condensables. The lower outlet was attached to a tank of prepurified N_2 and a slow passage of N_2 was continued throughout the experiment to aid in removing the noncondensables.

The mixture was then brought to reflux. After approximately 1.5 h, the ether solution was almost clear with only a slight turbidity. Essentially all of the Zn/Cu couple had gone into solution as some type of intermediate. Shortly after this point was reached, a black fluffy material began to settle out. In a previous experiment it was found that at this point $B(CH_3)_3$ was being evolved in large quantities. After 48 h the reaction was stopped.

Investigation of the traps showed only ether, $B(CH_3)_3$, and decomposition products of the Simmons–Smith reagent. The yield of $B(CH_3)_3$ was 25% based on the $(CH_3)_3N{\cdot}BH_3$ that reacted. Of the original 1.79 g of $(CH_3)_3N{\cdot}BH_3$ added only 0.17 g was obtained unreacted from the remaining ether solution. The $B(CH_3)_3$ was characterized by gas-phase infrared analysis[6] after purification by vacuum-line distillation through a −112 °C trap to remove diethyl ether.

Reaction of Trimethylamine–Borane with the Simmons–Smith Reagent—II. A one-necked flask was charged with Zn/Cu couple (2.76 g, 35 mmol), CH_2I_2 (5.36 g, 20 mmol), $(CH_3)_3N{\cdot}BH_3$ (1.46 g, 20 mmol), diethyl ether (50 ml), and a Teflon-coated stirring bar. After 18 h at gentle reflux, heating was stopped and the reaction vessel was allowed to cool.

The gas produced during the reaction occupied a volume of 145 ± 5 cm^3 at 25 °C and atmospheric pressure. The liquid nitrogen condensable portion was investigated. A gas-phase infrared spectrum was obtained and confirmed the presence of diethyl ether and the usual peaks observed from the gases produced during decomposition of the Simmons–Smith reagent. Absorption bands characteristic of $B(CH_3)_3$ were absent.

The material in the reaction flask consisted of two liquid phases. The denser layer was dried by vacuum evaporation for 1 h at 73 °C and weighed 2.44 g. This material was a very viscous liquid. The top layer was evacuated to dryness and produced a white solid weighing 3.74 g. Trimethylamine–borane (3.6 mmol, 18% recovery) was collected during drying of these two fractions.

The white solid obtained from the top layer of the original filtrate was recrystallized from CH_2Cl_2 solution by adding heptane. This solid gave one peak at 2.62 ppm in the NMR spectrum taken in CH_2Cl_2 solution with internal TMS as reference. The infrared spectrum taken in CH_2Cl_2 solution showed no absorption in the B–H stretching region. Anal. Calcd for $ZnI_2(CH_3)_3N$: C, 9.53; H, 2.40; N, 3.70; Zn, 17.28; I, 67.16. Found: C, 9.31; H, 2.32; N, 3.62; Zn, 15.30; I, 67.37.

The viscous liquid obtained from the bottom layer of the original filtrate was a mixture of the material found in the top layer and boron-containing compounds. Attempts to separate a pure material from this mixture were unsuccessful.

Reaction of Trimethylamine–Borane with the Simmons–Smith Reagent—III. A one-necked flask was charged with Zn/Cu couple (11.8 g, 162.2 mmol), CH_2I_2 (17.78 g, 66.4 mmol), a Teflon-coated stirring bar, and 50 ml of diethyl ether. The mixture was removed to the hood and refluxed gently. Formation of the Simmons–Smith reagent was monitored by NMR spectroscopy. The amount of CH_2I_2 was observed to decrease and finally to become undetectable in the NMR spectrum; this required approximately 1.5 h. During this time a total of 170 ± 5 cm^3 of gas was collected. Using the percentage composition of the gas produced from decomposition of the Simmons–Smith reagent[3] this quantity of gas would correspond to a loss of approximately 15–20 mmol of active methylene-transfer reagent; thus there was approximately 46 mmol of active methylene available for transfer to B–H bonds.

Trimethylamine–borane (0.73 g, 10 mmol) was added to the Simmons–Smith reagent; then the mixture was brought to gentle reflux and the over gas was slowly removed by a steady stream of prepurified nitrogen gas into a series of three liquid nitrogen traps. The nitrogen gas and other noncondensables were allowed to escape from the system through a mineral oil bubbler. After 2.3 h the flow of nitrogen was stopped and the material in the reaction flask was allowed to cool. The only boron-containing compound isolated was $B(CH_3)_3$, 0.63 mmol (6.3% yield), from vacuum-line measurements.

The $B(CH_3)_3$ was condensed into the first liquid nitrogen trap of the series. The system of traps was refilled with nitrogen gas and the reaction mixture was brought to gentle reflux again. After a total reaction time of 23 h the system was treated as before and a total of 0.69 mmol of $B(CH_3)_3$ was isolated. The amount of $B(CH_3)_3$ collected corresponded to a 6.9% conversion of the $(CH_3)_3N{\cdot}BH_3$ added.

