Ultraviolet Photoelectron Spectra of Square-Planar Complexes of Nickel Triad Metals. 3.[1a] He I and He II Spectra of trans-[(PEt₃)₂MXY] (M = Pd, Pt; X = Y = C≡C—H, C≡C—CH₃, C≡N; X = Cl, Y = C≡N) and Hartree–Fock–Slater Calculations on Model Compounds

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Ultraviolet photoelectron (UP) spectra of the title compounds and Hartree–Fock–Slater (HFS) MO calculations for the model compounds trans-[(PH₃)₂MXY] (M = Pd, X = Y = C≡C—H, C≡C—CH₃, C≡N and X = Cl, Y = C≡N; M = Pt (relativistic effects included), X = Y = C≡C—H and X = Cl, Y = C≡N) are reported. The upper valence bands in the spectra can be assigned in good agreement with the HFS calculations. Among the features demonstrated is a strong π interaction between metal and filled acetylide or cyanide ligand orbitals both in- and out-of-plane. No indication is found, however, for any significant amount of ML π back-bonding. Generally, a strong similarity exists between observed energy levels for corresponding Pd and Pt complexes and this is reflected in the HFS calculations. Also, for the Pt complexes, relativistic corrections to be applied to the nonrelativistic results appear to be very small.

Introduction

Square-planar complexes of palladium and platinum, which are among the earliest reported types of organometallic compounds, have been investigated extensively by both synthetic and spectroscopic means[1,2] and yet still continue to provide a challenge to both experimental and theoretical chemistry (see, e.g., ref 3). Because of the many interesting features of these compounds, insight into their electronic structure is of great importance, so it is surprising that, to date, only a few ultraviolet photoelectron (UP) studies on these compounds have been reported.[4-6]

In a previous study we reported the UP spectra of a series of square-planar complexes of Ni, Pd, and Pt with a σ-bonded phenyl group.[5] It was demonstrated that π interactions between ligand and metal orbitals of proper symmetry lead to a very low IE for the first band in the spectrum. With Pd and Pt, the band due to the d_z² orbital was also found at relatively low IE, probably due to σ-antibonding interactions, and this appears to correlate with the ability of related compounds to form donative metal–metal bonds with post-transition metals using this orbital.[5]

It is of obvious interest to test the generality of these observations in a wider range of square-planar divalent nickel triad complexes of the type [L₂MX₂]. In general, an assessment of the role of relativistic effects in third-row transition and post-transition metals is of great importance in discussing both the spectroscopy and the chemistry of these metals.[7] Therefore, the combination of UP spectroscopy and relativistic HFS calculations can yield detailed information regarding the bonding and the role being played by relativistic effects. Thus, we were prompted to investigate a series of bis(triethylphosphine) acetylide and cyanide complexes of Pd and Pt by means of UP spectroscopy in combination with HFS MO calculations. These particular compounds (which have the necessary volatility to be studied by UPS) were chosen for the following reasons.

First, the acetylide π orbitals have the proper symmetry to interact with d orbitals as well as an orbital energy[8] close to that indicated by UPS for transition-metal d orbitals in a wide range of organometallic complexes.[9] Therefore, possible π interaction between metal and ligand orbitals is strongly favored, as it was with a σ-bonded and rotationally hindered phenyl group in the previous series.[5]

Second, by using a PH₃ instead of a PEt₃ ligand, one obtains model compounds which are among the smallest molecules in which effects such as metal–ligand π interaction and the energy of d_z² orbital can be studied. Thus performing HFS calculations is much facilitated.

Finally, this class of compounds exhibits an interesting chemistry. By using ligands with two terminal acetylide moieties, inorganic polymers have been synthesized.[10-13]

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Also it has been demonstrated that metal-acetylide bonding is the first step in polymerization of PhC≡CH induced by either Pt(PPh₃)ₙ, [(PPh₃)₂PtCl₂], or [(PPh₃)₂Pt(C≡CPh)₂].[14]

Experimental Section

The compounds [(PEt₃)₂MX₂] (M = Pd, Pt; X = C≡C—H, C≡C—CH₃, C≡N) were synthesized according to literature procedures.[15,16] The compounds [(PEt₃)₂MCl(C≡N)] (M = Pd, Pt) were prepared by dropwise addition of 1 molar equiv of KCN dissolved in CH₃OH to a suspension of the corresponding dichloride complex[17] in CH₂Cl₂.

All compounds were sublimed prior to running the spectra, and purity and identity were checked by elemental analysis.

The spectra were recorded on a PS 18 Perkin-Elmer photoelectron spectrometer equipped with a hollow cathode Helectros Developments light source. All spectra were calibrated with respect to He, Ar, and Xe as internal references.

Calculations and Geometry. The calculations were carried out by using the Hartree–Fock–Slater method of Baerends et al.[18] This method differs from the Hartree–Fock method in using Slater's local exchange approximation. The resulting equations are then solved in an LCAO formulation, and the matrix elements are calculated by a numerical integration scheme. The exchange scaling factor was taken as α = 0.7. A double-ζ basis was used except for phosphorus d orbitals which were represented with a single-ζ basis (ζ = 1.3) and metal d orbitals for which a triple-ζ basis was employed. The triple-ζ basis was used since test runs indicated that results were somewhat dependent upon the basis set used for metal d orbitals. The calculated percentages of π acetylide character for the 3a₂ orbital in [(PH₃)₂Pd(C≡C—H)₂] differed by 6.5% (on a total percentage on the order of 20/25%) between double-ζ and triple-ζ runs. Otherwise, there were no significant differences between the double-ζ and triple-ζ results.

In the calculation of the Pt complexes the perturbation method of Snijders et al.[19] was used to analyze relativistic corrections to be applied to the numerical results.

Geometrical parameters were taken as follows. For all complexes the bond length R(P–H) was taken to be the same as in the free PH₃ ligand.[20] The angle ∠(HPH) was chosen to be 105° to correlate with the structure of a PMe₃ ligand coordinated to an oxygen atom.[21] Some test calculations were performed on the ligands. The first IE for the PH₃ molecule was calculated to be 10.23 eV with an angle of 93° (value for the free ligand[20]) and 9.41 eV with the value of 105°. The first IE for PMe₃ with ∠(CPC) = 105° was 7.64 eV (experimental value 8.62 eV). For the acetylide ligands R(C≡C) = 120 pm was taken in accord with crystallographic X-ray results for these and related ligands,[22] while R(C–H) was taken as 106 pm.[23] For the C≡C—CH₃ ligand the values taken were aliphatic R(C–C) = 146 pm, R(C–H) = 109 pm, and ∠(HCH) = ∠(CCH) = 109°.[23] Since the ionic radii of Pd²⁺ and Pt²⁺ are quite similar,[2] R(M–P) = 230 pm[24] and R(M–C) = 200 pm[25] for M = Pd and Pt. The geometry of the cyanide complexes was taken as that of the acetylide complexes with R(C≡N) = 116 pm.[23] R(M–Cl) was taken as 229 pm[26] for the (Cl)(C≡N) com-

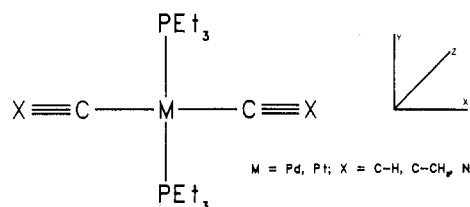**Figure 1.** Structure of the molecules with axis system used in the discussion. The structure of the (Cl)(C≡N) compounds is similar to that of the dicyanide compounds with one cyanide ligand replaced by a chloride.

plexes with other parameters similar to those in the dicyanide complexes.

The calculations were performed in C_{2v} symmetry. For the bis(acetylide) and bis(cyanide) complexes ligands were oriented so that the mirror planes pass through both the C–M–C and P–M–P axes, perpendicular to the coordination plane of the molecule. For the (Cl)(C≡N) compounds one mirror plane is coincident with the coordination plane, while the other is perpendicular to it and passes through the Cl–M–C axes.

Contour plots have been drawn by using contour lines for wave function values of 0.0, 0.02, 0.05, 0.1, 0.2, and 0.5.

