of a recently obtained crystal structure of the Ru/Co analogue of **2**[11] indicate that significant variation of the interplanar (and thus the metal–metal) distance can occur upon a screwlike C_4 distortion of the nicotinamide pickets. In the most extended conformation (rigorous C_{4h} symmetry), the metal–metal distance can approach 6 Å. Even in this conformation, normal "end-on" binding of an imidazole within the pocket is not possible due to steric restriction imposed by the chloride bound to the ruthenium at the internal site. Models indicate, however, that with a bent-bonding arrangement an imidazole can be accommodated within the pocket.

Given the steric restraint to one face of the porphyrin imposed by the $RuCl_2(nic)_4$ moiety, the magnitudes of the measured binding constants K_1 and β_2 are plausable for both the II and III oxidation states of iron.

An unusual feature of this complex is that it binds imidazole in the Fe(I) oxidation state. While nitrogenous bases have been demonstrated to bind to Fe(I) porphyrin in frozen solution,[12] we are unaware of any other evidence of nitrogenous base binding to Fe(I) in solution.[13] Because of the almost exact concurrence of the second imidazole binding (ostensibly within the pocket) by Fe(II) with the first binding by Fe(I), it is tempting to speculate that Fe(I) binds its single imidazole within the pocket. The unhindered face of the complex offers an environment that is, to a first approximation, no different from other Fe(I) porphyrins that do not bind nitrogenous bases. The pocket, on the other hand, provides a unique binding site. Irrespective of the exact site of imidazole binding, the behavior of the Fe(I) form of **2** is different from that of other capped and unhindered porphyrins.

Acknowledgment. Support of this work through the U.S. Department of Energy, Division of Chemical Sciences, Special Contract DE-AC02-81ER10968, is gratefully acknowledged.

Registry No. **2**, 102648-66-8; **3**, 102648-67-9; $RuCl_2((nic)_4H_2TPP)$, 97232-55-8; $RuCl_2((nic)_4Fe^{I}TPP)$, 102648-68-0; $Ru^{III}Cl_2((nic)_4Fe^{III}TPP)Cl$, 102648-69-1; $Ru^{III}Cl_2((nic)_4Fe^{III}TPP)(1\text{-}MeIm)$, 102682-01-9; $RuCl_2((nic)_4Fe^{III}TPP)(1\text{-}MeIm)$, 102681-99-2; $RuCl_2((nic)_4Fe^{II}TPP)(1\text{-}MeIm)$, 102648-70-4; $RuCl_2((nic)_4Fe^{I}TPP)(1\text{-}MeIm)$, 102648-72-6; $RuCl_2((nic)_4Fe^{II}TPP)(1\text{-}MeIm)_2$, 102648-71-5; $RuCl_2((nic)_4Fe^{III}TPP)(1\text{-}MeIm)_2$, 102682-00-8.

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UV PE Spectra and Pseudopotential ab Initio Calculations on *trans*-$Pt(PEt_3)_2X_2$ Complexes (X = Cl, Br, I)

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The He I/He II excited photoelectron spectra of *trans*-$Pt(PEt_3)_2X_2$ complexes (X = Cl, Br, I) are fully assigned with the aid of pseudopotential extended basis set ab initio calculations (including relativistic corrections for the Pt atom) on the whole series studied. Electronic reorganization energies upon ionization were estimated by means of a first-order perturbative treatment, which was revealed to be sufficiently accurate to allow a consistent interpretation of the experimental data. Moreover, the ab initio results provided new and interesting results that help to clarify the bonding scheme and its variation along the halide substituent series.

Introduction

Great attention has been focused on Pd(II) and Pt(II) square-planar (d^8) complexes[2] because of their catalytic[3] and anticancer[4] properties. However, despite the large number of investigations, many important features of their chemistry have not yet found an adequate understanding in terms of structure–activity correlations. Actually, definitive evidence concerning their electronic structures, on both experimental and theoretical grounds, is still lacking. Even the energy ordering of occupied molecular orbitals (MOs) and the nature of metal–ligand interactions still present open questions.

Aiming to clarify some of these arguments, we afforded the study of the electronic structures of some tetracoordinated planar complexes of Pd(II) and Pt(II) with simple monodentate ligands.[5] The present paper is devoted to *trans*-$Pt(PEt_3)_2X_2$ derivatives (X = Cl, Br, I), while related alkyl-substituted and hydrido compounds will be discussed in a subsequent paper.

