is the boron hybrid to X and

$$\bar{\phi}_h \left[= \frac{1}{1 + \lambda_x^2} [\bar{\phi}_s + \lambda_x^2 \bar{\phi}_p] \right]$$

signifies the average radial distance of ϕ_h. Using Slater functions for ϕ_s and ϕ_p $\{\phi = [(2\zeta)^{5/2}/(4!)^{1/2}]re^{-\zeta r}\}$, we find

$$\frac{d\bar{\phi}_h}{d\lambda_x} = 2[\bar{\phi}_p - \bar{\phi}_s] \frac{\lambda_x}{(1 + \lambda_x^2)^2}$$

Thus

$$\frac{dS_3}{dS_2} \cong (2\Delta R)K \frac{\lambda_x^2}{(1 + \lambda_x^2)^2} = 2(\Delta R)K(f_s f_p)$$

where f_s and f_p are the fractional s and p characters of the B hybrid to X. By including the variation in K with λ_x, we compute the curve in Figure 1 for $(S_3)_2 = f(f_s)$. This curve is developed by treating ΔR as a parameter, a value of 0.2 for which yields $dS_3/d\lambda_x$ = 0.06 Å for sp^2 boron and 0.04 Å for sp^3 boron, values which are in accord with chemical intuition.[6] When the experimental values of $(S_3)_2$ are placed on this curve, qualitatively reasonable results are obtained for the boron hybridization. With CN$^-$ as the donor the boron is seen to take on ~sp^3 character, a value consistent with the reported value[7] of $J_{^{11}BH}$ for BH_3CN^-. The isoelectronic BH_3CO is found to involve ~16% B s character in the hybrid to CO. (CNDO/2 calculations[4] give 26% and 19% s character for these hybrids, respectively.) Similarly F$^-$ and PF_3 are found to involve <25% B s characters in the B–X bonds, as expected. An especially low value for BH_3NC^- is to be noted. As mentioned above, there may be some error in the force field for this molecule which results in the low value. Values for the NH_3 and NMe_3 adducts[8] are included in Figure 1 but must be treated as tentative. Those values were not computed according to the same constraints as were those of the other adducts[4] and all force constants for these two adducts were reported in units of mdyn/Å with no indication of the value of r used in the unit conversion for bending coordinate constants. The per cents of s character for these adducts are not unreasonable, however.

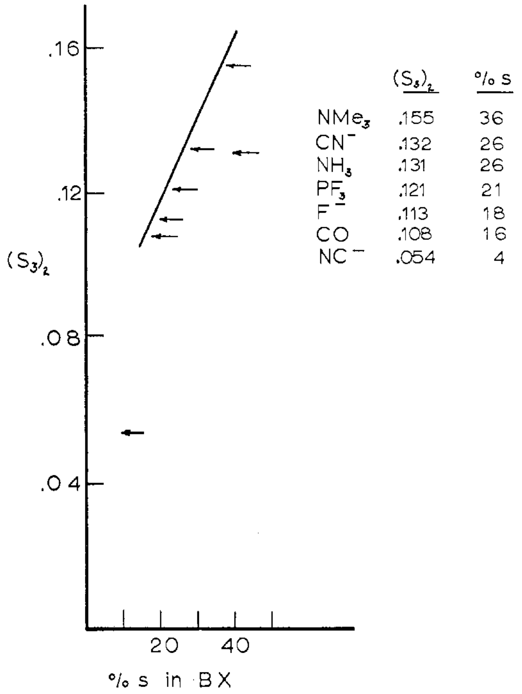

Figure 1.—Adduct bond stretch with respect to BH_3 bend interaction coordinate as a function of boron per cent of s character in the adduct bond. The solid line is the theoretical curve and experimental values of $(S_3)_2$ are indicated with arrows (see insert).

The effect of BH_3 hyperconjugation is expected to be barely discernible in Figure 1. While B–X back-donation would serve to reduce $(S_3)_2$, no drastic reduction is found for BH_3CO and BH_3PF_3. In fact, the per cent of s character for BH_3CO estimated from Figure 1 is in good agreement with that deduced from the CNDO/2 description of the B–C σ bond.