Results and Discussion

He I and He II photoelectron spectra of the acetylide, dicyanide, and chloride–cyanide complexes of Pd and Pt have been obtained and will be discussed in three separate sections. Unfortunately, the analogous Ni complexes[11] were found to decompose at elevated temperatures and no spectra of these could be recorded.

Throughout the discussion for each ionization a canonical molecular orbital is supposed to exist that indicates the electron to be ejected by the ionization. Since in HFS theory the eigenvalues of the canonical MO's are not equal to the Koopmans' ionization energies (see ref 27), the ionizations will be compared with transition states (removal of half an electron) calculated in the Slater Xα scheme by using Slater's method.[28] However, in many cases (costly) transition-state calculations result in an almost constant shift for all orbitals. Thus, in some cases transition states have been calculated only for some typical orbitals, and in other cases no transition-state calculations have been performed.

Although the HFS calculations have been carried out in C_{2v} symmetry (see Experimental Section), a center of inversion will sometimes be assumed in the discussion. This, however, only involves the trivial operation of rotating a phosphine or methyl group and does not affect the argumentation at all.

Breakdown into Fragments. It is convenient to discuss the molecules (Figure 1) as consisting of several fragments, and the molecular orbitals as consisting of fragment orbitals. Of these, the simplest fragment is the formal M²⁺ ion (M = Pd, Pt). This ion possesses four doubly occupied d orbitals in its valence shell. Furthermore, empty s and p orbitals and, especially, the empty $d_{x^2-y^2}$ orbital, located along the σ-bond axes in the molecule, are capable of accepting charge from the ligand fragments.

In mutual trans position are two phosphine molecules, whose relevant orbitals are the two lone-pair-type orbitals (n$_P$) and the higher σ$_{P–C}$ orbitals (e in local C_{3v} symmetry). In Figure 2a the interaction diagram for the (PEt₃)₂M²⁺ fragment is presented. The two lone-pair type orbitals split into a gerade and an ungerade combination, the first able and the second unable to mix with the empty $d_{x^2-y^2}$ orbital

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$(PEt_3)_2M$

M $\quad d_{x^2-y^2}\quad 2(PEt_3)$

d_{z^2}
n_p^u $\quad n_p^u,\ n_p^g$
$d_{xy},\ d_{yz}$
Md
d_{xz}

a

σ_{M-P}^g

e_{P-C} $\quad e_{P-C}$

$(PEt_3)_2M(C{\equiv}C-H)_2$

$(PEt_3)_2M^{2+}$ $\qquad\qquad 2(C{\equiv}C-H)^-$

π_{op}^-

π_{op}^u $\quad \pi^u,\ \pi^g$

d_{yz} $\quad d_{yz}$
d_{xz}

b

π_{op}^+

$(PEt_3)_2M(C{\equiv}C-H)_2$

$(PEt_3)_2M^{2+}$ $\qquad\qquad 2(C{\equiv}C-H)^-$

$d_{x^2-y^2}$ $\quad \pi_{ip}^-$

d_{z^2} $\quad d_{z^2}$

π_{ip}^u $\quad \pi^u,\ \pi^g$
n_p^u
d_{xy} $\quad n_p^u$ $\quad \sigma^u,\ \sigma^g$

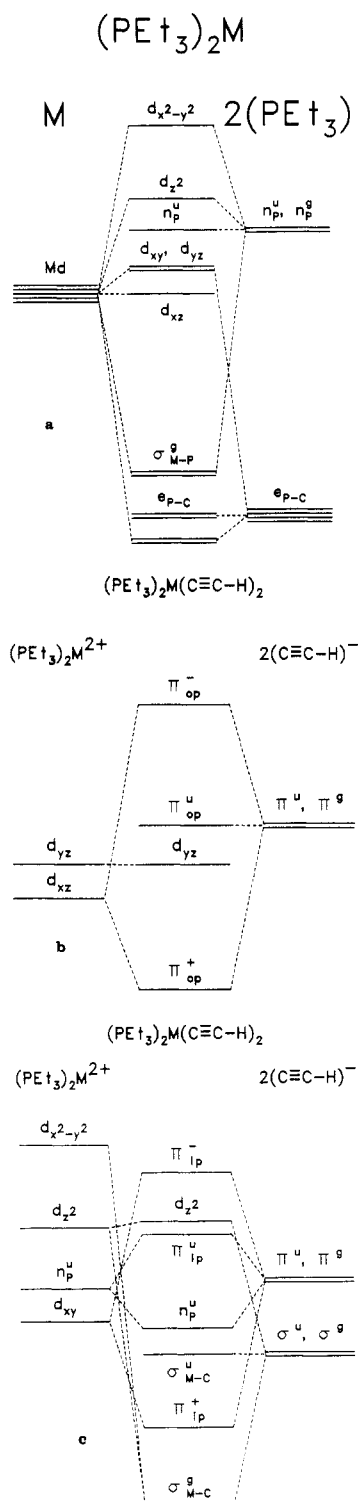σ_{M-C}^u

π_{ip}^+

c

σ_{M-C}^g

Figure 2. (a) Interaction diagram for fragment orbitals on the metal and phosphine fragments. (b) Interaction diagram for the out-of-plane fragment orbitals on the $(PEt_3)_2M^{2+}$ and the two $(C{\equiv}C-H)^-$ fragments. (c) Interaction diagram for the in-plane fragment orbitals on the $(PEt_3)_2M^{2+}$ and the two $(C{\equiv}C-H)^-$ fragments.

on the metal to provide M–P bonding. Due to the minor role of empty metal p orbitals in bonding, the ungerade combination will provide less M–P bonding than the gerade one.

The d_{z^2} orbital will be destabilized due to repulsive and antibonding interaction with the phosphorus lone pairs. Level interaction with the gerade σ_{P-C} orbitals will destabilize the d_{xy} and d_{yz} orbitals, although for these orbitals the possibility of stabilization due to π-back-bonding to-

ward the phosphine moieties exists in principle. This latter effect is expected to be insignificant. The d_{xz} orbital will have no interaction with phosphine orbitals.

The two acetylide or cyanide ligands in trans position provide six high-lying fragment orbitals. First, two σ orbitals interact in a fashion similar to the phosphorus lone pairs to provide M–C bonding. The other four orbitals are of local π symmetry. Only fragment orbitals for the acetylide fragments are presented (Figure 2b). Because of the complexity of the fragment interactions, they will be separated into two cases: in-plane and out-of-plane interactions. The out-of-plane interactions are depicted in Figure 2b. The two acetylide ligands provide two orbitals of local π symmetry that are also of π symmetry within the molecule. These split into a gerade and an ungerade combination. Due to the unavailability of M p orbitals for π bonding, the latter orbital is virtually nonbonding. The gerade combination, however, will interact with the d_{xz} orbital: this interaction results in one orbital that is antibonding between the fragments (π_{op}^-) and one that is bonding between the fragments (π_{op}^+). The M d_{yz} orbital is by symmetry unable to interact with acetylide orbitals.

In Figure 2c the in-plane fragment orbital interactions are presented. For the in-plane acetylide π orbitals the classification π will also be retained to emphasize the similar interactions for in- and out-of-plane acetylide π orbitals. As in the out-of-plane case the gerade combination of acetylide π orbitals mixes with the d_{xy} orbital to yield a bonding and an antibonding orbital [(π_{ip}^+) and (π_{ip}^-), respectively]. In contrast to the out-of-plane case, the ungerade acetylide π orbital can now interact with orbitals on the $(PEt_3)_2M^{2+}$ part. The n_p^u overlaps with the localized π orbital and is of about the same energy, and combinations of the two localized orbitals will arise. On the cyanide fragments two N lone pairs are also present but these, however, do not play a significant role in bonding.

The Cl fragment has been discussed extensively before;[6] here it may be noted that it possesses two nonbonding p orbitals, analogous to the π orbitals on the acetylide ligand, and one p orbital to provide M–Cl bonding.