The theoretical study of electronic structures of transition-metal compounds needs a rigorous MO approach, as provided by ab initio calculations, to take into due account bond covalency. This implies going beyond the simple atoms-in-molecule approach typical of early crystal field theory, which is still used to interprete UV–vis spectroscopic data. On the other hand, from the experimental point of view UV-photoelectron (PE) spectroscopy is by far the most direct tool to study the valence monoelectronic levels. However, two major problems must be examined to properly relate experimental PE evidence and theoretical results in a consistent way. First of all one has to override the computational problem arising from the large number of electrons to be included in the SCF procedure. In this regard we have adopted the well-known pseudopotential formalism,[6] so reducing the problem to few valence

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Table I. Bond Lengths Assumed in the ab Initio Calculations (Å)

	Pt(PH$_3$)$_2$Cl$_2$	Pt(PH$_3$)$_2$Br$_2$	Pt(PH$_3$)$_2$I$_2$
Pt-P	2.300[a]	2.315[a]	2.318[b]
Pt-X	2.294[a]	2.428[a]	2.612[b]
P-H	1.421[c]		

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electrons and allowing the use of more reliable extended basis sets (see Experimental Section).

The second problem is the expected occurrence of a large electronic reorganization upon ionization[7] so that ionization energies (IEs) are no longer related to ground-state monoelectronic energies as in Koopmans' frozen orbital approximation.[8] To take this into due account we had to improve our model by means of a first-order perturbative evaluation of reorganization effects.

To our knowledge, no other calculation of comparable accuracy has been reported on the title compounds, except one[9] on *trans*-Pt(PH$_3$)$_2$Cl$_2$, which was only devoted to molecular energy considerations. On the other hand, no detailed PE study has been reported on the title compounds, apart from a preliminary communication by Behan et al.[10]

Experimental Section

The *trans*-Pt(PEt$_3$)$_2$X$_2$ (X = Cl (**1a**), Br (**1b**), I (**1c**)) complexes were prepared according to literature methods.[2]

PE Spectra. He I (21.217 eV) and He II (40.814 eV) excited PE spectra were recorded on a Perkin-Elmer PS-18 spectrometer modified by the inclusion of a hollow-cathode discharge lamp giving high output of He II photons (Helectros Development Corp.). An heated inlet probe system has been used. The spectrometer was connected in line with a MINC 23 computer (Digital Equipment) with an interface built in our laboratory. Data were collected in the multiple scan mode by 3–5 sweeps over 500 distinct channels. Typical sweep times were about 10 min. The IE scale was calibrated by reference to peaks due to admixed inert gases (Xe, N$_2$, Ar) and to 1s^{-1} He self ionization.

Details of Calculations. SCF-MO-LCAO calculations were performed by using pseudopotentials to simulate all core electrons for each atom. The Barthelat et al. formalism[11] was chosen. For any atom C the local operator for each l value has the form

$$U_{l,c}(r) = \sum_i c_i r^{n(i)} \exp(-a_i r^2)$$

The adopted pseudopotential for Pt includes the major relativistic corrections[11a,b] (mass and Darwin corrections). The standard Huzinaga[12] double-ζ Gaussian basis set has been used for hydrogen atoms, while extended basis sets (double ζ for ligands and triple ζ for central metal) have been optimized for each valence shell by a pseudopotential version of the ATOM program.[13] Phosphorus 3d empty orbitals have been also taken into account in a calculation of **1a** using d polarization functions (ζ = 0.45). However, the very small changes in the eigenvalues and eigenvectors with respect to calculations without phosphorus polarization functions led us to exclude phosphorus 3d from the calculations of the whole series for economy reasons. Calculations have been carried out by running the PSHONDO program[14] on a VAX 11/780 computer. The geometrical parameters were taken from X-ray crystal data assuming a C_{2v} symmetry (Table I). A further time-saving and quite common[15] approximation was made by representing phosphine ethyl substituents by hydrogen atoms which were tetrahedrally disposed. The axis system adopted for the calculations is shown in Figure 1.

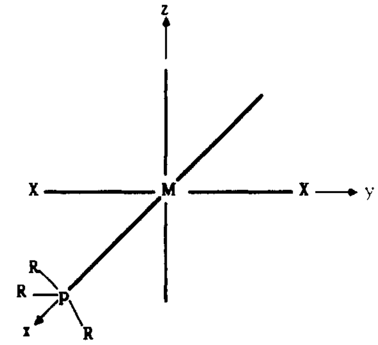

Figure 1. Axis system adopted for the ab initio calculations on *trans*-Pt(PH$_3$)$_2$X$_2$ complexes.

