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Registry No. Cu, 7440-50-8; 2,2′-bipyridyl, 366-18-7; iminodiacetic acid, 142-73-4; pyridine-2,6-dicarboxylic acid, 499-83-2.

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X-ray Photoelectron Spectra of Binuclear Palladium–Palladium-Bonded Complexes and Their Insertion Products

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X-ray photoelectron spectroscopic (XPS) data have been obtained for the binuclear Pd(I) complexes $Pd_2(dpm)_2Cl_2$ and $Pd_2(dam)_2Cl_2$ (dpm = bis(diphenylphosphino)methane and dam = bis(diphenylarsino)methane) and products resulting from the insertion of carbon monoxide, methyl isocyanide, sulfur dioxide, and atomic sulfur into the metal–metal bond. The insertion of these small molecules into the Pd–Pd bond results in either no change or modest increases in the Pd $3d_{5/2}$ binding energies (ΔE_B of 0.0 to +0.6 eV) while the Cl $2p_{3/2}$, P $2p_{3/2}$, or As 3d binding energies of the attendant ligands remain constant. The largest Pd $3d_{5/2}$ binding energy shifts arise from insertion of SO_2. When observable, the binding energies of atoms in the inserted ligands decrease, sometimes substantially (0.9–2.5 eV), compared with those of their precursors. The small binding energy shifts of the Pd 3d levels are reasonable because only half of the charge donated to the inserted ligand comes from each half of the dipalladium complex. Similarly the binding energy shifts of the atoms of the inserted ligands (compared to those of their free, neutral precursors) become smaller, where detectable, as the number of atoms which compose the ligand increases. Nitrogen 1s binding energies for bridging methyl isocyanide in $Pd_2(dpm)_2(\mu\text{-}CNCH_3)Cl_2$ and $[Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2](PF_6)_2$ are ~1 eV lower than those for terminal methyl isocyanide. For comparison, XPS data are also presented for $[Pd_2(CNCH_3)_6](PF_6)_2$, $[Pd(CNCH_3)_4](PF_6)_2$, $Pd(CNCH_3)_2I_2$, and $[Pt_2(CNCH_3)_6](BF_4)_2$, which contain only terminal, linearly bound $CNCH_3$ ligands.

Introduction

The unprecedented insertion of small molecules into the metal–metal bond of the dipalladium complexes $Pd_2(dpm)_2Cl_2$ (dpm = bis(diphenylphosphino)methane) and $Pd_2(dam)_2Cl_2$ (dam = bis(diphenylarsino)methane) via eq 1 has attracted widespread attention. As a consequence of the insertion reaction, the metal–metal bond is broken and the palladium ions move about 0.5 Å further apart. Carbon monoxide[2-5] and

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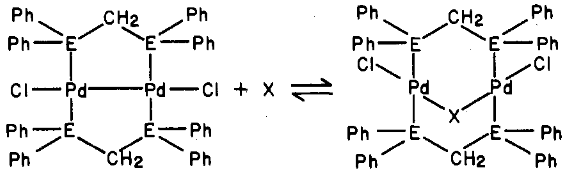


A B

E = P or As

(1)

sulfur dioxide[6,7] insert reversibly into the Pd–Pd bond while the insertions of isocyanides,[2,3] diazonium ions,[8] and sulfur atoms[7] are irreversible processes.

There has been some controversy over the assignment of formal oxidation states to the products of these reactions. Colton et al. have formulated the carbonyl-bridged compound $Pd_2(dam)_2(\mu\text{-}CO)Cl_2$ as a Pd(I) complex which is spin paired via the carbonyl bridge.[4,5] The insertion product has also been classified as a Pd(II) dimer with a keto or dimetalated formaldehyde bridge.[9] While we believe that the difference between these two formulations is largely semantic, there is a related question which is open to experimental test. That matter involves the alterations in atomic charge which occur as a result of these insertion reactions.

For this purpose we have obtained X-ray photoelectron spectra (XPS) of the dipalladium complexes and their insertion products. In the most general case, the binding energy difference ΔE_B of a core electron in a given atom in different solids can be expressed as

$$\Delta E_B = k\Delta Q + \Delta V + \Delta B + \Delta E_R \qquad (2)$$

where k is a constant, ΔQ is the difference in a ground-state charge associated with that atom, ΔV and ΔB are the differences in intramolecular and extramolecular Coulombic potentials, respectively, and ΔE_R is the difference in electronic relaxation energy. Looking at eq 2, it is clear that simple correlations of binding energy with ground-state charge are not generally possible and experimental results bear out this fact.[10,11] However, experience has shown[12-15] that judicious selection of the materials to be studied can lead to simplification in eq 2. In cases where the materials compared are structurally related, the relaxation energy contribution to all core level measurements is essentially constant; therefore $\Delta E_R \simeq 0$. A second simplification arises if the complexes studied are isocharged, in which case B is also constant. Under these conditions comparisons of ΔE_B between any two binding energy equations for a given core level can be expressed as

$$\Delta E_B = k\Delta Q + \Delta V \qquad (3)$$

Since the complexes studied are structurally very similar and are isocharged, eq 3 applies and binding energy shifts can be reasonably interpreted in terms of charge transfer between the complex and the inserted ligand.