Of indispensable use in the assignment of UP spectra of organometallic complexes are He I/He II intensity differences.[9] These are caused by differences in cross section at ionization from molecular orbitals with He I or He II photons. The cross section of a molecular orbital (as indicating a Koopmans' hole) is not, strictly speaking, equal to the sum of the respective contributions from the participating atomic (or fragment) orbitals (as two-center terms are involved), and the cross section is dependent upon the kinetic energy (and thus the IE) of the photoelectron. However, qualitative arguments in many cases have proven to be very enlightening, especially in cases of highly localized orbitals.

Thus, ionizations from metal d type orbitals are characterized by a strong enhancement in intensity upon going from the He I to the He II spectrum.[9] Halogen ionizations, on the other hand, will give rise to only very low intensity bands in He II.[29]

For the other ligand orbital ionizations the following rules hold:[30] σ orbitals on all fragments will have low He II intensities, because of the participations of C 2s, H 1s, or P 3s and 3p orbitals. C 2p type orbitals have about the same He I and He II cross section which means, however, that they will lose intensity on going from He I to He II

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Table I. Vertical Ionization Energies (eV) for $[(PEt_3)_2M(C{\equiv}X)_2]^a$

| | M, X | | | | | |
	Pd, C-H	Pt, C-H	Pd, C-CH$_3$	Pt, C-CH$_3$	Pd, N	Pt, N
π_{op}^-	7.98	7.49	7.43	7.05	9.07	8.99
π_{ip}^-	7.98	7.93	7.43	7.38	9.52	9.43
π_{ip}^u	7.98	8.26	7.68	7.89	9.97	9.99
d_{z^2}	8.33	8.26	8.05	8.01	9.23	8.77
π_{op}^u	9.03	9.02	8.36	8.46		
d_{yz}	9.31	9.16	9.21	8.99	10.19	10.33
σ_{M-C}^u	9.64		9.21	9.67	8.71	8.86
np^u	9.51	9.29	9.21	9.14		
π_{op}^+	~10.3	~10	~9.8	~9.9	11.50	11.40
π_{ip}	~10.3	~10	~9.8	~9.9	11.50	11.40
n_N					10.81	10.82

^{a} For assignments refer to text.
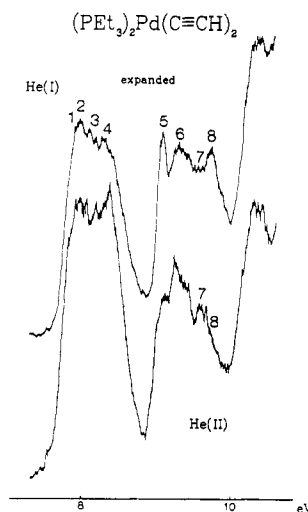
$(PEt_3)_2Pd(C{\equiv}CH)_2$

Figure 3. The He I and He II spectra of $[(PEt_3)_2Pd(C{\equiv}C—H)_2]$ (expanded first part only).
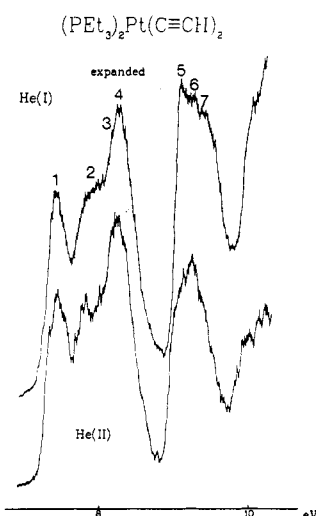
$(PEt_3)_2Pt(C{\equiv}CH)_2$

Figure 4. The He I and He II spectra of $[(PEt_3)_2Pt(C{\equiv}C—H)_2]$ (expanded first part only).

$(PEt_3)_2Pd(C{\equiv}C-CH_3)_2$

Figure 5. The He I and He II spectra of $[(PEt_3)_2Pd(C{\equiv}C—CH_3)_2]$ (expanded first part only).
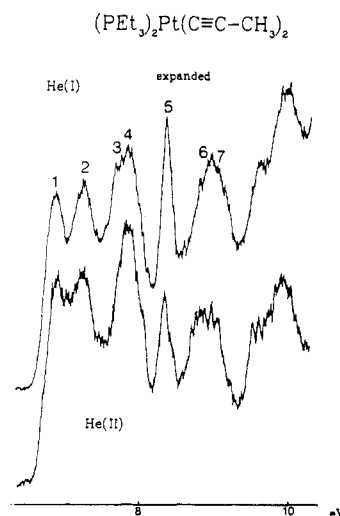
$(PEt_3)_2Pt(C{\equiv}C-CH_3)_2$

Figure 6. The He I and He II spectra of $[(PEt_3)_2Pt(C{\equiv}C—CH_3)_2]$ (expanded first part only).

with respect to transition-metal d type ionization bands. N 2p type orbitals have a slightly larger He II than He I cross section.

General Shape of the Spectra. In all spectra a more or less resolved region appears at 7–11 eV. At higher IE generally some very broad and unresolved bands can be observed. These consist of a large number of ionization bands that arise from the σ orbitals of the six ethyl groups on the phosphine ligands, together with some bands from the acetylide and cyanide ligand orbitals. In the case of
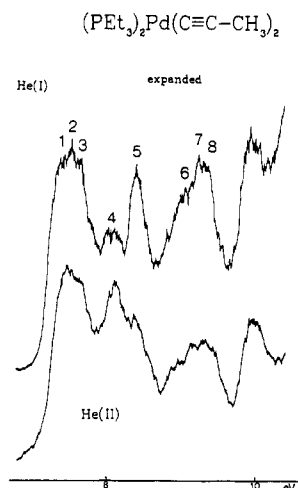
the acetylide compounds only the expanded first part of the spectrum is shown since no relevant information could be obtained from the region 11–20 eV.

The Spectra of $[(PEt_3)_2M(C{\equiv}C—R)_2]$ (M = Pd, Pt; R = H, CH$_3$). Because of their complexity and their similarity in shape, the spectra of the four acetylide type compounds can best be discussed in close relation to each other. For reasons of brevity, the following notations will be adopted. $[(PEt_3)_2M(C{\equiv}C—R)_2]$ will be notated as [M,R] (M = Pd, Pt; R = H, CH$_3$). Ionization energies (IE's) are listed in Table I, and the spectra are displayed

Table II. HFS Results for [(PH$_3$)$_2$Pd(C=C—H)$_2$]: Upper Valence Orbitals

orbital	orbital energy[a]	transitn-state energy[a]	% character PH$_3$	% character C≡C—H	% character Pd	classificatn[b]	exptl IE[a,c]
6b$_2$	5.04	7.70		69% π_z	27% d$_{xz}$	π_{op}^-	7.98
3a$_2$	5.21	7.83		76% π_y	23% d$_{xy}$	π_{ip}^-	7.98
5b$_1$	5.66	8.16	14% np	84% π_y		π_{ip}^u	7.98
8a$_1$	5.83	8.40	6% np		71% d$_{z^2}$, 16.8% s	d$_{z^2}$	8.33
7a$_1$	5.92	8.62		98% π_z		π_{op}^u	9.03
5b$_2$	6.76	9.65		78% σ	9% p$_x$	σ_{M-C}^u	9.64
4b$_1$	6.99	9.86	5% σ_{P-H}		85% d$_{yz}$	d$_{yz}$	9.31
4b$_2$	7.41	10.75		29% π_z	66% d$_{xz}$	π_{op}^+	10.3
3b$_1$	7.46	10.07	76% np	14% π_y		np^u	9.53
2a$_2$	7.58	10.54	11% σ_{P-H}	20% π_y	62% d$_{xy}$	π_{ip}^+	10.3

^{a} In eV. ^{b} op = out of plane; ip = in plane; + (−) = (anti)bonding between fragments; u = ungerade. ^{c} For the corresponding PEt$_3$ compound.

