the influence of the halogen on the palladium charge decreases in the order Cl → Br → I. The fact that the palladium $3d_{5/2}$ binding energy does not appear to decrease accordingly suggests that as the polarity of the palladium–halogen bond decreases in the series, another effect acts to minimize any overall change in the palladium charge. We suggest that this other effect is the balance of σ bonding from the phosphorus of the triphenylphosphine to the palladium and back-donation of palladium 4d electrons into available π orbitals of the phosphorus atom. We have previously invoked this back-donation to account for the constancy of the phosphorus 2p binding energy in a series of triphenylphosphine complexes with different metal atoms.[1] This balance of σ and π bonding can then serve to keep the relative electron distribution between the palladium and phosphorus fairly constant in the following manner. As the ligand attached to the palladium becomes more electron withdrawing (*e.g.*, Br → Cl) the palladium–halogen bond becomes more highly polarized, depleting the electron density around the palladium to some extent. The palladium to phosphorus π donation then becomes less efficient, and the phosphorus to palladium σ bonding more efficient, with the result that any depletion of electron density around the palladium atom is averaged over both the palladium and phosphorus atoms by this sharing process. In the same manner, if the ligand is less electron withdrawing (Br → I), the increased electron density of the palladium is again shared by both atoms. The overall effect noted, then, is that changing the polarity of the palladium–halogen bond causes very little change in the electron density of either palladium or phosphorus, which is borne out by Tables I and II and the line of almost zero slope of Figure 3.

TABLE II

MEASURED BINDING ENERGIES FOR POTASSIUM, BROMINE, AND PHOSPHORUS

Compound	Binding energies, eV K(2s)	Br($3p_{3/2}$)	P(2p)
$K_2[PdCl_4]$	377.8		
$K_2[Pd(NO_2)_4]$	377.8		
$K_2[Pd(CN)_4]$	377.7		
$K_2[PdBr_4]$	377.6	182.1 ± 0.2	
$PdBr_2$		182.6 ± 0.1	
$Pd(P(C_6H_5)_3)_2Br_2$		182.1 ± 0.1	131.8 ± 0.1
$Pd(P(C_6H_5)_3)_2Cl_2$			131.8 ± 0.3
$Pd(P(C_6H_5)_3)_2I_2$			131.6 ± 0.2
$Pd(P(C_6H_5)_3)_2(CN)_2$			131.9 ± 0.2

Replacing the halogen by CN provides a good check on the above reasoning. The CN ligand is well known[11] to be an effective π acceptor and is thus able to compete with the phosphorus for the palladium 4d electrons. Since the palladium is now bonded to four π-acceptor ligands, one would expect a net depletion of electron density from the palladium with a subsequent rise in binding energy. The π-bonding efficiency to the phosphorus is decreased somewhat, however, due to competition from the CN, and thus the phosphorus likewise suffers a loss of electron density and a rise in 2p binding energy. These effects are shown clearly in Tables I and II. Hendrickson,[12] *et al.*, arrived at a similar conclusion concerning the back-bonding nature of the cyanide ion by comparing the nitrogen 1s binding energies of CN in "coordinated" and "free" environments. They attributed a lower nitrogen binding energy in the coordinated cyanide to electron donation by the complexed metal into the π-acceptor orbitals of the cyanide ligand.

The palladium 3d binding energies are found to increase quite regularly with the oxidation state of the palladium. This is seen very clearly in the data obtained on the chloro compounds, which is shown in Figure 4. It must also be recalled that the coordina-

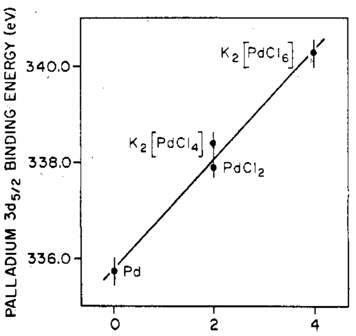


Figure 4.—Palladium $3d_{5/2}$ binding energies plotted against oxidation number.

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[11] L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963); **3**, 1581 (1964), and references therein.