Reaction of Trimethylamine with the Simmons–Smith Reagent. Methylene iodide (16.5 g, 62.5 mmol) and Zn/Cu (6 g, 81 mmol) were reacted in the hood in ether solution for 4 h. The reaction flask was then cooled and attached to the vacuum line where $(CH_3)_3N$ (65 mmol) was added at liquid nitrogen temperature. The mixture was allowed to warm to room temperature with stirring. After being stirred for 1 h, the mixture was pumped to remove unreacted $(CH_3)_3N$.

A compound insoluble in benzene but soluble in CH_2Cl_2 was the only product isolated. This compound was recrystallized from CH_2Cl_2 solution by adding heptane. A white solid (2.01 g), mp 165 °C, was obtained. The NMR spectrum in CH_2Cl_2 showed peaks at 3.23, 2.78, and 2.45 ppm in a 8.8:2:9 ratio, respectively, with internal TMS as reference. The infrared spectrum was obtained in CH_2Cl_2 solution: 2980 (m), 2920 (m), 2870 (w), 2810 (vs), 1485 (s), 1110 (m), 1010 (s), 965 (m), 910 (w), 822 (s) cm^{-1}.

Anal. Calcd for $C_7H_{20}N_2I_2Zn$: C, 18.63; H, 4.47; N, 6.21; I, 56.25; Zn, 14.49. Found: C, 18.53; H, 4.44; N, 6.05; I, 56.13; Zn, 14.09. Thus, the empirical formula is in good agreement with a complex containing one $(CH_3)_3N$, one ZnI_2, and a $(CH_3)_3NCH_2$ moiety as the simplest formulation.

Registry No. $B(CH_3)_3$, 593-90-8; $ZnI_2(CH_3)_3N$, 59389-43-4; $C_7H_{20}N_2I_2Zn$, 59389-44-5; $(CH_3)_3N{\cdot}BH_3$, 75-22-9; CH_2I_2, 75-11-6; $N(CH_3)_3$, 75-50-3.

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Ultraviolet Photoelectron Spectra of Nickel, Palladium, and Platinum Diethyl Dithiophosphate Complexes

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Uv photoelectron spectroscopy (UPS) is a powerful technique with which to probe the electronic structure of molecules.[1] Its use in transition metal chemistry has been, by necessity, limited to compounds that can be vaporized without decomposition. However, since the required vapor pressure is <0.1 Torr and the sample inlet probe can be easily heated several hundred degrees, there clearly exists a large number of transition metal complexes amenable to study. Our interest has been in studying the effect of changing the metal within a triad while keeping the ligand system constant. A number of such studies involving organometallic complexes have recently appeared.[2-10]

The electronic structure of planar d^8 metal complexes has been the subject of many discussions.[11-16] We have applied the UPS method to this problem and herein report the photoelectron (PE) spectra of the planar d^8 bis(diethyl dithiophosphato)metal(II) complexes, $M[S_2P(OEt)_2]_2$ (M = Ni, Pd, Pt), and the protonated ligand, $HS_2P(OEt)_2$. (Hereafter

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Table I. Ionization Energy Assignments (eV)[a]

Compd[b]	$d_{x^2-y^2,z^2}$	$d_{xz,yz}$	π_n (a_u)	π_n (b_{3g})	π_b (b_{1u})
$Ni(dtp)_2$	7.24	8.37	9.2	9.9	10.3
$Pd(dtp)_2$	7.90	8.7[c]	8.7[c]	9.7	10.4
$Pt(dtp)_2$	7.60	8.80	9.2	10.0	10.4

[a] Symmetry in D_{2h}; see Figure 2 for notation. IE's are vertical values. [b] IE's of Hdtp: n_0, π_n, 9.1; π_b, 10.2. [c] See text.

the abbreviations $M(dtp)_2$ and Hdtp are used.) Several workers[17,18] have analyzed the electronic spectrum of $Ni(dtp)_2$ with conflicting results.

Experimental Section

NH_4dtp and the metal complexes $M(dtp)_2$ were synthesized by standard methods and gave excellent elemental analyses. The PE spectra were obtained on two spectrometers of the Turner type,[20] incorporating a $\pi/2^{1/2}$ (10 cm) electrostatic cylindrical condenser analyzer. The spectra were excited with He Iα (21.2 eV) or He IIα (40.8 eV) photon radiation. The ionization energies (IE) were inferred from internal calibration with xenon and argon. In Table I are presented the IE's; the values may be taken as ±0.05 eV for well-separated bands whereas in the case of profuse, overlapping bands the values given are the estimated maxima as judged from the band profiles. The temperature required for each compound was as follows: NH_4dtp, 50 °C; $Ni(dtp)_2$, 130 °C; $Pd(dtp)_2$, 140 °C; $Pt(dtp)_2$, 120 °C. The PE spectra did not change over ±30 °C from the quoted value. The mass spectra were obtained on a Varian MAT CH-5 instrument using field desorption and electron impact sources.