Experimental Section

Materials. All of the complexes were prepared according to previously published procedures.[2,3,6,7,16,17]

X-ray Photoelectron Spectra. Spectra were obtained with a McPherson ESCA-36 photoelectron spectrometer interfaced to a PDP-12 computer with a Fabritek Model 8 extended memory. Spectrometer pressures between 1×10^{-8} and 3×10^{-7} atm were maintained during data collection. The vacuum pumping system consisted of an Air Products Displex cryopump for differentially pumping the sample chamber backed by two Sargent-Welch Turbomolecular pumps in series and a mechanical forepump. Spectra were generated with Mg Kα and Al Kα X-ray sources which were operated with the X-ray power supply output set at 200–240 W. The baffle settings and 0.1-mm analyzer entrance and exit slits employed gave a Au $4f_{7/2}$ line width of 1.05 eV. The spectrometer absolute binding energy scale was calibrated to the Au $4f_{7/2}$ level (84.0 eV)[18] of argon ion cleaned gold foil by using a spectrometer work function of 4.30 eV and analyzer constant k of 3.9940. For ambient spectrometer temperature spectra, samples were pressed onto etched aluminum or mechanically cleaned silver plates. For the $Pd_2(dpm)_2Cl_2$ and $Pd_2(dam)_2Cl_2$ complexes and their insertion products, binding energies were internally referenced to the C 1s line (285.0 eV) of the dpm and dam ligands.[12-14] Binding energies for the palladium and platinum methyl isocyanide complexes were referenced to the C 1s binding energy (285.0 eV) of an overlayer of carbon-containing material which is present in the residual atmosphere of the spectrometer and which adsorbs onto the surface of all samples.

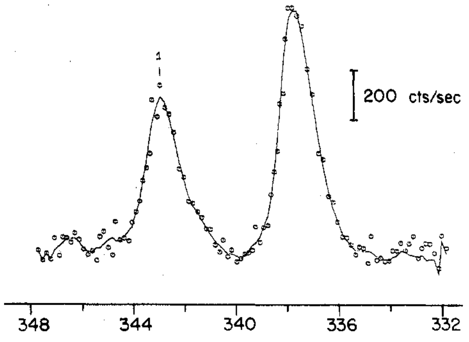


Figure 1. Pd $3d_{3/2}$,$3d_{5/2}$ spectrum of $Pd_2(dpm)_2Cl_2(\mu\text{-}S)$.

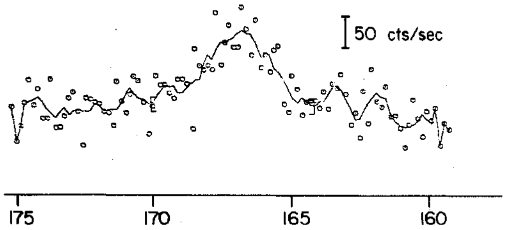


Figure 2. S 2p spectrum of $Pd_2(dam)_2Cl_2(\mu\text{-}SO_2)$.

During ambient-temperature data collection, samples of several of the insertion product complexes decomposed. Therefore, these complexes were crushed onto a copper clip attached to the McPherson ESCA-36G cryogenic probe. Probe temperatures were maintained between 100 and 160 K during data collection. Counting rates at these lower temperatures decreased and data collection times were longer but, on the basis of peak height, peak shape, and binding energy data, sample decomposition was judged to be minimal (≤10%). In cases where curves overlapped or were not resolved, the envelope was deconvoluted by using an iterative procedure of the McPherson curve-generating subroutine.

Results

The XPS data for $Pd_2(dpm)_2Cl_2$, **1**, and $Pd_2(dam)_2Cl_2$, **2**, and their insertion products are summarized in Table I. Data for four methyl isocyanide complexes are organized in Table II. Some representative spectra are shown in Figures 1–4.

In the course of ambient-temperature (ca. 35 °C) data collection, it became obvious that several of the complexes examined were unstable under the conditions of the experiment. For example, a N 1s signal could not be found for $Pd_2(dpm)_2Cl_2(\mu\text{-}CNCH_3)$, **8**, or $Pd(CNCH_3)_2I_2$, **13**. S 2p signals were not observed for $Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$, **5**, or $Pd_2(dam)_2(\mu\text{-}SO_2)Cl_2$, **6**, except on one occasion when a signal of the expected intensity was observed in the S 2p region. However, this peak was located at 170.5 eV, a binding energy which is suspiciously high for coordinated SO_2.[19] Since coordinated SO_2 is known to undergo oxidation by dioxygen[20] and since the S 2p binding energy of SO_4^{2-} is 169.0 eV,[21] we believe that in this instance the S 2p signal was due to oxidation of sulfur dioxide to sulfate with the possible formation of $Pd_2(dpm)_2(\mu\text{-}SO_4)Cl_2$.