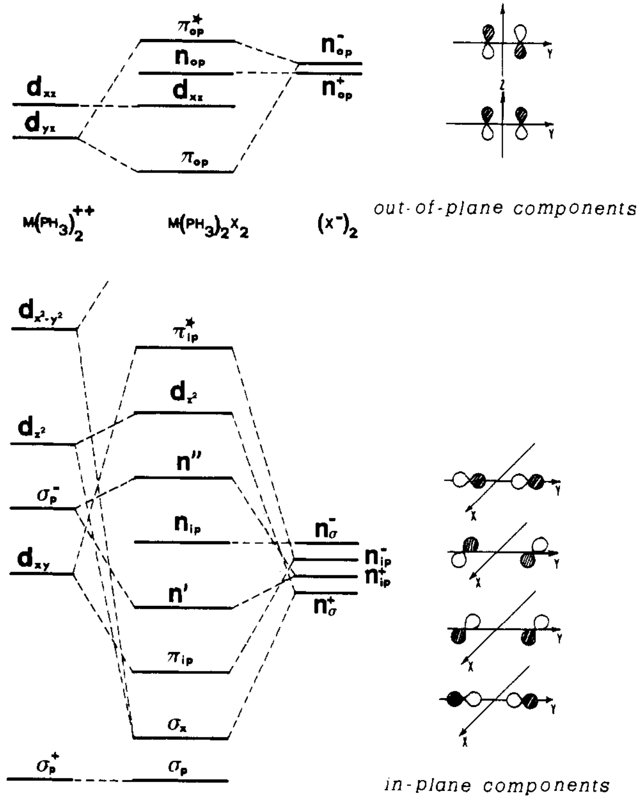

Figure 2. Qualitative correlation diagram between the outermost orbitals of the two [Pt(PH$_3$)$_2$]$^{2+}$ and (X$^-$)$_2$ fragments (X = halogen). The MO nomenclature here reported is adopted for the discussion. In-plane and out-of-plane interactions are reported separately for clarity.

The evaluation of reorganization energies upon ionization has been carried out by first-order perturbative treatment of repolarization and pair correlation effects.[16] Repolarization energies are by far the most important corrections to Koopmans' values for these molecular species. They were evaluated by using the Nesbet operator[17] as a perturbation Hamiltonian, so that the extimated repolarization energy is

$$E_r(k) = \sum_i^{\text{occ}} \sum_j^{\text{empty}} 2\langle i|F^+_k|j\rangle^2/(\epsilon_i - \epsilon_j)$$

where F^+_k is the Nesbet operator for the ion obtained by removing one electron from the kth MO

$$F^+_k = H^\circ + \sum_{l \neq k} 2J_l - K_l + \tfrac{1}{2}(2J_k - K_k)$$

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Table II. $Pt(PEt_3)_2X_2$ Ionization Energies and Band Assignments[a]

X = Cl			X = Br			X = I		
band	IE, eV	assgnt	band	IE, eV	assgnt	band	IE, eV	assgnt
A	7.59	d_{z^2}	A	7.49	d_{z^2}	A	7.19	d_{z^2}
B	8.12	d_{xz}	B	8.13	d_{xz}	B	7.82	π^*_{op}
B′	8.40	π^*_{op}	B′	8.44	π^*_{op}	B′	8.14	$\left.\right\} d_{xz} + \pi^*_{ip} + \pi_{op}$
C	9.32	π^*_{ip} (d_{xy})	C	9.21	π^*_{ip}	C	8.41	
D	9.97	$n'' + n_{ip} + n_{op}$	D	9.67	$n'' + n_{ip} + n_{op}$	D	9.18	$\left.\right\} n'' + n_{ip} + n_{op}$
						D′	9.38	
						D″	10.17	π_{ip}
E	10.77	$\sigma(PEt_3)$	E	10.81	$\sigma(PEt_3)$	E	10.85	$\sigma(PEt_3)$

[a] See Figure 2 for MO nomenclature.

The largest correlation term is the lack of pair correlation energy in the ion, and it is evaluated as

$$E_{\text{corr}}(k) = \sum_{j,l}^{\text{empty}} \langle kj^* | r_{1,2}^{-1} | kl^* \rangle / (2\epsilon_k - \epsilon_{j^*} - \epsilon_{l^*})$$

Additional correlation terms should be smaller, and thus they can be safely assumed as negligible. Since the neglected correlation terms have negative values, the reorganization energy computed in this way is an overestimate of the "true" value. However, it has the great advantage that it can be evaluated by low computational effort, since it requires just one SCF iteration for each IE.

Results and Discussion

In order to define a consistent MO nomenclature for the subsequent analysis of the spectral data and the description of the theoretical results, we report in Figure 2 a qualitative correlation diagram between $[Pt(PH_3)_2]^{2+}$ and $(X^-)_2$ fragment outermost orbitals. For convenience, Figure 2 has been separated into two portions corresponding to in-plane and out-of-plane interactions.