Results and Discussion

The PE spectra are given in Figure 1. The field desorption mass spectra of the $M(dtp)_2$ complexes, obtained at a variety of temperatures, show only mass peaks corresponding to isotopes of the parent ion, $M(dtp)_2^+$. The electron impact mass spectrum of $Ni(dtp)_2$ has been reported[21] and shows the parent ion as the major species present. To ensure further that the PE spectra are genuine, we found that heating $M(dtp)_2$ complexes *in vacuo* at the temperature used in the PE experiments caused no detectable decomposition.

Gentle heating (~50 °C) of NH_4dtp was found to cause decomposition to NH_3 and Hdtp. The electron impact mass spectrum of NH_4dtp at 50 °C consists of a complicated fragmentation pattern with the principal mass peak due to $Hdtp^+$. In contrast, the field desorption spectrum of NH_4dtp at about 50 °C contains the parent ion ($Hdtp^+$) as the only significant mass peak. Thus NH_4dtp represents a convenient way to "store" the less stable Hdtp.

The analysis of the first few bands in the PE spectrum of Hdtp is relatively simple. The lowest IE orbitals should be the P=S sulfur lone pair (n_0) and the nonbonding π orbital (π_n) consisting mainly of the sulfur p orbitals perpendicular to the SPS plane. Previous theoretical[22,23] and experimental[24,25] work has shown that n_0 and π_n are nearly degenerate in simple acids, esters, and amides. Accordingly, we assign the 9.1-eV band to ionization from n_0 and π_n. The next MO is most likely the π-bonding orbital, π_b, which we assign to the 10.2-eV band. In agreement with these assignments, the area ratio of the first two PE bands is close to 2:1. It would seem possible that the oxygen lone-pair orbitals could be responsible for the 10.2-eV band, but in this case it is more likely that the area ratio of the first two bands would be nearer 1:1. The oxygen lone-pair IE's seem to occur at ≳10.8 eV, a reasonable value considering that the lone-pair IE in ethanol is 10.8 eV.[26] The He IIα excited spectrum of Hdtp (Figure 1) strongly supports these assignments. The first two PE bands suffer a large decrease in intensity relative to higher IE bands when the ionizing radiation is changed from He Iα to He IIα. Such changes are characteristic of third-row 3p AO photoionization cross sections, in marked contrast to 2p AO's, and are often used diagnostically.[27-29] Finally, we note that a small portion of the third PE band may be due to NH_3 generated as NH_4dtp decomposes.

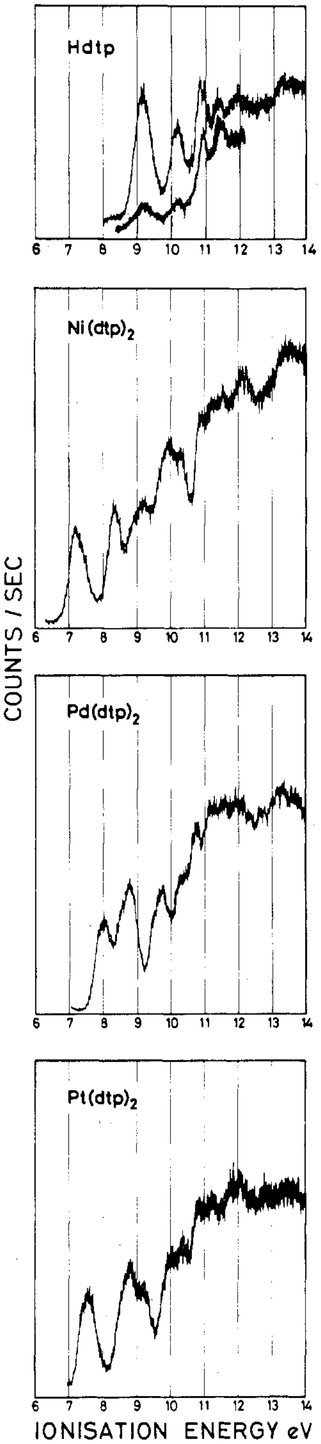

Figure 1. He Iα PE spectra of $M(dtp)_2$ and both He Iα (upper) and He IIα (lower) PE spectra of Hdtp.