Due to the difficulties encountered in the collection of ambient-temperature data, the following precautions were im-

Table I. X-ray Photoelectron Spectroscopic Data for Dipalladium Complexes

	core level binding energies, eV						
	Pd 3d						
complex	3/2	5/2	L[a]	P 2s	Cl $2p_{3/2}$	X[b]	C 1s
1 $Pd_2(dpm)_2Cl_2$	342.7 (1.9)[c]	337.3 (1.9)	131.9 (1.5)	189.3 (2.2)	198.1 (1.5)		285.0 (1.6)
2 $Pd_2(dam)_2Cl_2$	342.7 (1.9)	337.4 (2.1)	43.8 (2.1)		198.1 (1.6)		285.0 (1.9)
3 $Pd_2(dpm)_2Cl_2(\mu\text{-}CO)$	342.7 (1.5)	337.5 (1.6)	131.9 (1.5)		197.8 (1.6)		285.0 (1.7)
4 $Pd_2(dam)_2Cl_2(\mu\text{-}CO)$	343.0 (2.1)	337.7 (2.1)	44.0 (2.1)		198.1 (1.5)		285.0 (1.9)
5 $Pd_2(dpm)_2Cl_2(\mu\text{-}SO_2)$	343.2 (1.8)	337.9 (1.9)	131.9 (1.6)		197.8 (1.6)	166.8 (1.8)	285.0 (2.2)
6 $Pd_2(dam)_2Cl_2(\mu\text{-}SO_2)$	343.0 (1.8)	337.8 (1.9)	44.0 (1.9)		197.9 (1.6)	166.9 (1.7)	285.0 (2.1)
7 $Pd_2(dpm)_2Cl_2(\mu\text{-}S)$	342.9 (1.6)	337.6 (1.6)	131.8 (1.5)	189.5 (2.3)	198.2 (1.6)	161.6 (1.7)	285.0 (1.5)
8 $Pd_2(dpm)_2Cl_2(\mu\text{-}CNCH_3)$	342.7 (1.7)	337.2 (1.8)	131.9 (1.5)	189.0 (2.2)	198.1 (1.5)	399.9 (2.1)	285.0 (1.6)
9 $[Pd_2(dpm)_2(CNCH_3)_2(\mu\text{-}CNCH_3)](PF_6)_2$	343.0 (1.4)	337.8 (1.7)	132.0 (1.6) 136.3 (1.6)			401.0 (1.8) 399.8 (1.9)	285.0 (1.6)

[a] L is P $2p_{3/2}$ or As 3d. [b] X is S $2p_{3/2}$ or N 1s. [c] Values in parentheses are peak full widths at half-maxima (fwhm) in eV.

Table II. X-ray Photoelectron Spectroscopic Data for Methyl Isocyanide Complexes

	core level binding energies, eV				
complex	M[a]	C 1s	N 1s	P $2p_{3/2}$	X[b]
10 $[Pd(CNCH_3)_4](PF_6)_2$	339.5 (1.9)[c]	287.0 (2.0)	400.7 (1.9)	136.4 (1.5)	
11 $[Pd_2(CNCH_3)_6](PF_6)_2$	338.0 (1.8)	287.0 (2.1)	400.9 (1.7)	136.6 (1.5)	
12 $[Pt_2(CNCH_3)_6](BF_4)_2$	73.7 (1.7)	287.0 (1.9)	400.7 (1.5)		685.8 (1.8)
13 $Pd(CNCH_3)_2I_2$	338.9 (1.9)	287.1 (2.2)	401.3 (2.0)		619.9 (1.7)

[a] M is Pd $3d_{5/2}$ or Pt $4f_{7/2}$. [b] X is F 1s or I $3d_{5/2}$. [c] Values in parentheses are peak full widths at half-maxima (fwhm) in eV.