Table III. HFS Results for [(PH$_3$)$_2$Pd(C≡C—CH$_3$)$_2$]: Upper Valence Orbitals

orbital	orbital energy[a]	% character PH$_3$	% character C≡C—CH$_3$	% character Pd	classificatn[a]	exptl IE[a,c]
8b$_2$	4.33		72% π_z	26% d$_{xz}$	π_{op}^-	7.43
4a$_2$	4.57		80% π_y	15% d$_{xy}$	π_{ip}^-	7.43
6b$_1$	4.95	11% np	86% π_y		π_{ip}^u	7.68
10a$_1$	5.15		97% π_z		d$_{z^2}$	8.05
9a$_1$	5.27	6% np		72% d$_{z^2}$, 21% s	π_{op}^u	8.36
7b$_2$	6.19		81% σ	10% p$_x$	σ_{M-C}^u	9.21
5b$_1$	6.36	8% σ_{P-H}		86% d$_{yz}$	d$_{yz}$	9.21
6b$_2$	6.84		26% π_z	72% d$_{xz}$	π_{op}^+	9.8
4b$_1$	6.95	76% np	12% π_y	6% p$_y$	np^u	9.21
3a$_2$	7.19	10% σ_{P-H}	15% π_y	67% d$_{xy}$	π_{ip}^+	9.8

^{a} In eV. ^{b} op = out of plane; ip = in plane; + (−) = (anti)bonding between fragments; u = ungerade. ^{c} For the corresponding PEt$_3$ compound.

in Figures 3–6. In the spectra of [Pd,H] (Figure 3) and of [Pt,H] (Figure 4) two composite bands are found with IE below 10 eV. The region around 8 eV in the spectrum of [Pd,H] (bands 1–4) has little structure, but the corresponding region in the spectrum of [Pt,H] (also bands 1–4) shows more detail, an observation which seems quite general when a transition metal is replaced by its third-row triad member.[31] At lowest IE in the spectrum of [Pt,H] there is a more or less separated band at 7.49 (1) and a shoulder at 7.93 (2). These two bands strongly shift to lower IE upon methyl substitution (~0.5 eV), thus giving rise to the bands at 7.05 (1) and 7.38 (2) eV in the spectrum of [Pt,CH₃] (Figure 6).

In the spectra of both [Pt,H] and [Pt,CH₃] bands 3 and 4 are found to be strongly overlapping. With [Pt,CH₃] it can be seen that the lower IE side (band 3) of this composite band (bands 3 and 4) exhibits a relatively low He II cross section, effectively narrowing the band in He II. With [Pd,H] all four corresponding bands are located within one composite band, while upon methyl substitution (to [Pd,CH₃]) bands 1–3 shift to form the composite band at about 7.6 eV and one (band 4), with large He II cross section, is located at 8.05 eV.

The strong shift upon methyl substitution of bands 1 and 2 in the spectrum of [Pt,H] indicates a significant amount of acetylide localization of the corresponding orbitals. The rather high He II cross section, however, is in keeping with a substantial degree of metal d character. As before[5] the combination of these two features indicates that the orbitals giving rise to these ionization bands are antibonding combinations of ligand π orbitals with metal d orbitals of appropriate symmetry. In the spectra of [Pd,H] and [Pd,CH₃] bands 1 and 2 can also be assigned to π^- orbitals, by comparing the He I and He II spectra.

(PH$_3$)$_2$Pd(CCH)$_2$ xy—plane

3a$_2$ (π_{ip}^-)
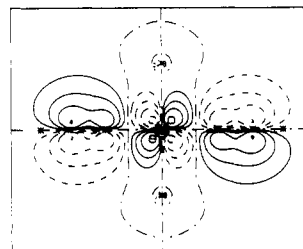
Figure 7. Contour plot of the π_{ip}^- orbital in the XY plane for [(PH$_3$)$_2$Pd(C≡C—H)$_2$].

Of the other two bands in the low IE parts of all the spectra one (band 4) exhibits a very large He II cross section, and thus it is assigned to a metal d type orbital.

The remaining band in this region exhibits a shift comparable to that of the π^- bands in the spectrum of the Pd complexes and shows in the spectra of the Pt complexes a shift which is at least larger than that of the metal-localized ionization (since the composite 3 and 4 band is broadened upon methyl substitution).

In keeping with previous data on *trans*-[(PEt₃)₂PtCl₂],[6] we assign this band to an orbital that consists of the antibonding combination of the ungerade in-plane acetylide π orbital and the ungerade np orbital. The antibonding character between the fragments of this orbital explains its high energy (and hence low IE).

For the four complexes the band due to the π_{op}^u orbital can easily be recognized by its sharpness and large shift upon methyl substitution (compare e.g., ref 32). In the

(31) Böhm, M. C.; Gleiter, R. *Angew. Chem.* 1983, 95, 334; *Angew. Chem., Int. Ed. Engl.* 1983, 22, 329.

(32) Böhm, M. C.; Gleiter, R.; Morgan, G. L.; Lusztyk, J.; Starowieyski, K. B. *J. Organomet. Chem.* 1980, 194, 257.

Table IV. HFS Results for [(PH$_3$)$_2$Pt(C≡C—H)$_2$]: Upper Valence Orbitals

	orbital energy[a]	transitn-state energy[a]	% character			classificatn[b]	exptl IE[a,c]
			PH$_3$	C≡C—H	Pd		
6b$_2$	5.01	7.67		76% π_z	22% d$_{xz}$	π_{op}^{-}	7.49
3a$_2$	5.23	7.93		84% π_y	15% d$_{xy}$	π_{ip}^{-}	7.93
5b$_1$	5.67	8.20	14% np	85% π_y		π_{ip}^{u}	8.26
8a$_1$	5.79		7% np		67% d$_{z^2}$, 25% s	d$_{z^2}$	8.26
7a$_1$	5.90			98% π_z		π_{op}^{u}	9.02
5b$_2$	6.76	9.71		83% σ	7% p$_x$	σ_{M-C}^{u}	
4b$_1$	7.34		8% σ_{P-H}		84% d$_{yz}$	d$_{yz}$	9.16
3b$_1$	7.49	10.68	82% np	12% π_y		n$_p^{u}$	9.29
4b$_2$	7.94	11.26		23% π_z	73% 5d$_{xz}$	π_{op}^{+}	10
2a$_2$	8.20	11.02	22% σ_{P-H}	11% π_y	62% d$_{xy}$	π_{ip}^{+}	10

[a] In eV. [b] op = out of plane; ip = in plane; + (–) = (anti)bonding between fragments; u = ungerade. [c] For the corresponding PEt$_3$ compound.
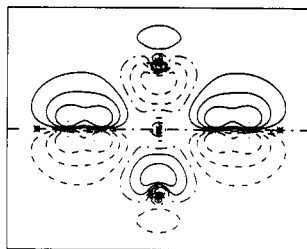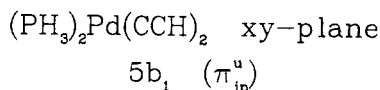
(PH$_3$)$_2$Pd(CCH)$_2$ xy–plane

5b$_1$ (π_{ip}^{u})

Figure 8. Contour plot of the π_{ip}^{u} orbital in the XY plane for [(PH$_3$)$_2$Pd(C≡C—H)$_2$].

(PH$_3$)$_2$Pd(CCH)$_2$ xy–plane

5b$_2$ (σ_{M-C}^{u})

Figure 9. Contour plot of the σ_{M-C}^{u} orbital in the XY plane for [(PH$_3$)$_2$Pd(C≡C—H)$_2$].

(PH$_3$)$_2$Pd(CCH)$_2$ xy–plane

3b$_1$ (n$_p^{u}$)

Figure 10. Contour plot of the n$_p^{u}$ orbital in the XY plane for [(PH$_3$)$_2$Pd(C≡C—H)$_2$].

spectra of [Pt,H] and [Pt,CH$_3$] band 5 due to this ionization is found at 9.02 and 8.46 eV, respectively.

