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X-RAY PHOTOELECTRON SPECTRA OF PALLADIUM AND PLATINUM COMPLEXES OF CARBENOID AND RELATED LIGANDS

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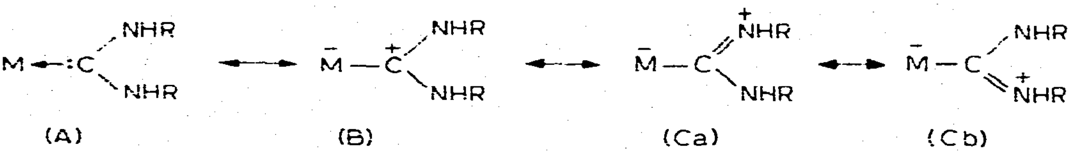
Summary

X-ray photoelectron spectra have been obtained for a series of palladium and platinum complexes involving carbenoid and related ligands. The Pt $4f_{7/2}$ and Pd $3d_{5/2}$ binding energies indicate that carbenoid ligands are better donors of electron density to the metal than methyl isocyanide. The C 1*s* binding energies show that the carbenoid carbon atoms are less positively charged than the carbon atom of coordinated methyl isocyanide.

Introduction

The chemistry of transition metal complexes of carbenoid ligands has developed rapidly in recent years [1,2]. In our laboratories we have been particularly interested in the palladium and platinum complexes of ligands obtained by addition of nucleophiles to coordinated isocyanides [3—5]. Such complexes have been alternatively described as metal carbenes [1,2] (A) stabilized carbonium ions (B) [8,9] or metallated amidinium ions (C) [3].



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Various physical methods have been employed in an effort to distinguish between the possible bonding schemes and charge distributions suggested by the valence bond structures. An early infrared study of chromium and tungsten pentacarbonyl alkoxycarbenoid complexes [6] led to the conclusion that an alkoxycarbenoid ligand is both a strong σ donor and π acceptor. On the other hand, single crystal X-ray structural results on aminocarbenoid complexes [4,7] have been interpreted to indicate that these carbenoid ligands are strong σ donors but at best weak π acceptors. Carbon-13 NMR chemical shifts for carbenoid-carbon are similar to those found for free carbonium ions leading some investigators [8,9] to describe the complexes as a metal stabilized carbonium ions (B). Recently, a ^{57}Fe Mössbauer study involving carbenoid complexes was reported [10] and interpreted to indicate that diamino carbenoid ligands are good σ donors but weak π acceptors.

The various possible ground state charge distributions in carbenoid complexes make them interesting and appropriate candidates for X-ray photoelectron spectroscopy (XPS) because relative changes in the binding energy at a given atomic center in a closely related series of molecules can often be related directly to changes in the charge distribution of the ground state [11—13]. The deconvoluted C 1*s* X-ray photoelectron spectrum of $Cr(CO)_5[C(CH_3)(OCH_3)]$ in the gas phase has been reported [14]. However, the measurement of the C 1*s* and metal binding energies for a single compound provides little general insight into the charge distribution in carbenoid complexes and the relative effect of carbenoid ligands upon the electron density on the metal. Therefore, we have obtained high resolution solid-state XPS data for a series of carbenoid complexes of palladium and platinum. In addition to the carbenoid complexes investigated, we also report the XPS data for several methyl isocyanide complexes. To our knowledge, no previous XPS investigations of isocyanide complexes have been reported.

Experimental

All materials investigated were prepared according to previously published procedures [5,15—17] or purchased and used without further purification. All the compounds investigated are air stable. X-ray photoelectron spectra were obtained with a McPherson ESCA 36 Photoelectron Spectrometer equipped with a Sargent—Welch turbomolecular pumping system. Both Al-K_α (1486.6 eV) and Mg-K_α (1253.6 eV) radiation sources were used in conjunction with a 7.9 cm anode shield. Samples were mounted on doublestick tape (3M Company) or lightly pressed onto aluminium metal planchettes which had been previously etched with a hydrochloric acid solution and rinsed with distilled water. Standardization was achieved using MoO_3 (Mo $3d_{5/2}$, 232.5 eV) and/or a characteristic component of the C 1*s* spectrum (obtained in some cases by curve deconvolution) previously standardized with the Mo $3d_{5/2}$ line in MoO_3. The C 1*s* binding energy in coordinated triphenylphosphine was found to be 285.0 eV. Binding energy values reported are the average of two or more determinations, and the average standard deviation for a given reported binding energy is ±0.24 eV or less. Curve deconvolutions and relative area ratios were determined with a Dupont 310 Curve Resolver.