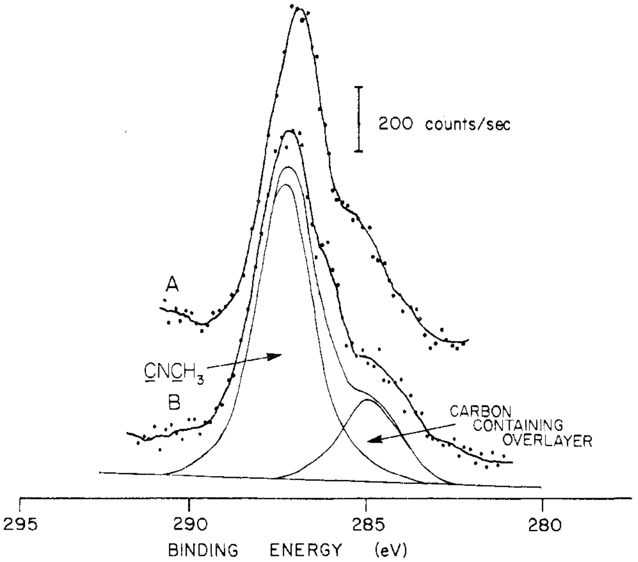


Figure 3. C 1s spectra of $[Pt_2(CNCH_3)_6](BF_4)_2$ (A) and $[Pd(CNCH_3)_4](PF_6)_2$ (B) and curve resolution of spectrum B.

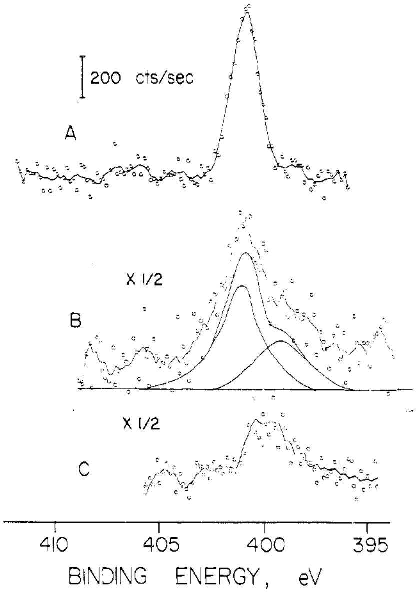


Figure 4. N is spectra of $[Pd_2(CNCH_3)_6](PF_6)_2$ (A), $[Pd_2(dpm)_2(CNCH_3)_2(\mu\text{-}CNCH_3)](PF_6)_2$ (B) (including curve resolution), and $Pd_2(dpm)_2Cl_2(\mu\text{-}CNCH_3)$ (C).

plemented. First, the spectra of all complexes which are products of insertion into the Pd–Pd bond (except $Pd_2(dpm)_2(\mu\text{-}S)Cl_2$, **7**) were recorded with the samples mounted on a cryogenic probe. Probe temperatures were maintained between 100 and 160 K during data collection. Second, relative peak heights of the core levels were tabulated for all the samples. The standardized core level intensity data published by Wagner[22] and Jørgensen and Berthou[23] were used to correct the relative peak heights to give atomic stoichiometries for each sample. The stoichiometries calculated from the XPS data are compared in Table III with the expected stoichiometries assuming no sample decomposition. Within the errors of the measurements and in spite of the variety of factors which can affect such measurements, the calculated stoichiometries at least roughly match those expected. Furthermore, the peak full widths at half-maxima (fwhm) and positions (for example, S $2p_{3/2}$ of $Pd_2(dam)_2(\mu\text{-}SO_2)Cl_2$ at 166.9 eV; Figure 2) are reasonable.[20] We are therefore confident that the data presented here are correct within the errors of the measurements (±0.2 eV).

Discussion

The palladium(I) complexes $Pd_2(dpm)_2Cl_2$, **1**, and $Pd_2(dam)_2Cl_2$, **2**, have, within experimental error, the same Pd $3d_{5/2}$ binding energies (337.3 and 337.4 eV, respectively). These values are 0.7–0.8 eV lower than that found for the related Pd(II) complex *trans*-$PdCl_2(PPh_3)_2$.[24] The decreased binding energy of the dinuclear Pd(I) complexes is consistent with the general observations concerning metal–phosphine–halide or metal–arsine–halide complexes (i.e., ~1 eV decrease in metal core level binding energy for each replacement of a halogen by a phosphine or arsine ligand).[12–14,25]

The dinuclear Pd(I) complexes **1** and **2** undergo insertion reactions with atoms or small molecules. Reactions of SO_2, $CNCH_3$, CO, or sulfur with **1** or **2** result in the formation of

Table III. Molecular Stoichiometries Based on Standardized[a] Core Level Peak Heights