The above assignments for bands 1–5 are in good agreement with calculations on the model compounds [(PH$_3$)$_2$M(C≡C—R)$_2$] (M = Pd, R = H, CH$_3$; M = Pt, R = H) (see Tables II–IV). These predict that the top two transition states are due to two orbitals of π-antibonding character resulting from a combination of metal d and acetylide π-fragment orbitals. A contour plot of the in-plane combination is shown in Figure 7. Furthermore, the calculations show a high-lying metal d type transition state which is of d$_{z^2}$ character with a significant amount of metal s participation. The presence of a low-energy ionization in square-planar complexes of Pd and Pt is of interest because a high-lying d$_{z^2}$ orbital is of potential use as a frontier orbital in donative metal–metal interactions and oxidation reactions at the metal site.[33]

In the calculations low-energy transition states are also encountered for the ungerade acetylide fragment π orbitals of which the in-plane one is destabilized with respect to the other due to level interaction with the n$_p^{u}$ orbital (Figure 8).

The measured methyl substitution shifts of the bands due to the out-of-plane ungerade acetylide π orbitals (which are almost totally localized upon the acetylide ligands) are less than those encountered in organic acetylene compounds[8,34] but are in agreement with the shift found for [(C$_5$H$_5$)BeC≡C—R] (R = H, Me).[32] Apparently, the inductive effect of the methyl substituent is impaired by charge acceptance of the metal. The shift in orbital energy of the π^- orbitals appears roughly proportional to the calculated amount of acetylide π character (see Tables II and III).
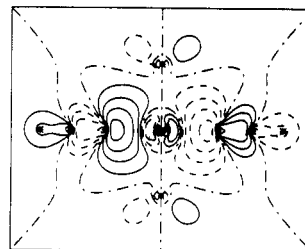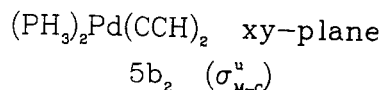
The calculations indicate that bands due to the σ_{M-C}^{u} orbital (Figure 9) and the orbital due to bonding combination of the n$_p^{u}$ and the π_{ip}^{u} orbitals (Figure 10) should be in the region around 9 eV. As regards the n$_p^{u}$ orbital it has to be taken into account that the calculated IE will be too high due to the less repulsive effect of a H vs. an Et group on P.

In the case of [Pd,H] band 8 at 9.64 eV exhibits a very low He II cross section, indicating it to be due to the σ_{M-C}^{u} orbital. Band 7 (9.54 eV) with a somewhat larger He II cross section is assigned to the n$_p^{u}$ orbital.

In the spectrum of [Pt,H] it can be seen by a comparison of the overall intensities of the region around 8 eV and the region around 9 eV that within the latter only three bands are present as opposed to four in the case of [Pd,H]. In this context the calculations indicate some amount of stabilization of the σ_{M-C}^{u} orbital upon going from Pd to Pt. Thus it is inferred that this orbital has now stabilized to such an extent that the corresponding band has now merged into the region 10 eV where due to strong overlapping of bands detailed assignments are not possible. In this [Pt,H] case the n$_p^{u}$ orbital ionization can be assigned

(33) A list of references on this subject has already been given in ref 5.

(34) Baker, C.; Turner, D. W. *Chem. Commun.* 1967, 797.

Table V. Analysis of Relativistic Effects in the Upper Valence Orbitals of $[(PH_3)_2Pt(C\equiv C-H)_2]^a$

	E_{NR}	Δmv^b	ΔDAR^c	$\Delta_{por}^{core\ d}$	$\Delta_{pot.}^{vale\ e}$	E_{rel}^{fo}	E_{rel}
$6b_2$	−5.02	−0.420	−0.018	0.910	−0.396	−4.94	−4.85
$3a_2$	−5.23	−0.274	−0.035	0.608	−0.310	−5.24	−5.25
$5b_1$	−5.67	−0.032	0.009	0.010	−0.104	−5.79	−5.79
$8a_1$	−5.79	−1.828	0.505	2.300	−0.844	−5.66	−5.64
$7a_1$	−5.90	−0.267	0.102	0.276	−0.173	−5.96	−5.98
$5b_2$	−6.76	−0.193	−0.012	0.180	−0.177	−6.97	−6.88
$4b_1$	−7.34	−1.120	−0.053	2.472	−1.016	−7.06	−7.03
$3b_1$	−7.49	−0.372	0.046	0.543	−0.333	−7.84	−7.71
$4b_2$	−7.94	−1.026	−0.023	2.259	−0.907	−7.64	−7.78
$2a_2$	−8.20	−0.846	−0.108	1.940	−0.859	−8.07	−8.15

^{a} Given are the nonrelativistic orbital energy (E_{NR}), the first-order corrections, the "first-order" relativistic orbital energy (E_{rel}^{fo}), and the full relativistic orbital energy (E_{rel}). For details see ref 19. ^{b} Correction due to increasing mass with velocity. ^{c} Darwin correction caused by the "Zitterbewegung". ^{d} Correction due to change in the electronic potential for core electrons. ^{e} Idem for valence electrons.

to the shoulder at 9.29 eV (band 7).

Comparison of overall intensities again indicates that in the spectrum of $[Pd,CH_3]$ the σ_{M-C}^u ionization band also has to be found within the region around 9 eV, while in the spectrum of $[Pt,CH_3]$ the band has merged as before within the overlapping bands at higher IE. The band due to the n_P^u orbital cannot be assigned with certainty in either of the spectra due to the very complicated overall band shapes. The same is true for the remaining band, a band with high He II intensity in the spectra of $[Pd,H]$ and $[Pt,H]$ (band 6 in both cases) that can not be assigned unambiguously in the spectra of the other two complexes.

The presence of a band with high He II intensity (apparently an ionization from a d type orbital) is in good agreement with the calculations which predict a transition state of predominantly metal d_{yz} character in that region and it is so assigned (see Table I). The calculated values for the energy of this orbital appear somewhat too negative relative to values for the other orbitals (see Tables II–IV), but this is not surprising since the calculations do not take into account level interaction between the d_{yz} orbital and σ_{P-C} orbitals.

In agreement with the calculations π-bonding combinations of gerade acetylide π orbitals and metal d orbitals of proper symmetry (the antibonding counterparts of which have been assigned in the first part of the spectrum) can be assigned to bands with IE > 10 eV that exhibit a relatively large He II cross section due to metal d participation and a significant shift upon methylation due to the partly acetylide π character. These bands are strongly overlapping with bands due to ionizations from high-lying σ orbitals on the PEt_3 units that do not show up in the calculations where PH_3 fragments were used. For details concerning the assignments see Table I.

In summary, the UP spectra for corresponding square-planar Pd and Pt compounds, as noted earlier,[5] are much alike. The most important difference is the IE for the σ_{M-C}^u orbital, which is significantly stabilized upon going from Pd to Pt, although no direct interaction with M d orbitals is possible. Apparently the role of Pd and Pt p orbitals in bonding can not be neglected, as it is the interaction of these orbitals with the localized ligand orbital that causes this difference. Similar findings were reported for the IE of the highest ungerade allylic π level in the UP spectra of MX_2 (M = Pd, Pt; X = C_3H_5, C_4H_7).[35] In agreement with this, differences between $[(PH_3)_2Pd(C\equiv C-H)_2]$ and $[(PH_3)_2Pt(C\equiv C-H)_2]$ are calculated to be rather small by HFS, except for the shifts in IE for three d type orbitals (d_{yz} and the two bonding combinations of d π and acetylide π). It appears from the spectra, however,
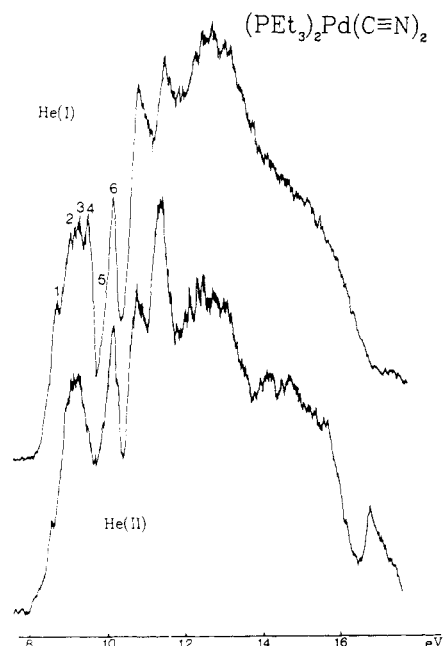

Figure 11. The He I and He II spectra of $[(PEt_3)_2Pd(C\equiv N)_2]$.

that these shifts are somewhat overestimated whereas the shift in the first IE on going from Pd to Pt is, on the other hand, somewhat underestimated. Shifts of acetylide π orbitals (or transition states) upon methyl substitution are also somewhat underestimated when comparing results for the acetylide and propylide complexes of Pd.

