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Communications

Assignment of the Valence Molecular Orbitals of *cis*-[PtR_2L_2] Complexes: UV Photoelectron Spectra and SCF-MS-Xα Calculations

Sir:

The complexes *cis*-[PtR_2L_2], where R = alkyl or aryl and L = a ligand such as a tertiary phosphine, alkene, or amine, have played an important role in studies of organometallic reaction mechanisms related to catalysis by d^8 complexes, and the more volatile compounds are useful precursors for chemical vapor deposition of platinum.[1-5] However, there has not been any experimental determination of the relative energies of the valence orbitals, in particular the σ-PtC and Pt 5d orbitals in these molecules,[6] although this is important in understanding reactivity and mechanism.[1-4,7] Accordingly, we have undertaken a detailed He I and He II photoelectron spectroscopic study of *cis*-[PtR_2L_2] complexes (R = Me, CF_3; L = PR_3, AsR_3, SbR_3, CNR, $P(OR)_3$, etc.). In this communication, we report the photoelectron spectra and SCF-MS-Xα calculations on [$PtMe_2$(cod)] (cod = 1,5-cyclooctadiene), which show that the HOMO has mostly metal–ligand character and that the Pt 5d orbitals lie at higher ionization potentials.

The He I and He II photoelectron spectra[8] of [$PtMe_2$(cod)] are shown in Figure 1. The experimental ionization energies, along with those calculated for the model compound *cis*-$PtMe_2(C_2H_4)_2$] by using the SCF-MS-Xα method with relativistic corrections[9] are shown in Table I. At least one peak is resolved for each molecular orbital. The increase in He II:He I intensity ratios for metal d ionizations is often used to assign the metal d peaks.[10] However in spectra of our [$PtMe_2L_2$] complexes (e.g. see Figure 1 and Table I), there are only small changes in relative intensities between He I and He II spectra, and the ratios are not useful in the assignment for these molecules. This is not surprising, considering the problems with the He II:He I ratios for molecules such as bis(π–allyl)nickel,[11] resonance effects recently seen in synchrotron radiation studies in many molecules,[12] and extensive mixing of the metal d levels in these covalent compounds.

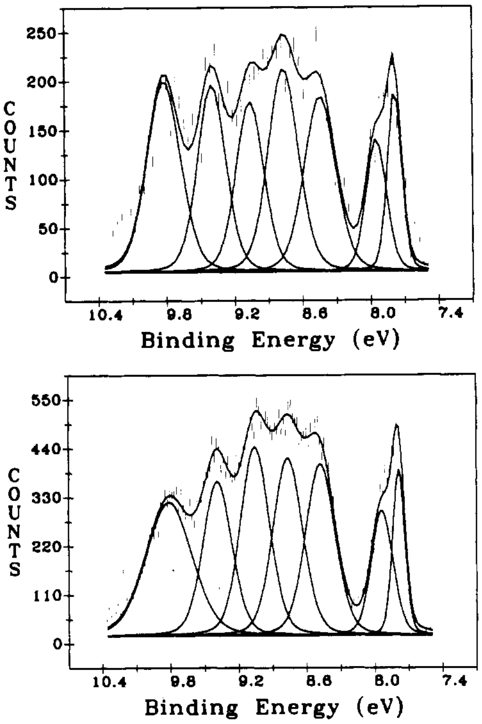

Figure 1. Curve-fitted He I (bottom) and He II (top) photoelectron spectra of *cis*-[$PtMe_2$(cod)], showing only the low-ionization-energy region.

The assignment of the spectrum can be readily made on the basis of the SCF-MS-Xα calculation for *cis*-[$PtMe_2(C_2H_4)_2$] (Table I) and the splitting of the lowest ionization band for the

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Table I. SCF-MS-Xα and Experimental Ionization Energies and He II:He I Intensity Ratios for *cis*-[$PtMe_2L_2$] Upper Valence Orbitals

	ionizn energy, eV			
orbital (C_{2v})	SCF-MS-Xα[a] L = C_2H_4	exptl L_2 = cod[c]	He II:He I L_2 = cod	compn[b]
$4a_1$	7.57	7.76, 7.93	1.00	spd (33%), σ_{Me} (16%), $\pi_{C=C}$ (24%)
$2b_2$	8.73	8.47	0.82	pd (9%), σ_{Me} (10%), $\pi_{C=C}$ (47%)
$3a_1$	8.93	8.76	1.05	sd (59%), σ_{Me} (7%), $\pi_{C=C}$ (8%)
$1b_1$	9.22	9.05	0.90	d (78%), $\pi_{C=C}$ (5%)
$1a_2$	9.41	9.39	1.05	d (66%), $\pi_{C=C}$ (11%)
$2a_1$	10.30	9.82	1.01	d (56%), $\pi_{C=C}$ (18%)

[a] The ionization energies were obtained by the removal of a half of an electron from the HOMO ($4a_1$). Geometric parameters assumed in the calculation: Pt-C_{Me} = 2.068 Å, Pt-ol [midpoint of C=C olefin (ol) bond] = 2.169 Å and $\angle C_{ol}$-Pt-C_{ol} = 91.25° (Day, C. S.; Day, V. W.; Shaver, A.; Clark, H. C. *Inorg. Chem.* **1981**, *20*, 2188); $\angle C_{Me}$-Pt-C_{Me} = 81.92° C=C = 1.375 Å, $C_{C=C}$-H = 1.087 Å, $\angle$H-$C_{C=C}$-H = 114.9°, and $\angle$H-$C_{1,C=C}$-$C_{2,C=C}$ = 121.08°: (Love, P. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653). Atomic and outer-sphere radii (bohr): outer, 6.8965; Pt, 2.6577; C, 1.6794; H, 1.2390. [b] Contributions in outer-sphere, intersphere, and hydrogen and contributions less than 5% are not included. [c] The ionization energy of the HOMO of free cod is 9.06 eV.