The levels of the former fragment (i.e. the five 5d metallic orbitals and the two σ M–P localized orbitals) have been extensively discussed elsewhere.[18] The adopted nomenclature and the shape of some relevant ligand-based orbitals are reported in Figure 2. A metal $d_{x^2-y^2}$ atomic orbital (AO) is involved in inner σ bonds with all four ligands giving rise to MOs labeled as σ_x and σ_p according to their prevalent localization. On the contrary, the metal d_{z^2} AO remains in a more localized "lone-pair" situation, because it can interact only through its equatorial ring (partially enlarged by an admixture with the s orbital). Within the π system, the metal d_{yz} AO gives rise to a π_{op} (out of plane) interaction with halides, whose bonding and antibonding terms are both occupied; on the other hand, d_{xz} can overlap only with inner occupied π-like PH_3 MOs, but it retains a "lone-pair" nature. The metal d_{xy} AO is in an intermediate situation, being involved in a π_{ip} (in plane) interaction, which will involve both phosphorus and halogen contributions.

As to the ligand-based MOs, those labeled as n_{op} and n_{ip} are representatives of halide p combinations (respectively out of plane and in plane), while n' and n'' involve both halogen and PH_3 p_x-based orbitals, giving rise to fully delocalized MOs.

***trans*-$Pt(PEt_3)_2X_2$ (X = Cl (1a), Br (1b)).** The He I and He II spectra of **1a** and **1b** are reported in Figure 3, while Table II contains the IEs and the final spectral assignments.

Qualitative spectral assignments can be proposed on purely experimental grounds by means of two main effects: (i) the well-known He I/He II cross section variations[19] that can help in discriminating ligand-based ionization bands, whose relative intensity decreases under He II radiation, with respect to d-based bands; (ii) substitution effects along isoelectronic series that shift the IE of "lone-pair" MOs according to the variations of electronegativity, thus allowing discrimination between metal- and halide-based ionization bands.

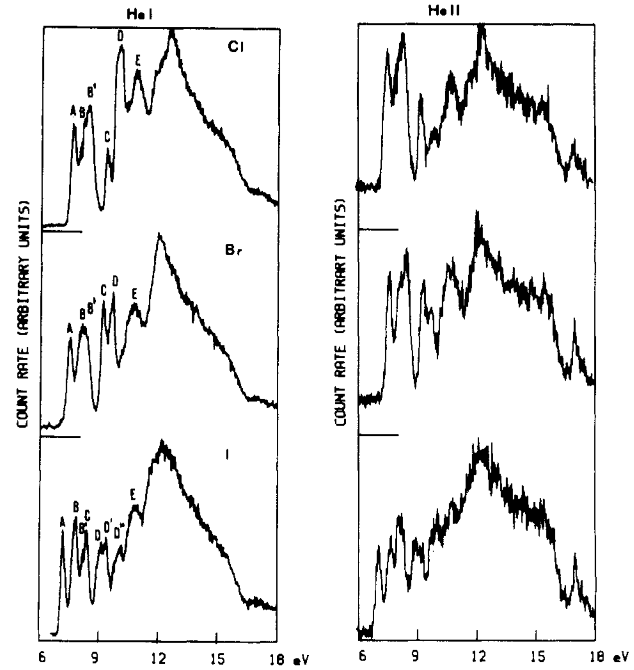

Figure 3. Gas-phase He I (left) and He II (right) PE spectra of *trans*-$Pt(PEt_3)_2X_2$ complexes (X = Cl, Br, I).

In the first region (at energies below 9 eV) of both spectra we have two resolved bands, labeled A and B, the second showing a larger intensity, which indicates two unresolved components. On the basis of their He II relative-intensity growth, both A and B are to be related to ionizations from MOs in which metal d orbitals are largely involved.

In the second spectral region (within the 9–10 eV energy range) two different bands (C and D) are present. Between them, D suffers the largest intensity decrease under He II radiation; thus, a marked halogen character is to be predicted for the corresponding MOs (n_{ip}, n_{op}). Such consideration is also confirmed by the energy shift of band D on going from **1a** to **1b**, which parallels the variation expected on the basis of electronegativity arguments. The C band shows an intermediate behavior and probably is to be assigned to an MO presenting a strong admixture of metal d and halogen orbitals. The third spectral region (above 10 eV) is similar to the free PEt_3 spectrum:[20] band E is thus assigned to P–C bonds, its broadening probably due to contributions from other ionizations. The intense convolution representing the ionizations from ligand C–C and C–H bonds hides any contribute from inner metal–ligand MOs present in the region over 12 eV.

Ground-state ab initio results for the outermost valence region for **1a** and **1b** are reported in Tables III and IV, where the orbital energies and percentage atomic populations are listed.