In conclusion, we find the HOFF model to be applicable to these BH_3X adducts with semiquantitative results. This approach to orbital following of nuclear displacement also indicates that BH_3 hyperconjugation is observable with X = CO or PF_3 but that the B–X π-bond interaction is much less significant to BH_3 electron reorganization during nuclear displacement than is the σ-bond interaction.

Acknowledgment.—We wish to thank the National Science Foundation for support of this research through Grant GP-28924.

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2-Substituted 1,3,2-Benzodioxaphosphole Derivatives of Tungsten Hexacarbonyl

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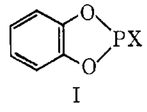
Received July 7, 1971

In connection with our current interest in phosphorus–transition metal chemistry, we wish to report some 2-substituted 1,3,2-benzodioxaphosphole (I) derivatives of tungsten hexacarbonyl of the type $C_6H_4O_2P(X)W(CO)_5$, where X = Cl or $N(C_2H_5)_2$.



I

The new compounds were obtained by the reactions of the appropriate ligands, I, with the tetrahydrofuran complex of tungsten pentacarbonyl, prepared *in situ* by the irradiation of a solution of tungsten hexacarbonyl in tetrahydrofuran.[1] Related metal complexes of I with X = F have been reported by Schmutzler.[2] The chlorophosphole[3] was prepared by the reaction of phosphorus trichloride with catechol and converted

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to the diethylamino derivative upon reaction with diethylamine.

In the reactions of the chlorophosphole with AgNCO, AgNCS, C_6H_5SH, CH_3SH, and CH_3OH,[4] spectroscopic data indicated that the isolated products were, respectively, I, where X = NCO, NCS, SC_6H_5, SCH_3, and OCH_3. However, these phospholes changed their identity rapidly, and we were unable to obtain pure samples for satisfactory identification and further reaction with $W(CO)_5 \cdot THF$. The literature contains many examples of the lability of phospholes toward Arbuzov and similar reactions.[5] Attempts to stabilize the labile ligands, by immediate reaction with the tetrahydrofuran complex of tungsten pentacarbonyl, in many cases gave isolatable complexes which decomposed rapidly both *in vacuo* and under nitrogen to give uncharacterized blue residues. In contrast, the new compounds $C_6H_4O_2P(Cl)W(CO)_5$ and $C_6H_4O_2P[N(C_2H_5)_2]W(CO)_5$ have been stable for up to 2 years in a nitrogen atmosphere.

The reactions of the chlorophosphole with silver cyanide (in dichloromethane and in xylene, under reflux) and with methyl- or phenylmagnesium bromide did not yield the desired derivatives of I. Furthermore, we were unable to obtain a pure sample of the phenylphosphole from the reaction of phenylphosphorus dichloride with catechol.[6,7]

The proton nmr spectrum of the aminophosphole-tungsten pentacarbonyl complex, when compared to that for the uncomplexed ligand, shows a downfield shift for all the ligand protons consistent with a formal oxidation state change from 3+ to 5+ for phosphorus upon complexation (assuming that phosphorus is coordinating to tungsten).

Experimental Section

Physical Measurements.—Infrared spectra were determined using a Perkin-Elmer Model 21 sodium chloride spectrophotometer and a Perkin-Elmer 621 grating spectrometer. Proton nmr spectra were obtained by means of a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were taken using a Perkin-Elmer Hitachi RMU-6D double-focusing spectrometer at 70-eV ionizing energy. Irradiation was carried out in a quartz vessel using a Hanovia 679A36 medium-pressure lamp. Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Micro-Tech Laboratories, Inc., Skokie, Ill.

Materials.—Tungsten hexacarbonyl was a generous gift from the Climax Molybdenum Co. 2-Chloro-1,3,2-benzodioxaphosphole was prepared by a literature method[4] and all solvents were dried before use by standard procedures. All manipulations were carried out under nitrogen.