	element					
compd	M[b]	L[c]	X[d]	S	N	C[g]
$Pd_2(dpm)_2Cl_2$	2.0[e]	5.0 (4.0)[f]	2.2 (2.0)			55.4 (50)
$Pd_2(dam)_2Cl_2$	2.0	4.8 (4.0)	1.3 (2.0)			57.6 (50)
$Pd_2(dpm)_2Cl_2(\mu\text{-CO})$	2.0	2.5 (4.0)	2.0 (2.0)			52.2 (51)
$Pd_2(dam)_2Cl_2(\mu\text{-CO})$	2.0	4.7 (4.0)	2.3 (2.0)			56.9 (51)
$Pd_2(dpm)_2Cl_2(\mu\text{-}SO_2)$	2.0	3.4 (4.0)	1.7 (2.0)	0.7 (1.0)		53.5 (50)
$Pd_2(dam)_2Cl_2(\mu\text{-}SO_2)$	2.0	4.9 (4.0)	1.9 (2.0)	1.1 (1.0)		58.1 (50)
$Pd_2(dpm)_2Cl_2(\mu\text{-S})$	2.0	3.9 (4.0)	1.5 (2.0)	1.0 (1.0)		53.0 (50)
$Pd_2(dpm)_2Cl_2(\mu\text{-}CNCH_3)$	2.0	3.6 (4.0)	2.9 (2.0)		1.4 (1.0)	61.5 (52)
$[Pd_2(dpm)_2(CNCH_3)_2(\mu\text{-}CNCH_3)](PF_6)_2$	2.0	6.2 (6.0)			2.3 (3.0)	53.6 (56)
$[Pd(CNCH_3)_4](PF_6)_2$	1.0	3.0 (2.0)			4.2 (4.0)	9.4 (8.0)
$[Pd_2(CNCH_3)_6](PF_6)_2$	2.0	3.2 (2.0)			4.9 (6.0)	10.8 (12.0)
$[Pt_2(CNCH_3)_6](BF_4)_2$	2.0		7.9 (8.0)		3.7 (6.0)	8.8 (12.0)
$Pd(CNCH_3)_2I_2$	1.0		1.6 (2.0)		1.6 (2.0)	3.5 (6.0)

[a] The relative core level peak height data of Wagner[22] and Jørgenson and Berthou[23] were used to calculate the molecular stoichiometries from the XPS data. The previously compiled standard peak heights were obtained with an Al Kα X-ray source whereas in the present study a Mg Kα X-ray source was employed. Corrections to account for the differences in relative core level peak heights due to the different X-ray source used are minor for the core levels examined[24] compared to the errors inherent in the peak height measurements and were not applied to the data. [b] M is Pd or Pt. [c] L is P or As. [d] X is Cl, F, or I. [e] The metal stoichiometry is taken as the reference and is set equal to the number of metal atoms in the complex. [f] Values in parentheses are the expected number of atoms of this element in the complex. [g] The number of carbon atoms determined from the experimental C 1s data for the dpm and dam complexes include carbon from material adsorbed onto the sample surface from the residual spectrometer atmosphere.

complexes having the general structure B (eq 1). The Pd $3d_{5/2}$ binding energies of the insertion products $Pd_2(dpm)_2(\mu\text{-X})Cl_2$ (X = CO, **4**; X = SO_2, **6**) fall within the narrow range 337.2–337.8 eV. Thus, in all cases insertion results in, at most, a modest increase in Pd $3d_{5/2}$ binding energy (0.0–0.6 eV). There are no detectable changes ($\leq$0.2 eV) due to insertion in the As 3d, P $2p_{3/2}$, or Cl $2p_{3/2}$ binding energies of the attendant ligands except for the μ-carbonyl complexes **3** and **4** in which the Cl $2p_{3/2}$ binding energies were found to be 0.3 eV lower than those in their respective precursors, **1** and **2**. These larger variations can arise due to the uncertainty involved in deconvoluting the Cl $2p_{1/2}$,$2p_{3/2}$ envelope.

The variations in the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ binding energies that result from these insertion reactions are clearly lower than those experienced by platinum[12,26] or nickel[27] centers when they undergo oxidative addition. For example, in the series $(Ph_3P)_4Pt$, $(Ph_3P)_2Pt(PhC_2Ph)$, $(Ph_3P)_2Pt(C_2H_4)$, $(Ph_3P)_2Pt(CS_2)$, $(Ph_3P)_2Pt(NC)_2CC(CN)_2$, $(Ph_3P)_2PtO_2$, $(Ph_3P)_2PtCl_2$, the Pt $4f_{7/2}$ binding energy smoothly increases by 1.6 eV.

Since any redistribution of charge caused by insertion into the Pd(I) dimers must be equally distributed over both metal centers, it is perhaps not surprising that the shifts in Pd binding energies are small. However, some comparisons do indicate that negative charge is transferred to the ligand which is inserted into the Pd–Pd bond. In particular, an examination of the binding energies associated with the inserted ligand and comparison of these binding energies with the binding energies of the free ligand offer independent information on the flow of charge upon insertion.

The most sensitive case for examining the inserted ligand involves $Pd_2(dpm)_2(\mu\text{-S})Cl_2$ in which the ligand is monatomic. The S $2p_{3/2}$ binding energy of the sulfur bridge in $Pd_2(dpm)_2(\mu\text{-S})Cl_2$, **7**, is 161.6 eV. This value is 2.4 eV lower than that of S_8 in which the charge of sulfur is zero. Consequently net negative charge has been transferred to sulfur.