Differences between relativistic and nonrelativistic energies calculated for the Pt compound are also found to be very small (see Table V). Among other things, this is caused both by mutual cancellation of separate relativistic effects and, as far as spin–orbit coupling is concerned, by the absence of degeneracies or "quasi-degeneracies". Thus, the sum of all relativistic perturbations to be applied to the nonrelativistic results is only slightly different from the first-order sum.

The Spectra of $[(PEt_3)_2M(C\equiv N)_2]$ (M = Pd, Pt). Again it may be noted that a strong similarity exists between the spectrum of the Pd compound (Figure 11) and that of the Pt compound (Figure 12). In both spectra a set of four strongly overlapping bands is observed between 8.5 and 10 eV. In Figure 13 the expanded first part of the spectrum of the Pd compound is presented. The lowest IE band of the four, band 1, visible as a shoulder at 8.71 eV, is seen to exhibit a very poor He II cross section which indicates this band to be due to ionization from a σ type orbital. Of the other three bands band 3 has a better He II/He I cross section ratio than bands 2 and 4. In view of the findings for the acetylide compounds, band 3 is

(35) Böhm, M. C.; Gleiter, R.; Batich, C. D. *Helv. Chim. Acta* 1980, 63, 990.

Table VI. HFS Results for [(PH$_3$)$_2$Pd(C≡N)$_2$]: Upper Valence Orbitals

orbital	orbital energy[a]	% character			classificatn[b]	exptl IE[a,c]
		PH$_3$	C≡N	Pd		
6b$_2$	6.10		57% π_z	34% d$_{xz}$	π_{op}^-	9.07
5b$_2$	6.12		89% σ		σ_{M-C}^u	8.71
3a$_2$	6.37		64% π_y	35% d$_{xy}$	π_{ip}^-	9.52
8a$_1$	6.42	8% n$_P$	34% σ	41% d$_{z^2}$, 19% s	d$_{z^2}$	9.23
5b$_1$	6.81	32% n$_P$	66% π_y		π_{ip}^u	9.97
7a$_1$	6.94		60% σ	31% d$_{z^2}$	n$_N^g$	
6a$_1$	7.15		98% π_z		π_{op}^u	
4b$_1$	7.44	6% σ_{P-H}		88% d$_{yz}$	d$_{yz}$	10.19
3b$_1$	8.10	59% n$_P$	32% π_y	4% p$_x$	np^u	
4b$_2$	8.21		42% π_z	56% d$_{xz}$	π_{op}^+	11.3
2a$_2$	8.31	14% σ_{P-H}	31% π_y	49% d$_{xy}$	π_{ip}^+	11.3
3b$_2$	8.82	10% σ_{P-H}	81% σ	6% p$_x$	n$_N^u$	

[a] In eV.   [b] op = out of plane; ip = in plane; + (−) = (anti)bonding between fragments; u = ungerade; g = gerade.   [c] For the corresponding PEt$_3$ compound.
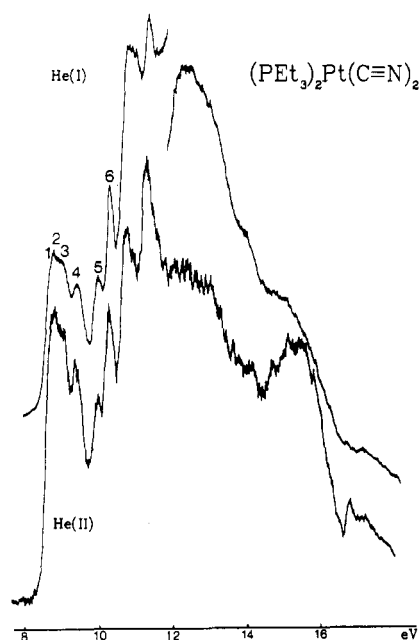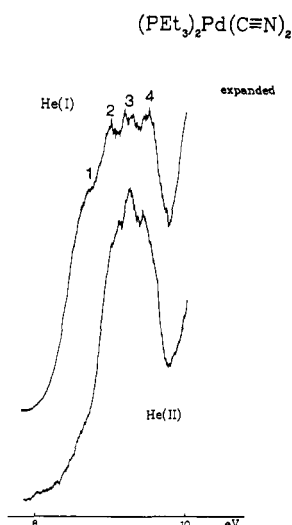

Figure 12. The He I and He II spectra of [(PEt$_3$)$_2$Pt(C≡N)$_2$].

Figure 13. The He I and He II spectra of [(PEt$_3$)$_2$Pd(C≡N)$_2$] (expanded first part).

assigned to an ionization from a d$_{z^2}$ type orbital, while bands 2 and 4 are assigned to the out-of-plane (2) and the in-plane (4) antibonding combinations of gerade cyanide π orbitals and metal d orbitals of proper symmetry.

These empirical assignments are in good agreement with results from the HFS calculations on the model compound [(PH$_3$)$_2$Pd(C≡N)$_2$]. As can be seen in Table VI all valence orbitals are calculated to be stabilized with respect to the corresponding orbitals in the acetylide compound, with the exception of the σ_{M-C}^u orbital. This orbital has become destabilized since (antibonding) level interaction of the localized σ_{M-C} orbital with n$_N$ is stronger than with σ_{C-H}. The overall result of the destabilization of this orbital and stabilization of all other orbitals with respect to the acetylide case is that this orbital has now become the HOMO (accidentally degenerate with a π type orbital in the HFS results). Thus, for the lowest IE band in the spectrum of the Pd compound an assignment to the σ_{M-C}^u level is proposed.

The occurrence of two π type orbitals and a d$_{z^2}$ orbital is also predicted. The metal/ligand ratio in the two π type orbitals is now calculated to be 35/65 as opposed to 25/75 in the case of the acetylide ligand.

In the spectrum of the Pt compound bands 1–3 are strongly overlapping, while band 4, assigned to the out-

of-plane π type orbital, is now observed separately. The other assignments that are of necessity tentative because they are based upon He I/He II band shape differences for a very complex band are as follows.

The d$_{z^2}$ ionization is assigned to the lowest IE maximum at 8.77 eV (band 1) with both the σ_{M-C}^u and π_{op}^- ionization bands at 8.99 eV (bands 2 and 3).

Band 5, which is a separate band in the spectrum of the Pt compound, and a shoulder at 9.97 eV in the spectrum of the Pd compound is assigned to the in-plane ungerade cyanide π orbital, both on the basis of its He I/He II intensity ratio and the results from the calculations. It is seen (Table I) that the shift in energy for corresponding C≡X π type ionization energies upon going from an acetylide to a cyanide ligand is about the order of magnitude one would expect in view of the difference in IE for the π orbitals in H$_2$C$_2$ (11.43 eV[8]) and HC≡N (13.61 eV[36]) and the respective percentages of ligand π participation in the orbitals (see Tables II and VI).

Band 6 at 10.19 eV with Pd and 10.33 eV with Pt exhibits a strong enhancement in the He II spectrum and is correspondingly assigned to the metal d$_{yz}$ orbital, analogous to the acetylide complexes and in agreement with the calculations.

No band due to the n$_N^u$ orbital can be traced in either of the spectra, although such ionization events are pre-

(36) Frost, D. C.; Lee, S. T.; McDowell, C. A. *Chem. Phys. Lett.* 1973, 23, 472.