It is clearly evident that the interpretation of the PE data based

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Table III. Pseudopotential ab Initio Outermost MOs of *trans*-Pt(PH$_3$)$_2$Cl$_2$

MO	$-\epsilon$, eV	E_r,[a] eV	E_{corr},[b] eV	IE,[c] eV	% pop. Pt	P	Cl	H	descripn
5b$_2$ HOMO	9.66	1.27 (0.95)[d]	−0.05	8.44	35	0	65	0	π^*_{op}
3a$_2$	10.26	0.90 (0.75)[d]	−0.04	9.40	21	0	79	0	π^*_{ip}
5b$_1$	10.37	0.50 (0.45)[d]	−0.04	9.92	2	40	53	5	n″
7a$_1$	10.41	3.42 (2.18)[d]	−0.23	7.23	89	5	5	1	d_{z^2}
4b$_2$	11.24	0.85	−0.11	10.51	8	0	91	1	n_{ip}
6a$_1$	11.27	0.72	−0.04	10.59	2	0	97	1	n_{op}
4b$_1$	11.93	3.89	−0.11	8.15	89	3	0	8	d_{xz}
3b$_1$	12.46	0.49	−0.04	12.00	6	45	45	4	n′
3b$_2$	13.52	2.44	−0.05	11.13	67	0	33	0	π_{op}
2a$_2$	13.76	1.97	−0.06	11.85	59	10	12	19	π_{ip}
5a$_1$	14.13	1.12	−0.17	13.18	43	3	54	0	σ_x
4a$_1$	15.68	1.13	−0.08	14.63	41	44	7	8	σ_p

[a] Perturbative repolarization energy (see text). [b] Perturbative pair correlation energy (see text). [c] $-IE = \epsilon + E_r + E_{corr}$. [d] According to fully relaxed ΔSCF calculations.

Table IV. Pseudopotential ab Initio Outermost MOs of *trans*-Pt(PH$_3$)$_2$Br$_2$

MO	$-\epsilon$, eV	E_r,[a] eV	E_{corr},[b] eV	IE,[c] eV	% pop. Pt	P	Br	H	descripn
5b$_2$ HOMO	9.19	0.88	−0.04	8.36	24	0	76	0	π^*_{op}
3a$_2$	9.65	0.64	−0.03	9.04	13	1	86	0	π^*_{ip}
5b$_1$	9.87	0.46	−0.03	9.44	1	21	74	4	n″
7a$_1$	10.38	0.55	−0.03	9.86	3	0	97	0	n_{op}
4b$_2$	10.44	0.71	−0.11	9.84	11	0	88	1	n_{ip}
6a$_1$	10.46	3.57	−0.23	7.12	87	5	8	0	d_{z^2}
4b$_1$	11.98	3.95	−0.11	8.13	85	6	1	8	d_{xz}
3b$_1$	12.16	0.69	−0.06	11.53	11	60	23	6	n′
3b$_2$	13.10	3.37	−0.07	9.79	78	0	22	0	π_{op}
5a$_1$	13.51	1.22	−0.18	12.47	47	2	51	0	σ_x
2a$_2$	13.54	2.82	−0.07	10.79	69	8	6	17	π_{ip}
4a$_1$	15.70	1.29	−0.09	14.50	42	46	4	8	σ_p

[a] Perturbative repolarization energy (see text). [b] Perturbative pair correlation energy (see text). [c] $-IE = \epsilon + E_r + E_{corr}$.