From the sulfur-bridged complex **7**, one can derive the bridging SO_2 complex $Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$, **5**, by oxidation of the sulfur bridge by peracids.[7] While this oxidation of sulfur only marginally affects the palladium and attendant ligand core level binding energies ($\leq$0.2 eV), it results in an increase in the S $2p_{3/2}$ binding energy of 5.3 eV. The S $2p_{3/2}$ binding energies of $Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$, **5**, and $Pd_2(dam)_2(\mu\text{-}SO_2)Cl_2$, **6**, are similar to that recorded for $Ir(SO_2)(CO)Cl(PPh_3)_2$ (166.8 eV)[19] and 1.4–1.5 eV lower than that found for free sulfur dioxide (168.3 eV).[21] Due to complications arising from the presence of an overlayer of oxygen-containing contaminants, oxygen 1s binding energies for coordinated sulfur dioxide in **5** or **6** were not obtained. Additionally the oxygen 1s binding energies of solid sulfur dioxide or dioxygen have also not been reported, so relevent comparisons cannot be made.

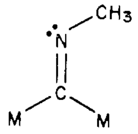
Attempts were made to extend measurements of inserted ligand binding energies by examining the C 1s regions of $Pd_2(dpm)_2(\mu\text{-CO})Cl_2$, **3**, $Pd_2(dam)_2(\mu\text{-CO})Cl_2$, **4**, and $Pd_2(dpm)_2(\mu\text{-}CNCH_3)Cl_2$, **8**. Due to the low concentration of carbonyl and methyl isocyanide carbons in these complexes and the likely proximity of the μ-CO and μ-$CNCH_3$ C 1s peaks to those for the phenyl and methylene carbons in the dpm and dam ligands, no peaks which might be attributed to the μ-CO or μ-$CNCH_3$ ligands in **3**, **4**, and **8** could be found. Although the C 1s and O 1s peaks were not located, the Pd $3d_{5/2}$ binding energies of **3**, **4**, and **8** were observed between 337.5 and 337.9 eV. These values are only 0.0–0.3 eV greater than those of their dipalladium precursors, $Pd_2(dpm)_2Cl_2$, **1**, and $Pd_2(dam)_2Cl$, **2**, and suggest that the charge transferred from the complex to CO or $CNCH_3$ is small or negligible within the limits of XPS.

In hopes of comparing C 1s data for linear, terminally bound $CNCH_3$ and bent, bridging $CNCH_3$, we recorded C 1s spectra for the methyl isocyanide complexes $[Pd(CNCH_3)_4](PF_6)_2$ (**10**), $[Pd_2(CNCH_3)_6](PF_6)_2$ (**11**), $[Pt_2(CNCH_3)_6](BF_4)_2$ (**12**), and $Pd(CNCH_3)_2I_2$ (**13**). Representative spectra are shown in Figure 3. We have reported the C 1s and metal core level binding energy data for **10**–**12** in an earlier study.[24] As in the previous study, two C 1s peaks of variable relative intensity were observed: one between 286.9 and 287.1 eV and another situated at 285.0 eV. However, in the previous study, the relative peak intensities varied between 0.7:1.3 and 1.2:0.8 (higher E_B/lower E_B) whereas in the present spectra, the peak areas varied from ~1.7:0.3 to ~1.0:1.0. As before, the peak at higher binding energy is assigned to both the cyano and methyl carbons and that at 285.0 eV to the carbon-containing material(s) which are present in the residual atmosphere of the spectrometer and which adsorb on the sample surface. Due to the lower sample chamber pressure attainable in the present study, the lower binding energy peak (285.0 eV) due to adventitious carbon is weaker than in the previous study.

The assignments for the two peaks can be independently corroborated from the relative core level peak height–stoichiometry calculations in Table III. In the cases of complexes **10**–**13** it is found that the carbon-to-metal ratio that was determined from the height of the higher binding energy peak is consistent with the expected stoichiometry of the complexes. Although the peak at 286.9–287.1 eV is caused by two structurally different forms of carbon, no attempts to deconvolute the peaks were made because the peaks were symmetrical and not unusually broad.

While a resolved C 1s signal attributable to the bridging ligands could not be found in the spectra of **3**, **4**, or **8**, a N 1s signal having the expected intensity (Table III and Figure 4) and located at 399.9 eV was found for $Pd_2(dpm)_2(\mu\text{-}CNCH_3)Cl_2$, **8**. The N 1s value reported for free $CNCH_3$ (standardized to Au $4f_{7/2}$ of 83.8 eV) is 400.0 eV.[28] N 1s binding energies for linear, terminally bound methyl isocyanide in $[Pd(CNCH_3)_4](PF_6)_2$, $[Pd_2(CNCH_3)_6](PF_6)_2$, $[Pt_2(CNCH_3)_6](BF_4)_2$, and $Pd(CNCH_3)_2I_2$ fall in the range 400.6–401.3 eV (Table II). Although the complexes **10**–**13** are only remotely related to $Pd_2(dpm)_2(\mu\text{-}CNCH_3)Cl_2$, **8**, and simplifying assumptions which lead to eq 3 may not apply, one can make the qualified judgement that, as expected on the basis of simple valence bond arguments (Ia and Ib), the charge on the nitrogen in the bridging methyl isocyanide is more negative than the charge on nitrogen in terminally bound $CNCH_3$.