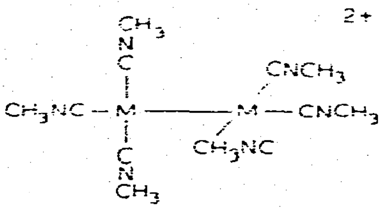
Results and discussion

Platinum binding energies

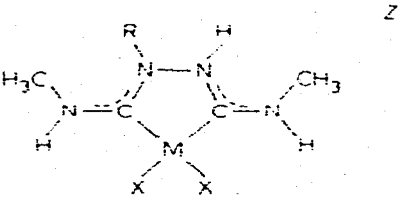
Table 1 lists the XPS data for the platinum complexes investigated. All of the carbenoid complexes (3,4,7,9,10,11,13,15,16) are produced by nucleophilic addition to coordinated methyl isocyanide [5]. The XPS data for two isocyanide complexes of platinum, 2 and 14, are also given in Table 1. The Pt $4f_{7/2}$ binding energies of 2 and 14 imply a marked decrease of electron density on the metal relative to the carbenoid complexes. The addition of four equivalents of methylamine to 14 leads to compound 7, the only tetrakis-carbenoid platinum complex investigated. Differences in binding energy due to lattice effects should be minimized for 7 and 14 because both are dipositive cations isolated as their PF_6^- salts. Thus, the large decrease in the Pt $4f_{7/2}$ binding energy (2.0 eV) in going from 14 to 7 presumably reflects the much stronger total electron donating ability of the carbenoid ligand versus the isocyanide ligand. Additional evidence for the differing electron donating and accepting ability of carbenoid and isocyanide ligands is provided by compound 2. This formally platinum(I) complex has a Pt $4f_{7/2}$ binding energy similar to 7, and significantly higher than 3 and 4.

Other comparisons of the effect of a carbenoid ligand on the metal charge relative to other ligands can be made from the data in Table 1. Compounds 4, 6, 8 and 12 are all formally square planar platinum(II) compounds containing the *cis*-$PtCl_2$ fragment. Variations in relaxation effects should be minimized in this series, and the differences in metal binding energies should be primarily due to differences in the electron donating ability of the coordinated ligands. The data for 4, 6, 8 and 12 indicate that the chelating carbenoid ligand is as good or better donor of electron density than bipyridyl, PR_3 or Cl^-. This result is reinforced by the Pt $4f_{7/2}$ binding energy for compound 3.

In light of the ~1 eV decrease in binding energy when two Cl^- ligands are replaced by carbenoid ligands in going from 12 to 4 it is somewhat surprising that the binding energy of 7 is similar to 12. The possibility that there are greater relaxation or reorganization effects on the platinum binding energies for species 3, 4, 5, and 6 cannot be ruled out, although differences in relaxation energies are usually minimized for a closely related series of molecules [18,19]. It is also important to note that in 7 each carbenoid ligand must be *trans* to another carbenoid



(I a) M = Pt
(I b) M = Pd



(II a) M = Pt, X = Cl, R = H, Z = 0
(II b) M = Pt, X = Br, R = H, Z = 0
(II c) M = Pd, X = Cl, R = H, Z = 0
(II d) M = Pd, X = Br, R = H, Z = 0
(II e) M = Pt, X = CNCH$_3$, R = nothing, Z = +1