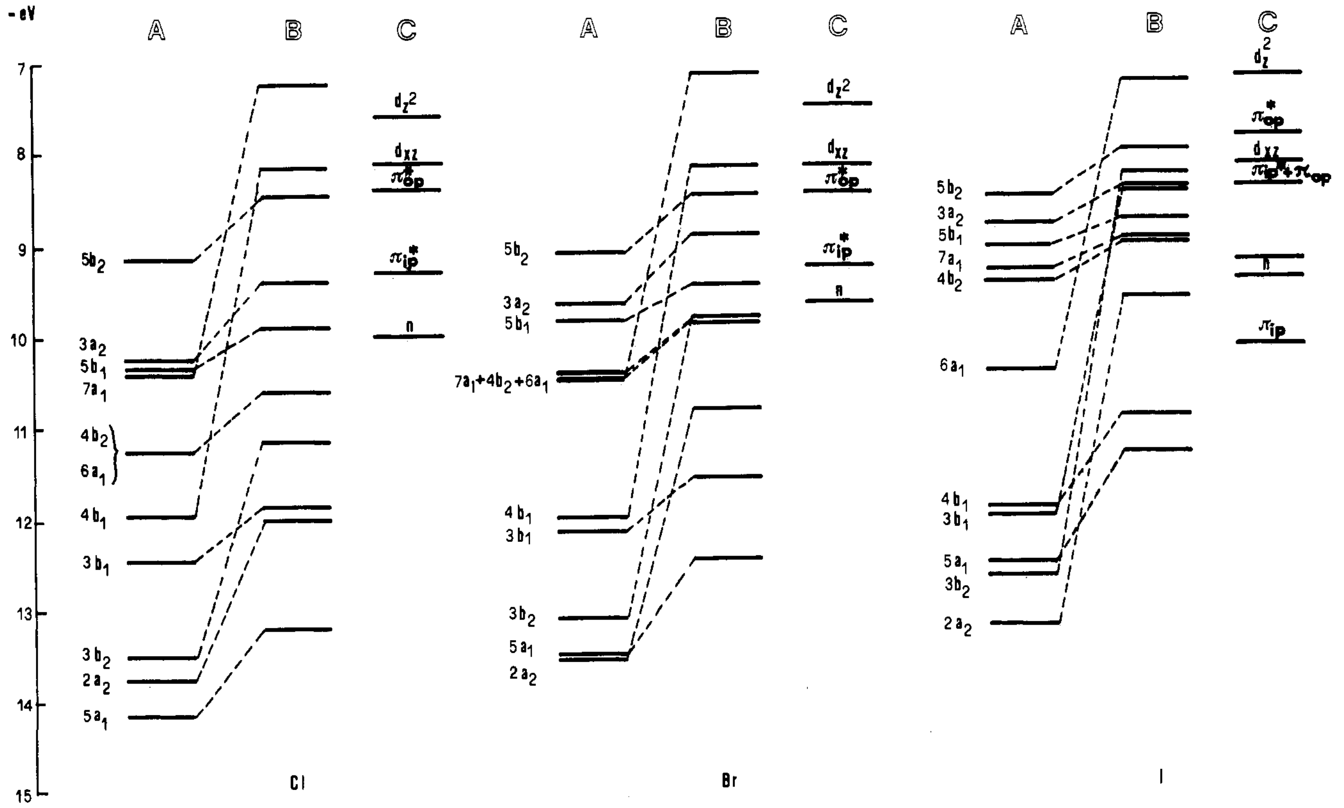

Figure 4. Correlation diagram between Koopmans' (A), perturbatively computed (B), and experimental (C) IEs of *trans*-Pt(PEt$_3$)$_2$X$_2$ complexes (X = Cl, Br, I).

on Koopmans' theorem does not match at all the experimental trend just discussed. Actually, computed reorganization energies (see Tables III and IV and Figure 4) contribute to a large extent (from about 0.5 up to 5 eV), with the greatest part of them being

Table V. Pseudopotential ab Initio Outermost MOs of *trans*-$Pt(PH_3)_2I_2$

MO	$-\epsilon$, eV	E_r,[a] eV	E_{corr},[b] eV	IE,[c] eV	% pop. Pt	P	I	H	descripn
$5b_2$ HOMO	8.48	0.52	-0.03	7.99	16	0	84	0	π^*_{op}
$3a_2$	8.79	0.40	-0.03	8.42	9	2	89	0	π^*_{ip}
$5b_1$	9.04	0.34	-0.03	8.73	2	9	86	3	n''
$7a_1$	9.29	0.36	-0.03	8.96	4	0	96	0	n_{op}
$4b_2$	9.43	0.53	-0.10	9.00	11	0	87	2	n_{ip}
$6a_1$	10.41	3.37	-0.22	7.25	83	3	14	0	d_{z^2}
$4b_1$	11.91	1.16	-0.08	10.83	21	63	8	8	n'
$3b_1$	12.00	3.57	-0.10	8.53	75	14	3	8	d_{xz}
$5a_1$	12.50	1.36	-0.19	11.32	51	1	48	0	σ_x
$3b_2$	12.64	4.48	-0.08	8.24	87	0	13	0	π_{op}
$2a_2$	13.31	3.78	-0.08	9.61	78	5	3	14	π_{ip}
$4a_1$	15.68	1.43	-0.10	14.36	42	47	3	8	σ_p

[a] Perturbative repolarization energy (see text). [b] Perturbative pair correlation energy (see text). [c] $-IE = \epsilon + E_r + E_{corr}$.

related to repolarization contributions.[21] As shown in Figure 4, reorganization effects reorder the IE sequence in a manner consistent with the proposed interpretation of PE spectra (see assignments in Table II).