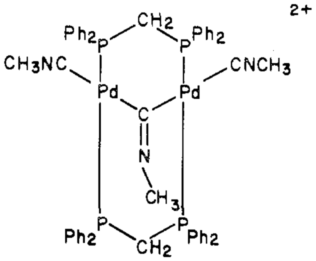
Ia



Ib

Avanzino and Jolly[29] reported gas-phase oxygen 1s data for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $Co_2(CO)_8$, complexes which contain both terminal and bridging carbon monoxide. The spectra could be resolved into two peaks of appropriate intensity which correspond to the two modes of CO coordination. In each case, the lower binding energy peak could be attributed to the bridging carbonyl ligand. Oxygen 1s peak separations were ca. 1.2 eV.

In the above comparisons of isocyanide complexes terminally bound and bridging methyl isocyanide are not present in the same complex, so complications regarding changes in *V* and *B* arise. $[Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2](PF_6)_2$, **9**, offers the best opportunity to compare N 1s spectra of terminal and bridging $CNCH_3$ ligands because both are present in the same molecule so differences in *V* and *B* terms are minimal. The N 1s spectrum of **9** is shown in Figure 4. Although two resolved N 1s peaks were not found, the peak observed was consistently skewed to lower binding energies and broadened compared to peaks in spectra of complexes in which a single form of $CNCH_3$ was present. Therefore as shown in Figure 3, the peak was deconvoluted into two Gaussian curves with enforced area ratio of 2:1. The two resultant peaks have binding energies of 401.0 and 399.9 eV. As in the previous comparisons, the N 1s binding energy of the bridging $CNCH_3$ is lower than that of the terminally bound $CNCH_3$. It is surprising that the N 1s binding energies of $Pd_2(dpm)_2(\mu\text{-}CNCH_3)Cl_2$, **8**, and $[Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2](PF_6)_2$, **9**, which are of dissimilar charge, are essentially identical.



9

$[Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2](PF_6)_2$, **9**, can be synthesized from $[Pd_2(CNCH_3)_6](PF_6)_2$, **11**, by reaction with dpm. Although **9** has three fewer $CNCH_3$ ligands, which are moderately good π-back-bonding ligands, and two dpm bridging ligands, which are excellent σ donors, the Pd $3d_{5/2}$ binding energies of **9** and **11** are the same within experimental error. In a recent review Brisk and Baker[30] speculated that ligand core level satellites due to M → L charge transfer should be found in the X-ray photoelectron spectra of complexes with π-acceptor ligands. Several investigators have reported the presence of C 1s satellites in carbonyl complexes[30,31] and there has been one report of C 1s satellites in hexacyano complexes.[32] In the present study, spectra of the C 1s (300–280 eV) and N 1s (415–395 eV) regions of $[Pd_2(CNCH_3)_4](PF_6)_2$ (**10**), $[Pt_2(CNCH_3)_6](PF_6)_2$ (**11**), and $[Pt_2(CNCH_3)_6](BF_4)_2$ (**12**) were carefully examined, but no satellites were found ($S/N \approx 15\text{–}30$). Neither were satellites encountered in the metal core level spectra. While we believe satellites are likely present in these regions, these results indicate that their intensities relative to the primary peak are less than 0.05.

In summary, the results indicate that insertion in the Pd–Pd bonds of $Pd_2(dpm)_2Cl_2$ and $Pd_2(dam)_2Cl_2$ occurs with minimal changes in the atomic charges. Thus these reactions offer excellent examples of the application of the Pauling principle of electroneutrality. In view of these results it would appear unprofitable to discuss these reactions in terms of an oxidation state change for the palladium centers. Rather we prefer to emphasize the similarity of $Pd_2(dpm)_2Cl_2$ or $Pd_2(dam)_2Cl_2$ with their insertion products. In all cases the palladium centers are surrounded by 16 valence electrons, have a square-planar geometry, and appear to undergo facile ligand substitution. Finally it should be noted that similar bonding considerations must pertain to the platinum analogues, several of which have been reported.[3,6,7,33]

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Registry No. **1**, 64345-29-5; **2**, 67415-28-5; **3**, 64345-32-0; **4**, 66706-37-4; **5**, 67414-86-2; **6**, 71171-28-3; **7**, 71171-39-6; **8**, 64345-34-2; **9**, 68228-56-8; **10**, 38317-62-3; **11**, 56116-48-4; **12**, 60767-37-5; **13**, 30142-15-5.