TABLE 1

BINDING ENERGIES FOR PLATINUM COMPLEXES

Compound		Structure[a]	Pt $4f_{7/2}$ (eV)[b]	C 1s
1	Pt metal		71.2(1.6)[c], 71.1[d], 71.0[e]	
2	$[Pt_2(CNCH_3)_6][PF_6]_2$	Ia	73.6(1.9)	287.1(1.7), 285.0(1.7)
3	$C_4H_{10}N_4PtBr_2$	IIb	72.6(2.0)	286.6(1.8), 285.0(1.9)
4	$C_4H_{10}N_4PtCl_2$	IIa	72.7(1.8)	286.6(1.8), 285.0(2.0),
5	$Pt(bipy)Cl_2$		72.9(1.8)	285.0(1.7)
6	*cis*-$Pt[P(C_2H_5)_3]_2Cl_2$		72.9(1.9)	284.8(1.7)
7	$[Pt\{C(NHCH_3)_2\}_4][PF_6]_2$		73.2(2.0)	286.6(1.9), 285.0(1.9)
8	*cis*-$Pt[P(C_6H_5)_3]_2Cl_2$		73.1(1.9)	285.0(1.6)
9	$[C_4H_9N_4Pt(CNCH_3)_2]Cl \cdot 4H_2O$	IIc	73.2(2.3)	
10	$[C_4H_9N_4Pt(CNCH_3)_2]I \cdot 4H_2O$	IIc	73.2(1.9)	
11	$[C_4H_9N_4Pt(CNCH_3)_2][B(C_6H_5)_4]$	IIc	73.2(2.2)	
12	K_2PtCl_4		73.4(2.0)	
13	*trans*-$[Pt(CNCH_3)_2\{(C(NHCH_3)(SCH_2CH_3)\}][PF_6]_2$		74.1(1.8)	
14	$[Pt(CNCH_3)_4][PF_6]_2$		75.2(2.1)	287.5(1.8), 285.0(1.8)
15	$C_4H_{10}N_4PtBr_4$		73.2(2.2)	286.7(1.9), 285.0(1.9)
16	$C_4H_{10}N_4PtCl_4$		73.3(1.9)	286.5(1.9), 285.0(1.9)

[a] See structure key. [b] Binding energies are in electron volts. The number in parentheses is the full width of the peak at half maximum (FWHM). [c] This work. [d] Ref. 30. [e] Ref. 31.

ligand. Structural studies show that carbenoid ligands exert a strong *trans* influence [4]. Table 1 shows that the binding energy for the *trans*-dicarbenoid complex (13) is about 1 eV larger than the energies for the related *cis* complexes (9, 10, 11). If the Pt binding energy is indeed sensitive to the stereochemistry of the carbenoid ligands then the expected decrease of ~1 eV per pair of Cl^- ligands of $PtCl_4^{2-}$ (12) replaced by carbenoid ligands will be nearly counterbalanced by an ~1 eV increase for *trans* geometry, and the binding energies of 7 and 12 will be little different.

Replacing the *cis* halogens in compounds 3 and 4 by CH_3NC produces complexes which are acidic [3,5] and lose a proton to give the cationic species 9, 10, and 11. These compounds contain the same cation in different environments. The electronic spectra of the solids 9 and 10 contain additional electronic transitions (at 21000 and 17000 cm^{-1} respectively) that are not present in 9, 10 and 11 in various solvents or in 11 in the solid state. In addition 9 and 10 show color changes from red to green upon dehydration. It is likely that 9 and 10 contain cations which are associated through metal—metal interactions [5]. However, these interactions do not manifest themselves in the XPS spectra. Not only are the Pt $4f_{7/2}$ binding energies nearly identical in 9, 10 and 11 but the Pt $4f_{7/2}$ and I $3d_{5/2}$ binding energies of 10 in hydrated and dehydrated form are not detectably different.

The results in Table 1 also demonstrate the inherent difficulties and ambiguities in using XPS data to probe chemical bonding. For example, the binding energies of dicarbenoid complexes 3 and 4 are ~0.6 eV less than those of 9, 10, and 11 which are in turn 0.9 eV less than that of 13. The observed binding energy increases for these three kinds of dicarbenoid complexes could be due to the change in the overall charge on the complex from 0 to +1 to +2, to the change in the ligands, and/or to the change in stereochemistry about the metal. The relative importance of each of these changes to the observed differences in binding energy cannot be specified from the XPS data.

Addition of halogen to complexes 3 and 4 produces the formally platinum(IV) complexes 15 and 16. The increase in platinum binding energy of 0.6 eV on oxidation is much less than the increase of ~2.5 eV reported for oxidative addition of halogen to other square planar complexes [20].