External ionizations are in fact due to metal d "lone pairs", the outermost one (band A) being related to d_{z^2} ($7a_1$ for **1a** and $6a_1$ for **1b**) and the other (band B) to d_{xz} ($4b_1$ in both cases). The higher intensity of band B is justified by the superimposition of a further ionization related to the highest occupied MO (HOMO) $5b_2$, which is a π^*_{op} orbital of fairly covalent character. Band C is related to the π^*_{ip} ($3a_2$ MO) interaction, slightly more localized on halide atoms than the previous one; band D contains ionizations from halide quasi-degenerate lone pairs n_{ip} ($4b_2$ MO) and n_{op} ($6a_1$ for **1a** and $7a_1$ for **1b**) as well as from the nonbonding n'' ($5b_1$ MO).

***trans*-$Pt(PEt_3)_2I_2$ (1c).** The He I and He II spectra of **1c** are reported in Figure 3, while Table II contains the IEs and spectral assignments; as compared to preceding compounds, the iodine complex shows an increased spectral complexity, thus compelling a separate discussion.

In the first spectral region below 9 eV three resolved bands are evident instead of the preceding two, and the highest IE one (B′ + C) shows an ill-resolved structure. It is likely that the inner C component, previously associated with π^*_{ip} ionization, has now moved into this region, according to the higher electronegativity of iodine, which will destablize π^* orbitals. On the other hand, D and D′ bands can be assigned to ligand-based MOs on the basis of their He II intensity decrease; the shift towards lower IEs with respect to preceding lone pairs ionizations confirms this assingment. The internal band labeled D″, which was not seen separately in **1a** and **1b**, can be assigned to an inner MO with a high metal d percentage (probably a π interaction) because of its He II intensity increase. The remaining portion of the spectrum is just the same as in the previously discussed cases.

Ground-state calculations, reported in Table V, as well as the comparison between perturbatively computed and experimental IEs (Figure 4 and Table V), once again confirm and specify these qualitative arguments.

The metal d_{z^2} AO is involved in stronger σ antibonding interactions, due to the presence of more diffuse 5p iodine AOs, giving rise to a $6a_1$ MO, which still retains enough d character to allow large reorganization effects. Thus the lowest ionization (band A) still relates to such MO, and the absence of He II intensity growth can be explained by the presence of larger ligand components. The proposed destabilization of π^* MOs, due to high-energy iodine components, is fully confirmed by calculations.

Table VI. Pt–X Overlap Populations according to Mulliken's Population Analysis

X	total overlap	σ overlap	π overlap
Cl	0.56	0.53	0.03
Br	0.60	0.60	0.00
I	0.77	0.61	0.16

On this ground, band B relates to the π^*_{op} $5b_2$ HOMO ionization. As to bands B′ and C, assignments remain tentative because of strong peak overlap: probably peak C relates to π^*_{ip} $3a_2$ ionization and the B′ shoulder to the $3b_1$ one. The latter MO is based on the metal d_{xz} AO, to some extent admixed with a noninteracting close in energy n′ lone-pair combination of the same symmetry. As far as we can rely on perturbative extimates of IEs, this band envelope should also contain the $3b_2$ MO ionization, representing the internal π_{op} d-based orbital; however, we do not have enough experimental evidence (i.e. band intensity) supporting this theoretical suggestion. In tune with the above arguments, band D″ must be related to π_{ip} $2a_2$ MO ionization.

Conclusions

The core pseudopotential formalism applied to the ab initio SCF scheme has confirmed its validity in providing reliable calculations, with low computational effort, on molecules containing heavy atoms. This approach allowed us to describe properly the electronic structures of the title compounds and their variations along the halide substituent series. As a matter of fact, π-bond covalency, here meant as mixing degree, decreases on going from chlorine to iodine, thus reversing the order that could be inferred by simple overlap considerations. A total overlap population analysis, reported in Table VI, confirms the Pt–X bonds become stronger as the halogen atoms increase their covalent radii, as a result of both σ and π contributions. π-overlap population is nearly zero for X = Cl, Br, and suddenly increases for X = I. These arguments suggest that MO localization depends more on the energy matching of constituent AOs than on pure overlap considerations.

These ground-state theoretical considerations have been related to PE experimental data by means of a computationally efficient perturbative estimate of reorganization energies. This approach has provided sufficient accuracy, permitting detailed discussions of spectral data. Because of large reorganization effects, the lower IE processes are those from inner MOs of prevailing metal character, as confirmed by relative-intensity variations under He I and He II ionizing radiations.

A comparison with PE data of analogous palladium compounds[5] shows significant differences, expecially concerning the intermediate region of ligand-based and π^* MOs. In order to account for these differences, we have performed an ab initio pseudopotential calculation for the $Pd(PH_3)_2Cl_2$ compound.[22] Both the

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(21) As a check of the repolarization effects, we have performed separate SCF calculations on the lowest positive cations of each symmetry of $Pt(PH_3)_2Cl_2$ (see Table III). The perturbation theory E_r values reproduce satisfactory the fully relaxed ΔSCF results, even if they overestimate them. This is expecially true for the ionization from the strongly localized metal d pair ($7a_1$ MO). This comparison demonstrates that the perturbation theory corrections, which are quite inexpensive to obtain, can be taken as semiquantitative estimates of the reorganization effects.