As Figure 1 shows, ionization from the filled d orbitals in the $M(dtp)_2$ complexes is clearly discernible. A simple molecular orbital diagram we propose to explain the spectra is given in Figure 2 and some tabulated assignments are given in Table I. At this point a comment on Koopmans' theorem is in order. It has become clear from recent work[6,7,30-34] that, due to large relaxation energies, Koopmans' theorem frequently fails quite badly for MO's consisting of mostly metal d AO's. The theorem seems to work reasonably well, however, for delocalized ligand MO's. Because of this problem, MO diagrams of the neutral complex inferred from PE spectra are qualitative at best. However, in a set of closely related

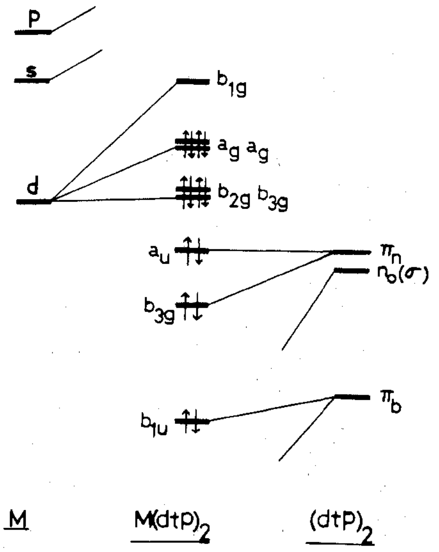

Figure 2. Qualitative MO scheme for M(dtp)$_2$ accounting for the first five PE bands.

compounds, like the M(dtp)$_2$ series, it is likely[6,34] that deviations from Koopmans' theorem are similar so that changes in orbital energies inferred from the PE spectra should be valid.

Figure 1 shows that Ni(dtp)$_2$ and Pt(dtp)$_2$ have very similar PE spectra, and it is convenient to discuss these first. In Ni(dtp)$_2$ the two d-orbital bands have equal areas, suggesting the splitting scheme shown in Figure 2. The d–d separation is 1.1 eV and compares with a splitting of approximately 1.3 eV proposed by Tomlinson and Furlani,[17] based on an analysis of the electronic spectrum. In Pt(dtp)$_2$ the two d-orbital bands again have equal area and the splitting is 1.2 eV. Both PE spectra have the third band at 9.2 eV which we assign to the nonbonding π orbital of a_u symmetry, which occurs at 9.1 eV in Hdtp. The a_u orbital is prevented by symmetry from mixing with any of the metal orbitals. The next two bands in the PE spectra of Ni(dtp)$_2$ and Pt(dtp)$_2$ are assigned to the b_{3g} (π_n) orbital lowered from 9.1 eV in Hdtp by interaction with the metal b_{3g} orbital and the b_{1u} (π_b) orbital shifted from 10.2 eV in Hdtp. We place the oxygen lone-pair IE's at $\gtrsim$10.8 eV, as in Hdtp.

The PE spectrum of Pd(dtp)$_2$ differs markedly from the others. The major differences are (1) the absence of the π_n IE at about 9.2 eV as seen in Ni(dtp)$_2$ and Pt(dtp)$_2$ and (2) the area ratio of the first two bands, which is about 1:1.8 for Pd(dtp)$_2$. We believe the most likely explanation of these facts is that the π_n (a_u) IE occurs within the second PE band. This accounts for its absence at 9.2 eV and the area ratio exceeding 1:1. The second PE band for Pd(dtp)$_2$ has a shoulder at 8.5 eV and a maximum at 8.7 eV. The 8.5-eV shoulder may be the a_u orbital or may result from d-orbital splitting. We do not attempt a distinction in Table I.

In planar d^8 systems it is usually found[11-16] that the $M \rightarrow L(\pi^*)$ charge-transfer transitions in the electronic spectrum follow the order Ni < Pd > Pt while the $L(\pi) \rightarrow M$ transitions have the order Ni > Pd < Pt. For all three metals the $L(\pi) \rightarrow L(\pi^*)$ transitions, where seen, occur at about the same energy. This suggests that the d–π_n separation in the M(dtp)$_2$ series should be least for Pd, in accord with our results. The only unanticipated result in our work is the small d-orbital separation found for Pd(dtp)$_2$.

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Registry No. Ni(dtp)$_2$, 16743-23-0; Pd(dtp)$_2$, 21312-72-1; Pt(dtp)$_2$, 37583-01-0; Hdtp, 298-06-6.

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Decarbonylation of β-Carbomethoxypropionylpentacarbonylmanganese(I)

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We recently reported the bisdecarbonylation of *o*-carbomethoxybenzoylpentacarbonylmanganese(I), **1**, to give **2** in which the carbomethoxy group acts as a chelating ligand.[1] A monodecarbonylated compound could be trapped with external phosphite but could not be directly observed by spectral means. The more rapid loss of the second CO from **1** might be related to the formation of a particularly stable chelated product (Scheme I).

β-Metallo-α,β-unsaturated carbonyl compounds with a chelating carbonyl group, **3**, are readily formed in many diverse