Table VII. HFS Results for [(PH₃)₂PdCl(C≡N)]: Upper Valence Orbitals

orbital	orbital energy^a	% character				classificatn^b	exptl IE^{a,c}
		PH$_3$	Cl	C≡N	Pd		
4b$_1$	5.49		60% p$_x$		24% d$_{xz}$	π_{op}^{Cl}	8.55
6b$_2$	5.56		79% p$_y$			π_{ip}^{Cl}	8.55
9a$_1$	6.12			25% σ	37% d,^{d} 13% s	d$_{z^2}$	8.95
8a$_1$	6.34		30% p$_x$	38% σ	16% d^d	σ_{M-C}	8.24
5b$_2$	6.49	17% n$_p$		65% π_y	12% d$_{xy}$	π_{ip}^{CN}	9.69
3b$_1$	6.65		27% p$_z$	75% π_z		π_{op}^{CN}	
2a$_2$	6.95				88% d$_{yz}$	d$_{yz}$	9.98
7a$_1$	7.46		41% p$_x$	37% σ		σ_{M-Cl}	
4b$_2$	7.62	61% n$_p$	12% p$_y$		12% d$_{xy}$	n$_p^u$	
2b$_1$	7.95			33% π_z	58% d$_{xz}$	π_{op}^+	11.66
3b$_2$	8.23	10% σ_{P-H}		26% π_y	47% d$_{xy}$	π_{ip}^+	11.66

^{a} In eV. ^{b} op = out of plane; ip = in plane; + (–) = (anti)bonding between fragments; u = ungerade. ^{c} For the corresponding PEt$_3$ compound. ^{d} A mixture of d$_{z^2}$ and d$_{x^2-y^2}$.

Table VIII. HFS Results for [(PH₃)₂PtCl(C≡N)]: Upper Valence Orbitals

orbital	orbital energy^a	% character				classificatn^b	exptl IE^{a,c}
		PH$_3$	Cl	C≡N	Pt		
4b$_1$	5.21		61% p$_z$		23% d$_{xz}$	π_{op}^{Cl}	8.36
6b$_2$	5.56		82% p$_y$			π_{ip}^{Cl}	8.93
9a$_1$	5.97			28% σ	33% d;^{d} 17% s	d$_{z^2}$	8.36
8a$_1$	6.31		28% p$_x$	37% σ	17% d^d	σ_{M-C}	8.66
5b$_2$	6.54	18% n$_p$		69% π_y		π_{ip}^{CN}	9.78
3b$_1$	6.70		26% p$_z$	61% π_z		π_{op}^{CN}	
7a$_1$	7.46		44% p$_x$	37% σ		σ_{M-Cl}	
2a$_2$	7.49				85% d$_{yz}$	d$_{yz}$	10.26
4b$_2$	7.88	71% n$_p$				n$_p^u$	
2b$_1$	8.28			25% π_z	65% d$_{xz}$	π_{op}^+	
3b$_2$	8.59	21% σ_{P-H}		15% π_y	55% d$_{xy}$	π_{ip}^+	

^{a} In eV. ^{b} op = out of plane; ip = in plane; + = bonding between fragments; u = ungerade. ^{c} For the corresponding PEt$_3$ compound. ^{d} A mixture of d$_{z^2}$ and d$_{x^2-y^2}$.

dicted by the calculations. This result, however, is not surprising since previous experience with HFS calculations in combination with UP spectra of Se(C≡N)$_2$ has shown that n$_N$ orbitals may not be predicted well. The problem is due to an error in the orbital energy introduced by the HFS scheme in the case of delocalized orbitals with a very small differential overlap between constituting fragment orbitals. The error may amount to several electron volts,[37] and it was shown that a better description of experimental results was reached when calculations were carried out symmetry unrestricted (ionization holes localized to one part of the molecule). It is likely that for the dicyanide Pt and Pd complexes a similar situation also arises and (rather than two separate ionization bands due to gerade and ungerade combinations of lone-pair type orbitals) two degenerate localized orbitals give rise to one double band, at much lower IE values than predicted. Tentatively, the maximum at 10.81 (Pd) or 10.85 eV (Pt) is assigned to these coinciding ionization bands, while the maximum at 11.49 (Pd) or 11.40 eV (Pt) should be assigned to the two π-bonding combinations between metal and acetylide π orbitals on the basis of the large He II intensity. The band due to the n$_p^u$ orbital should, according to the calculations, be overlapping with these bands.

The Spectra of [(PEt₃)₂MCl(C≡N)] (M = Pd, Pt). Although it is tempting to treat the replacement of a cyanide by a chloride ligand as a perturbation because of the similarity in valence orbitals with comparable IE in the HX molecules,[29,36] the calculations (Tables VII and VIII) indicate that the character of the molecular orbitals

(37) Jonkers, G.; Lange, C. A. de; Noodleman, L.; Baerends, E. J. *Mol. Phys.* 1982, 46, 609.

Table IX. Vertical Ionization Energies (eV) for [(PEt₃)₂MCl(C≡N)] (M = Pd, Pt)^a

	Pd	Pt
σ_{M-C}	8.24	8.66
π_{op}^{Cl}	8.55	8.36
π_{ip}^{Cl}	8.45	8.93
d$_{z^2}$	8.95	8.36
π_{ip}^{CN}	9.69	9.78
d$_{yz}$	9.98	10.26
π_{op}^+	11.66	
π_{ip}^+	11.66	

^{a} For assignments refer to text.
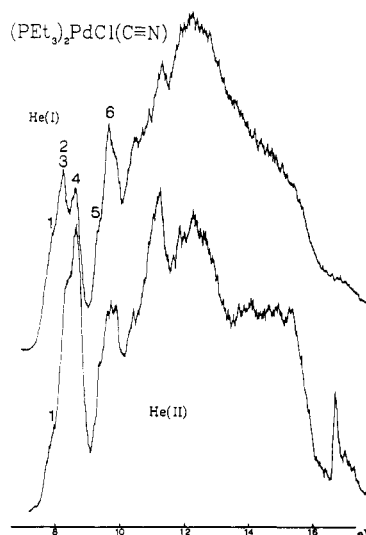
Figure 14. The He I and He II spectra of [(PEt₃)₂PdCl(C≡N)].
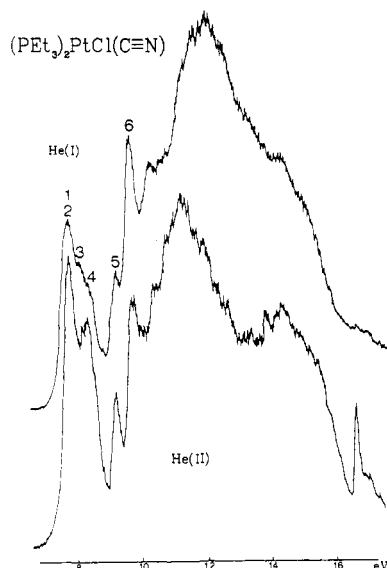
Figure 15. The He I and He II spectra of [(PEt₃)₂PtCl(C≡N)].

has also changed in that they have become more localized.

In the spectrum of the Pd compound (Figure 14) it is seen that all but one of the bands in the low IE part of the spectrum (around 8.5 eV) have a very poor He II cross section. The only band with large He II intensity, 4 at 8.95 eV, is assigned to a d_{z^2} type orbital.

At lowest IE in this complex is a shoulder (band 1) on the band at 8.24 eV with apparently very low He II intensity. This band is assigned to a σ orbital, corresponding to the $\sigma_{M-C}{}^u$ orbital in the dicyanide complexes.

At somewhat higher IE (8.55 eV) is a band with high He I and relatively low He II intensity that is assigned to two coincident ionization bands (2 and 3) from the π type orbitals. These bands seem to have much Cl character as can be judged by the very low He II cross section of the overall band.

As stated before, band 4 can readily be assigned to the d_{z^2} orbital, due to its large He II intensity. At 9.69 eV a shoulder is present (band 5), corresponding to the band at 9.97 eV in the spectrum of the dicyanide compound, and it is accordingly assigned to a π type orbital. In view of the rather large He II intensity of the band, the corresponding orbital is expected to reside mainly on the cyanide and not so much on the chloride ligand. The results from the calculations agree with this.

In the region around 10 eV several overlapping bands are observed. On the basis of data on the dicyanide complexes, the band due to the d_{yz} orbital ionization is to be expected here and a comparison of the He I and He II spectra indicates a value of 9.98 eV (band 6) for this ionization.

A strong He II enhancement of a composite band at 11.66 eV suggests the presence of the two ionizations due to orbitals that are analogous to the π-bonding orbitals in the dicyanide complexes.