[12] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *ibid.*, **8**, 2642 (1969).

tion number of the palladium changes in this sequence. The effect of oxidation state on binding energy is in complete conformity with data previously published on such trends.[9]

During the course of these studies, we also determined the binding energies of the potassium 2s, bromine 3p, and phosphorus 2p levels and the results are given in Table II. The potassium is present in these compounds as the cation component of the ionic lattice; hence, we expect its inner-shell binding energies to be almost constant unless crystal field effects bring about differences. The observed K(2s) binding energy is constant to within 0.2 eV, which we take as weak evidence that crystal field effects can be ignored.

The data show that there is essentially no difference in the $3p_{3/2}$ level of bromine in the compounds $K_2[PdBr_4]$ and $[Pd(P(C_6H_5)_3)_2)Br_2]$, but the Br $3p_{3/2}$ level of these compounds is about 0.5 eV lower than the Br $3p_{3/2}$ level in $PdBr_2$. We attribute the higher value for $PdBr_2$ to the effect of each bromine being coordinated to two palladium atoms in a bridging structure. This conclusion is supported by the expectation that such bridging-type bonds should result in higher binding energies for the electrons in the bridging atoms as they are coordinated to two close acceptor atoms and thus have lower electron densities than in cases where they are coordinated to only one acceptor atom.

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CONTRIBUTION FROM THE CENTRO STABILITÁ E REATTIVITÁ COMPOSTI DI COORDINAZIONE, CNR,
ISTITUTO CHIMICA GENERALE, UNIVERSITY OF PADUA, PADUA, ITALY

Zwitterion Complexes of the Cation Dicyanobis[1,2-bis(diphenylphosphino)ethane]cobalt(III)

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The cobalt(III) complex $L^+ = [Co\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\}_2(CN)_2]^+$ acts as positively charged ligand giving compounds of the stoichiometry $M(L^+)X_3$, where M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II) and X = halogen or pseudohalogen. On the basis of their electronic and vibrational spectra, magnetic susceptibilities, and X-ray diffraction patterns, these compounds are formulated as pseudotetrahedral zwitterion complexes in which the cobalt(III) cation is bound to MX_3^- moieties through the nitrogen atom of one cyanide group.

Introduction

We have recently reported the preparation of the compound $Co(dpe)_2(CN)_2$ (dpe = $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$) which we formulated as a low-spin five-coordinate complex of cobalt(II) where one of the two diphosphines acts as a monodentate ligand.[1] Methanol solutions of the compound were found to react with oxygen giving the hexacoordinate cobalt(III) species $[Co(dpe)_2(CN)_2]^+$. Investigations have now been extended to the reactions of the complex with oxygen in 1,2-dichloroethane. We find that the reaction yields *inter alia* the compound $Co^{III}(dpe)_2(CN)_2Co^{II}Cl_3$ which can be formulated as a zwitterion made by the cation $[Co^{III}(dpe)_2(CN)_2]^+$ bound through the nitrogen end of one CN group to the Co(II) atom of the $CoCl_3^-$ moiety. Several recent reports have been concerned with zwitterion systems in transition metal complexes containing positively charged nitrogen and phosphorus ligands.[2-9] In the present paper we report the preparation and the characterization of a series of compounds in which the ionic species $[Co(dpe)_2(CN)_2]^+$ acts as a positively charged ligand for MCl_3^- anions. The general composition of the complexes is $M(L^+)X_3$ where $L^+ = [Co(dpe)_2(CN)_2]^+$; M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II); X = halogen or pseudohalogen.

Experimental Section

Apparatus.—The magnetic moments were determined at 25° by using the Gouy method and were corrected for the diamagnetism of the ligands.[10] Electronic spectra were recorded on an Optica CF4NI spectrophotometer. The reflection spectra were measured with a Beckman DU spectrophotometer using solid compounds ground with $MgCO_3$ as the inert diluent. Ir spectra were recorded using a Beckman IR 9 spectrophotometer. Conductivity measurements were made at 25°. X-Ray powdered diffractograms were taken using a Siemens diffractometer, Model F-Nr. The uptake of oxygen was measured as described previously.[11]

Starting Materials.—Metal salts were analytical reagent grade.

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