Palladium binding energies

The XPS data obtained for the palladium complexes are presented in Table 2. A comparison of the Pd $3d_{5/2}$ binding energies for the complexes 21, 22, and 23 which contain the *cis*-$PdCl_2$ unit indicates that the chelating carbenoid is as good a donor of electron density as the other ligands, similar to the results for the platinum series. The relatively high Pd $3d_{5/2}$ binding energies for the two isocyanide complexes 18 and 25 are consistent with the Pt $4f_{7/2}$ binding energies found for the isostructural platinum complexes, 2 and 14, and support the classification of the isocyanide ligand as a moderate π acceptor of electron density. As found for the platinum analogs, addition of four equivalents of methylamine to 25 produces the tetracarbenoid complex 19, and decreases the Pd $3d_{5/2}$ binding energy markedly.

Other binding energies

The C 1*s* spectra of the methyl isocyanide complexes 2, 14, 18 and 25 dis-

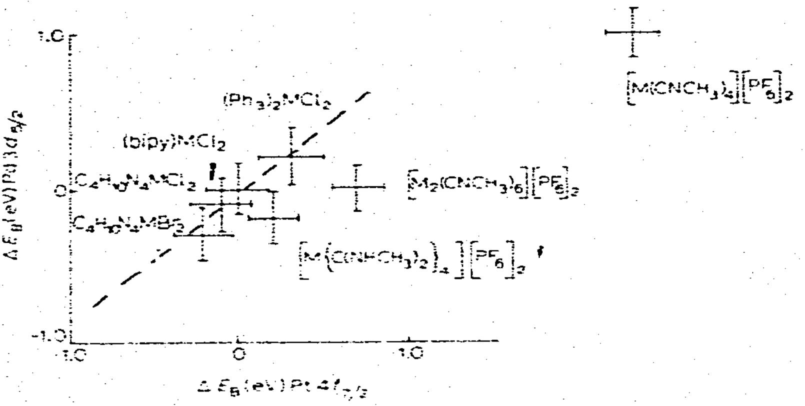


Fig. 1. Plot of ΔE_B (eV) Pd $3d_{5/2}$ vs. ΔE_B (eV) Pt $4f_{7/2}$. The binding energy of M(bipy)Cl_2 had been chosen as the arbitrary reference point. The horizontal and vertical bars for each compound indicate the estimated error in the measurement.

played two distinct peaks at ~287 and 285.0 eV with an area ratio between 1.2 : 0.8 and 0.7 : 1.3 (higher E_B/lower E_B). Relative intensities varied according to the sample support material, binding energy standardization procedure and thickness of the sample. X-ray photoelectron spectra of CH_3NC in the solid and gas phase were reported by Barber et al. [21]. Two peaks were found in the gas phase at 293.8 and 293.1 eV, and two deconvoluted peaks were reported for the solid state at 287.5 and 287.0 eV. The binding energies found in this investigation for coordinated CH_3NC (~287 eV) are approximately the same as that reported for solid CH_3NC. The peaks were not deconvoluted because the FWHM values were not unusually large.

All complexes involving carbenoid ligands gave broad C 1s spectra (FWHM * ~2.4 eV) centered at 285.5—285.8 eV. Curve deconvolution for the "simpler" carbenoid complexes such as 7 gave an average binding energy for the carbenoid carbon of 286.5 ± 0.4 eV. Similar values were obtained for samples mounted on aluminum plates and for thick samples on double-stick tape. No attempts

TABLE 2

BINDING ENERGIES FOR PALLADIUM COMPLEXES

Compound		Structure	Pd $3d_{5/2}$	C 1s
17	Pd metal		335.1(1.6)	
18	$[Pd_2(CNCH_3)_6][PF_6]_2$	Ib	338.1(1.7)	286.9(1.7), 285.0(1.7)
19	$[Pd\{C(NHCH_3)_2\}_4][PF_6]_2$		337.9(1.9)	286.4(1.9), 285.0(1.9)
20	$C_4H_{10}N_4PdBr_2$	IIc	337.8(1.7)	
21	$C_4H_{10}N_4PdCl_2$	IId	338.0(1.8)	
22	Pd(bipy)Cl_2		338.1(1.6)	285.0(2.1)
23	K_2PdCl_4		338.2(1.5)	
24	*trans*-Pd$[P(C_6H_5)_3]_2Cl_2$		338.2(1.5)	285.0(1.6)
25	$[Pd(CNCH_3)_4][PF_6]_2$		339.1(1.8)	287.2(2.0), 285.0(1.9)

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* FWHM = full width at half maximum.

were made to deconvolute the C 1*s* spectra of 9, 10 or 11. Since the carbenoid C 1*s* binding energies reported are determined by deconvolution and involve inherently large standard deviations, internal comparison of these binding energies cannot be made. However, a general comparison of the binding energy difference between isocyanide carbon and carbenoid carbon is valid. As expected, the addition of a nucleophile to the methyl isocyanide ligand decreases the binding energy of the coordinated carbon significantly.