A striking feature in the spectrum of [(PEt₃)₂PtCl(C≡N)] (Figure 15) is the change in shape of the lowest IE composite band, brought about by the decrease in He II intensity of band 3 (a shoulder at 8.66 eV in the He I spectrum). In view of this, this band is assigned to the analogue of the σ ungerade orbital in the dicyanide complexes. As before it is seen that the ungerade σ type orbital is found at significantly higher IE in the spectrum of the Pt than in that of the Pd compound.

Although three other bands should be present in the low IE part of the spectrum, only two can be discerned. Thus
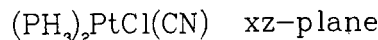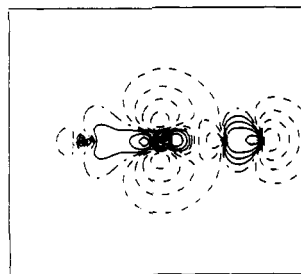

Figure 16. Contour plot of the d_{z^2} orbital in the XZ plane for [(PEt₃)₂PtCl(C≡N)].

it must be concluded that the band at 8.36 eV consists of two coinciding bands (1 and 2). Band 4, in view of its large He II intensity, must be due to an in-plane π type level, while the bands due to the other π type ionization and the d_{z^2} band give rise to the composite band at 8.36 eV. It may be noted that He II cross sections for the two π type orbitals are much higher with Pt than with Pd, indicating a much larger degree of metal d participation. As a consequence, no high IE band with strong He II enhancement is observed (such as the 11.66 eV band in the spectrum of the Pd compound) since the d participation will be proportionally less in the lower π type orbitals.

In the region around 10 eV bands due to the in-plane π type orbital (band 5, at 9.78 eV) and the d_{yz} orbital (band 6, at 10.26 eV) can again be observed.

It can be seen from Tables VII and VIII that, although there still exists a fair agreement between results from the HFS calculations on the model compounds and the spectra, this agreement is less than that for the other compounds. In particular, the relative IE of the highest σ orbital is calculated as being too stable. The calculations correctly predict for both compounds two low IE π ionizations which are mainly localized on the chloride ligand. It is also indicated that significant mixing of the d_{z^2} type orbital with σ levels takes place. This mixing, a good example of which is shown in Figure 16 for the d_{z^2} type orbital in the Pt compound, was symmetry forbidden in the previous compounds since the higher σ levels are strictly ungerade.

This mixing may explain why for the Pd and Pt compounds IE's for the d_{z^2} type orbital are significantly different while they were rather similar for the two metals in the previous compounds. Obviously, mixing between pure d_{z^2} and σ levels is different for Pd and Pt.

All IE's for the (Cl)(C≡N) compounds are lower than those of corresponding orbitals in the dicyanide complexes for both Pd and Pt. This is in agreement both with results from the HFS calculations and UP data on ClSeC≡N and Se(C≡N)₂.[37]

The Question of Back-bonding. In many studies on these and related compounds the existence of a significant amount of MX (X = C≡C—R or C≡N) back-bonding has been postulated in rationalizing experimental data,[38-41] although conflicting evidence has likewise been put forward.[42] For a general discussion on π back-bonding in

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acetylide complexes refer to ref 22. In this study no indication for such an interaction has been found. The Mulliken population of the π^* orbitals on the ligand fragments is calculated as 0.05 e or less in all cases by HFS.

Since UP data in combination with reliable MO calculations is the most direct method to study the electronic structure of compounds, these data shed some doubt upon the existence of π back-bonding in this type of complex, at least with cyanide and alkyl or unsubstituted acetylides.

In some cases X-ray data on palladium and platinum acetylide complexes has shown unusually short M–C distances.[43-45] Although ligands and/or coligands in these cases were much different from those used in this study, we still feel an alternative explanation from π back-bonding may be offered on the basis of the present data.

It has been shown that the highest π orbitals in all complexes were orbitals with M–C antibonding character. If π withdrawing substituents are added to the acetylide part, then charge will be withdrawn from this type of orbital and the M–C bond order will thus be increased. Replacement of one acetylide ligand by another ligand with similar fragment orbitals might have the same effect.

Conclusions

By using empirical criteria and the results from HFS calculations on model compounds, the UP spectra of a

series of square-planar Pd(II) and Pt(II) complexes of acetylide and cyanide ligands can be assigned.

It is shown that there exists strong interaction between metal d orbitals and the coordination environment, leading to delocalized orbitals of π symmetry with respect to the M–C bond in one case and a very high-lying d_{z^2} type orbital in another.

It is shown that, despite π interaction between occupied orbitals on metal and ligand fragments, π back-bonding plays only a very minor role in the complexes studied.

Energy levels are very similar for corresponding palladium and platinum complexes, in agreement with results from the calculations. One important exception is the IE of the ionization due to the $\sigma_{M–C}{}^u$ orbital in the bis(acetylide) and dicyanide complexes. Since no metal d orbitals are involved in this orbital, apparently the role of Pd and Pt p orbitals in bonding is not insignificant.

Registry No. [(PEt₃)₂Pd(C≡C—H)₂], 34230-57-4; [(PEt₃)₂Pt(C≡C—H)₂], 34230-58-5; [(PEt₃)₂Pd(C≡C—CH₃)₂], 34230-60-9; [(PEt₃)₂Pt(C≡C—CH₃)₂], 34230-61-0; [(PEt₃)₂Pd-(C≡N)₂], 15638-57-0; [PEt₃)₂Pt(C≡N)₂], 15712-02-4; [(PEt₃)₂PdCl(C≡N)], 89579-33-9; [(PEt₃)₂PtCl(C≡N)], 68225-04-7; [(Ph₃)₂Pd(C≡C—H)₂], 89579-34-0; [(Ph₃)₂Pd(C≡C—CH₃)₂], 89579-35-1; [(Ph₃)₂Pt(C≡C—H)₂], 89579-36-2; [(Ph₃)₂Pd(C≡N)₂], 89579-37-3; [(Ph₃)₂PdCl(C≡N)], 89579-38-4; [(Ph₃)₂PtCl(C≡N)], 89596-63-4.

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The Isomerization of Methylsilene to Dimethylsilylene. Further Evidence

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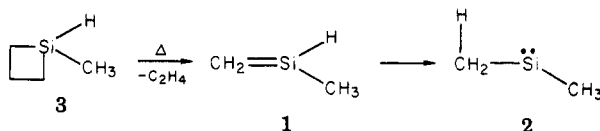
Methylsilene, generated thermally from three different precursors 1-methylsilacyclobutane, 2,3-bis-(trifluoromethyl)-7-methyl-7-sialabicyclo[2.2.2]octa-2,5-diene, and 1-methoxy-1-methyl-1-[(trimethyl-silyl)methyl]silane, isomerizes to dimethylsilylene. Trapping studies with butadiene and trimethylsilane lead to products expected from dimethylsilylene.

Introduction

Following our preliminary report that generation of 1-hydrido(1-methyl)silene from low-pressure pyrolysis of 1-methylsilacyclobutane (3) leads to products characteristic of the isomeric dimethylsilylene,[1] the proposed hydridosilene to methylsilylene isomerization has become a controversial reaction mechanism. Matrix isolation studies

of Drahnak, Michl, and West[2] on photogenerated[3] methylsilene (1) and dimethylsilylene (2) were interpreted as evidence for rapid thermal conversion of 1 to 2 at 100 K. These gas-phase and condensed-phase experiments appeared to complement the earlier theoretical studies from the groups of Gordon[4] and Schaefer[5] which indicated methylsilene and dimethylsilylene to be nearly isoenergetic.

(2) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1845. Further work on matrix-isolated dimethylsilylene and methylsilene has been reported recently. Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176. In this communication the authors offer the interesting suggestion that the act of trapping the hydridosilene induces a hydrogen shift from silicon to carbon.

(3) Photochemical conversion of 2 to 1 was also reported in ref 2 and the reversibility of the photoisomerization between hydridosilenes and methylsilylenes has recently been described. Reisenauer, H. P.; Mihm, G.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 854.

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