(22) Granozzi, G.; Zangrande, G., unpublished results.

theoretical and PE differences between platinum and palladium derivatives are in agreement with a higher π covalency of the former, so that π^* MOs in the latter compounds are strongly localized on halide ligands and very near in energy to n_{ip} and n_{op} lone pairs.

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Registry No. *trans*-$Pt(PEt_3)_2Cl_2$, 13965-02-1; *trans*-$Pt(PEt_3)_2Br_2$, 13985-90-5; *trans*-$Pt(PEt_3)_2I_2$, 15636-79-0.

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Dinuclear Fe, Ru, and Co Complexes with C- and S-Bonded Bridging $C(SR)_2$ Carbene Ligands

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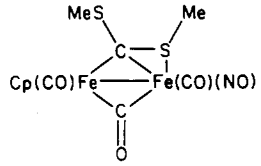
The dithiocarbene complex $Cp(CO)(MeCN)Fe{=}C(SMe)_2^+$ reacts with $Fe(CO)_3(NO)^-$ to give the dinuclear complex $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(CO)(NO)$ in which the $C(SMe)_2$ ligand bridges the two metal atoms via the C atom and an S atom is also coordinated to the NO-bearing Fe:



IV

Analogously bridged complexes $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SR)_2]Fe(CO)(NO)$ are prepared from cyclic dithiocarbene complexes, $Cp(CO)(MeCN)Fe{=}\overline{CSCH_2CH_2S}^+$ and $Cp(CO)(MeCN)Fe{=}\overline{CSCH_2CH_2CH_2S}^+$, and $Fe(CO)_3(NO)^-$. Reactions with $Co(CO)_4^-$, instead of $Fe(CO)_3(NO)^-$, give the related $C(SR)_2$-bridged $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SR)_2]Co(CO)_2$ complexes. Likewise, $Cp(CO)(MeCN)Ru{=}C(SMe)_2^+$ reacts with $Co(CO)_4^-$ to yield $Cp(CO)Ru(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Co(CO)_2$. Spectroscopic studies indicate that all of the dinuclear complexes contain the unusual bridging $C(SR)_2$ ligand, as in structure IV. Reactions of IV and other $C(SR)_2$-bridged complexes with PEt_3 result in CO substitution but no displacement of the coordinated sulfur atom. The remarkable stability of the unusual bridging $C(SR)_2$ group can be understood in terms of competing π-donation by the S and metal atoms into the carbene C atom. Two-electron oxidation by $[Cp_2Fe]FeCl_4$, I_2, Ph_3C^+, and $C_7H_7^+$ of the dinuclear complexes results in metal–metal bond cleavage to yield the terminal carbene complexes $Cp(CO)_2Fe{=}C(SR)_2^+$ and $Cp(CO)_2Ru{=}C(SMe)_2^+$.

Introduction

Polynuclear transition-metal compounds containing bridging methylene (CH_2) ligands have been proposed as models for intermediates in several heterogeneously catalyzed reactions.[2] Homodinuclear metal complexes containing μ-methylene units are now known for nearly all the transition elements.[3] Polynuclear metal complexes containing a bridging carbon atom with group 15 or 16 heteroatoms such as O, S, N, or P are less well explored. Exceptions to this include compounds containing the μ-CR(OR) ligand, the chemistry of which has been amply demonstrated.[4] To date, no compounds containing bis(alkoxy)- or bis(thioalkoxy)–μ-methylene ligands have been reported. This is in contrast to terminal carbene complexes, of which several $C(OR)_2$ and $C(SR)_2$ derivatives are known.[5]

Theoretical calculations on dinuclear μ-methylene compounds imply that heteroatoms on the methylene carbon would influence the bonding in the dimetallocyclopropane ring.[6] For μ-CH_2 complexes, back-bonding from the metal pi* system into the unoccupied high-lying p_π orbital of the μ-methylene carbon atom makes a large contribution to the overall bonding. This back-bonding is also thought to be responsible for the large negative charge found on the μ-carbon atom in a Mulliken electron population analysis. The negative charge on the μ-carbon is chemically manifested in the facile reaction of these compounds with electrophiles.[3c] The presence of heteroatoms which can serve as π-donors on the carbon atom in μ-methylene compounds could result in altered patterns of reactivity. Competition for the "vacant" p_π orbital on the μ-carbon atom between the heteroatoms and the dimetal center would be expected to weaken the bonding within the dimetallocyclopropane ring.

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