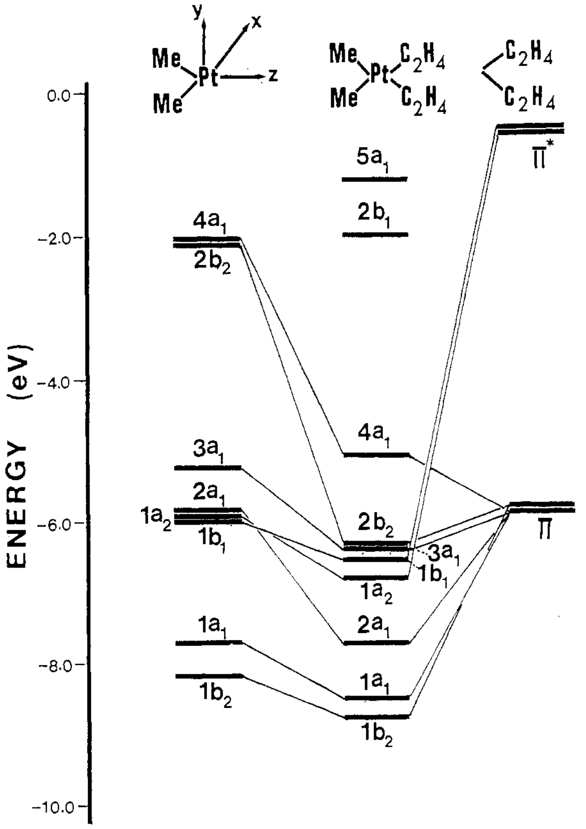

Figure 2. Orbital interaction diagram for *cis*-[$PtMe_2(C_2H_4)_2$]. For *cis*-[$PtMe_2$] the HOMO is $3a_1$. For *cis*-[$PtMe_2(C_2H_4)_2$] the HOMO is $4a_1$. For simplicity, only the major correlations are shown; for example, a correlation between $3a_1$ of the Me_2Pt fragment and $4a_1$ of *cis*-[$PtMe_2L_2$] is expected but is not shown in the diagram. This will be discussed in more depth in the full paper.

cod compound. This band shows resolved vibrational structure, and the observed splitting of 0.17 ± 0.02 eV (~1400 cm^{-1}) correlates well with the expected C=C stretching frequency for [$PtMe_2$(cod)][6] of 1428 cm^{-1}. This is strong evidence that the HOMO has substantial Pt-L character, and this is supported by the calculation. Although such a ligand vibrational splitting is not common, CO vibrational splittings have been seen on M-C MO's in $W(CO)_6$.[13] This vibrational structure has also been observed on the lowest IE band of [$PtMe_2$NBD] (NBD = norbornadiene) and [$Pt(CF_3)_2$(cod)], again strongly suggesting that the splitting is due to C=C bond vibrations.

The agreement between the calculations and experiment for the remaining five peaks is again good. However, with the orbitals so closely spaced, the exact ordering cannot be considered highly reliable, even when the calculations allow for relaxation and relativistic effects.[11]

An orbital correlation diagram is shown in Figure 2, with values calculated by the SCF-MS-Xα method for the ground state only for both of the fragments *cis*-$PtMe_2$ and (C_2H_4) and for *cis*-[$PtMe_2(C_2H_4)_2$]. This illustrates the mixing of the "d" and "σ" orbitals in the complex. As for *trans*-[$PtCl_2L_2$] complexes,[10] the HOMO shows large mixing of Pt 5d and ligand orbitals (Table I). The next orbital has high $\pi_{C=C}$ character, while the mainly 5d orbitals have higher ionization energies. Because of the small differences in energy in this and other *cis*-[$PtMe_2L_2$] complexes, interpretation of the reactivity of these molecules based on selective attack of electrophiles at the HOMO is problematic.[14] However, when electronic effects are dominant electrophilic attack on the σ orbitals rather than on the d orbitals might be predicted.

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Rational Synthesis of Monooxo Thioanions from [$OMo(SPh)_4$]$^-$. Structural Characterization of the [Ph_4P]$^+$ Salts of the [$(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)$]$^{2-}$, [$(\eta^2\text{-}S_2)MoO(MoS_4)$]$^{2-}$, [$(S_4)MoX(\mu\text{-}S)_2MoSX(\eta^2\text{-}S_2)$]$^{2-}$ (X = S, O), and [$(S_4)MoO(MoS_4)$]$^{2-}$ Anions

Sir:

In a previous communication we reported[1] on the systematic synthesis and chemical interconversions of the [$Mo_2(S)_n(S_2)_{6-n}$]$^{2-}$ anions and various isomeric forms of these compounds. More recently we have been able to obtain many of the corresponding [$Mo_2(O)_2(S)_n(S_2)_{4-n}$]$^{2-}$ complexes by a rational synthesis that employs the recently characterized[2] [$Mo_2O_2S_4(DMF)_3$] and [$Mo_2O_2S_2(DMF)_6$]$^{2+}$ complexes.

The availability of series of related Mo/S and Mo/O/S complexes is highly desirable for systematic studies that probe the

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