Resonance structures Ca and Cb suggest the possibility of distributing positve charge over the hetero atoms of the carbenoid ligand. In this study the atoms bound to the carbenoid carbon were N and S. The N 1*s* binding energy of 399.8 ± 0.4 eV for 7 and 19 is slightly higher than those observed for most amines and slightly lower than common values for amides [22]. The S $2p_{3/2}$ binding energy of 163.9 eV for 13 is more positive than in thioethers such as $(C_6H_5)S(t\text{-}Bu)$ (162.4 eV) [23].

It has been demonstrated previously [24] that a plot of ΔE_BPt $4f_{7/2}$ versus ΔE_BPd $3d_{5/2}$ for corresponding platinum and palladium halide and pseudohalide complexes yields a straight line with a slope of unity. A plot of ΔE_BPt versus $\Delta E_B Pd$ (referenced to M(bipy)Cl_2) for the two series of complexes is shown in Fig. 1. A least-squares fit of the data for the series $M(PPh_3)_2Cl_2$, M(bipy)-Cl_2, $C_4H_{10}N_4MCl_2$, and $C_4H_{10}N_4MBr_2$ produces a straight line of slope 0.93 ± 0.04. This plot implies that the chelating carbenoid ligand is a slightly better σ donor than bipyridyl or triphenylphosphine. The deviations of $[M\{C(NHCH_3)_2\}_4]^{2+}$, $[M_2(CNCH_3)_6]^{2+}$ and $[M(CNCH_3)_4]^{2+}$ from the line in Fig. 1 clearly suggest that these dications are fundamentally different from the neutral compounds containing the *cis*-MX_2 fragment. The deviations to larger ΔE_B for isocyanide complexes of platinum compared to palladium (Fig. 1) contrast with a previous study [24] in which smaller ΔE_B values for platinum were observed for π-acceptor ligands.

Conclusions

The data obtained clearly indicate that the carbenoid ligands studied are good donors of electron density to palladium and platinum. It can be inferred that the carbenoids are, at best, weak π acceptors. In comparison, the isocyanide ligands remove charge from the metal with the removal being greater for platinum complexes than the palladium analogs. These results are consistent with isocyanides being moderate π acceptors [26].

The XPS results also show that a carbenoid carbon is less positively charged than the carbon of a coordinated methyl isocyanide molecule. Recent non-parameterized molecular orbital calculations [27] on $(OC)_5Cr[C(CH_3)(OCH_3)]$ have likewise concluded that the carbenoid carbon atom is not positively charged. The primary reasons for postulating a positively charged carbon atom in carbenoid ligands have been the reactivity of such ligands with nucleophiles [1,2,28] and the similarity of the ^{13}C chemical shifts to carbonium ions [8,9]. The reactivity with nucleophiles can be rationalized by the nature of the lowest unoccupied molecular orbital (LUMO) of the complexes [27], but the ^{13}C chemical shifts have yet to be adequately explained.

The metal binding energies for closely related pairs of compounds increase with increasing formal metal oxidation state[*]. Thus, the Pd $3d_{5/2}$ and Pt $4f_{7/2}$ binding energies are lower in the metal(I) dimers 18 and 2 than in the tetrakis(methyl isocyanide)metal(II) species 25 and 14. Similarly 15 and 16 exhibit higher Pt $4f_{7/2}$ binding energies than do 3 and 4.

Finally, there is some evidence from Tables 1 and 2 that *cis* and *trans* complexes of four coordinate platinum and palladium may exhibit detectably different metal binding energies. This point needs to be verified by a more extensive study of *cis* and *trans* isomers of a series of ligands.

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[*] Similar results have been observed for other complexes of metals of the second and third transition series. See for example ref. 29.