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Hyperfine Quadrupole Coupling and π Bonding in Dodecahedral Chelates of Hafnium(IV)

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Time-differential-perturbed angular correlation experiments using the 133–482-keV γ–γ cascade of the ^{181}Ta nucleus have been performed in order to determine the hyperfine quadrupole couplings in various d^0 dodecahedral chelates of hafnium(IV). The hyperfine data are analyzed within the frame of both the point-charge model considering the actual geometry of the coordination polyhedra and the valence bond picture. Our analysis indicates a significant contribution of π bonding to the stabilization of these systems. The charge transferred onto the metal via $\pi \rightarrow d_{x^2-y^2}$ interactions is estimated at about 20% of the overall charge donated by the ligands in the tetrakis(*N*-benzoyl-*N*-phenylhydroxylaminato)hafnium(IV) and 16% in the tetrakis(*N*-nitroso-*N*-phenylhydroxylaminato)hafnium(IV). The overall charge donated by the ligands onto the valence orbitals of the metal stands between -0.7 and $-1.2e$, which attests the important ionic character of the hafnium–oxygen bonds in these eight-coordinate chelates.

Introduction

The decisive role played by d–π interactions in determining the stereochemistry of eight-coordinate dodecahedral complexes of transition elements was first suggested by Orgel.[1] Initially developed for complexes of d^1 or d^2 metal ions, Orgel's ideas have been later on extended to d^0 complexes and may be summarized as follows: in dodecahedral complexes of the type MA_4B_4, the distribution of the two different ligands onto the two nonequivalent coordination sites A and B[2] should depend on both the electronic configuration of the metal ion and the relative π-bonding capabilities of the ligands. For d^0 complexes, the better π-donor ligands (or ligating atoms for polydentate ligands) should occupy the B positions on the dodecahedron. The inverted situation would be expected in complexes of d^1 or d^2 metal ions. Such predictions are based on the following ligand-field argument: in dodecahedral complexes of D_{2d} (or lower) symmetry, the b$_1$ ($d_{x^2-y^2}$) level is more stable than any other and is capable of forming strong π bonds with the ligands placed on the B coordination sites. However, as pointed out by Archer, Bonds, and Hamilton,[3] a full picture of π bonding in dodecahedral complexes of transition metals must include all the d orbitals of the central atom. Thus, according to the results of angular overlap calculations, both the A and B ligands would be substantially involved in π-bonding interactions.[3] From the experimental point of view, several structures obeying completely[3–6] or only partially[7] Orgel's rules have been reported, but the number of MA_4B_4 complexes whose structures are known is still too small for valid conclusions to be reached about the importance and the nature of π bonding in these molecular species.

The determination of the electric field gradient (efg) at the nucleus of the central atom can provide a new insight into metal–ligand bonds in dodecahedral complexes. Effectively, the efg tensor is directly related to the charge distribution around the nuclear probe. Measurements of electric field gradients in dodecahedral d^0 complexes are of particular interest for (i) the charge distribution around the metal is expected to be significantly influenced by any eventual charge transfer from the ligands onto the $d_{x^2-y^2}$ orbital of the metal via specific d–π interactions and (ii) this influence would result in specific modifications of the efg tensor which could be reasonably interpreted by using a simple efg model such as the donated-charge model.[8] Moreover, such experiments can provide valuable information concerning the importance of π-bonding effects in complexes involving identical monodentate or symmetrical bidentate ligands to which Orgel's rule does not apply.

For eight-coordinate d^0 complexes of the group 4B transition metals, the study of the angular correlations of the γ rays emitted from the radioactive ^{44}Ti and ^{181}Hf isotopes is the only way available for determining accurately both the magnitude and the asymmetry of the electric field gradient at the site of the central nucleus. When the quadrupole moment of the intermediate level in a γ_1–γ_2 nuclear cascade couples with an electric field gradient, one observes a perturbation in the anisotropic angular distribution of the intensity of the second radiation (γ_2) with respect to the direction at which the first radiation (γ_1) is detected. In order to obtain the values of the quadrupole-coupling parameters, we determined the time evolution of this perturbation during the lifetime of the intermediate nuclear state by performing time-differential-perturbed angular correlation (TDPAC) experiments. Typically, when ^{181}Hf is used as nuclear probe, this technique allows one to measure quadrupole frequencies ω_Q within the range 20–200 Mrd·s^{-1} with an accuracy of about 1%. TDPAC measurements of electric field gradients in several chelates[9–13] and organometallic compounds[14] of hafnium(IV) have been already reported. Recently, Vulliet, Baudry, Boyer, and Tissier[11] have been able to give a coherent interpretation of the quadru-

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