Preparation of $C_6H_4O_2P(Cl)W(CO)_5$ (II).—A solution of 1.76 g (5 mmol) of tungsten hexacarbonyl in 50 ml of tetrahydrofuran was irradiated for 5 hr, during which time 5 mmol of carbon monoxide was evolved. The resulting yellow solution was added quickly to 0.87 g (5 mmol) of $C_6H_4O_2PCl$ and the mixture was stirred for 20 min at ambient temperature. Solvent was removed *in vacuo* and the residual yellow solid sublimed. Unreacted tungsten hexacarbonyl (0.35 g) was collected at 30° (0.05 mm) and identified by it sinfrared spectrum. Fine colorless needles of product (0.75 g, 40%) were collected at 50–55° (0.05 mm), mp 80–81°. *Anal.* Calcd for $C_{11}H_4ClO_7PW$: C, 26.5; H, 0.8; Cl, 7.1. Found: C, 26.5; H, 1.1; Cl, 7.2. Ir spectrum (hexane solution): $\nu(CO)$ 2083 (m), 1981 (vs), 1950 (m sh) cm^{-1}. A parent ion was observed in the mass spectrum at 500 (calcd: 500 for ^{184}W and ^{37}Cl).

Preparation of 2-Diethylamino-1,3,2-benzodioxaphosphole, $C_6H_4O_2PN(C_2H_5)_2$.—A 2.9-g (40-mmol) sample of diethylamine in 20 ml of benzene was added dropwise, over a 4-hr period, to 3.5 g (20 mmol) of 2-chloro-1,3,2-benzodioxaphosphole in 20 ml of benzene, cooled to 0° in a two-necked flask equipped with a mechanical stirrer. Vigorous stirring was maintained for a further 16 hr at ambient temperature under nitrogen. Solvent was removed *in vacuo* and the residue was shaken with pentane. The mixture was filtered, solvent was removed, and the residual oil was distilled under reduced pressure. The product (1.9 g, 46%) was collected at 113–115° (0.25 mm). *Anal.* Calcd for $C_{10}H_{14}NO_2P$: C, 56.9; H, 6.6; N, 6.6; P, 14.7. Found: C, 58.4; H, 6.9; N, 6.4; P, 14.0. Proton nmr (carbon tetrachloride solution): τ 3.23 (four phenyl protons), 7.14 (six methylene protons), 9.02 (six methyl protons).

Preparation of $C_6H_4O_2P[N(C_2H_5)_2]W(CO)_5$.—The preparation was essentially the same as for II above [0.88 g (2.5 mmol) of tungsten hexacarbonyl, 7 hr irradiation, and 0.52 g (2.5 mmol) of ligand]. After removal of solvent the pink solid was sublimed to give 0.13 g of unreacted tungsten hexacarbonyl (40° (0.05mm)) and fine colorless needles of product (0.76 g, 67%) at 75° (0.05 mm), mp 67°. *Anal.* Calcd for $C_{15}H_{14}NO_7PW$: C, 33.7; H, 2.6; P, 5.8; W, 34.4. Found: C, 33.9; H, 2.6; P, 5.9; W, 33.3 Ir spectrum (hexane solution): $\nu(CO)$ 2081 (m), 1962 (vs) cm^{-1}. A parent ion was observed in the mass spectrum at 535 (calcd: 535 for ^{184}W). Proton nmr (carbon tetrachloride solution): τ 3.07 (four phenyl protons), 6.82 (four methylene protons), 8.84 (six methyl protons).

Reaction of 2-Chloro-1,3,2-benzodioxaphosphole with Silver Isothiocyanate.—A 8.73-g (50-mmol) sample of 2-chloro-1,3,2-benzodioxaphosphole and 8.30 g (50 mmol) of silver isothiocyanate in 100 ml of benzene were heated under reflux for 16 hr. The cooled mixture was filtered, solvent was removed *in vacuo*, and the residual viscous liquid was distilled. The main fraction (5.15 g) was collected at 70° (1.5 mm). The mass spectrum showed a parent ion at 197 which agrees with the calculated value of 197 for $C_7H_4NO_2PS$. However, this product rapidly turned into a yellow-orange oil upon standing at room temperature, *in vacuo*, in the dark.

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The Nitrogen 1s Binding Energies of Transition Metal Nitrosyls

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Received July 15, 1971

The bonding and electronic structure of transition metal nitrosyls have been frequently studied in recent years.[1–6] Two limiting situations have been identified: linearly coordinated NO^+ groups and angularly coordinated ("bent") NO^- groups. We have investigated the X-ray photoelectron spectra[7] of a series of these compounds to attempt correlations of the nitro-

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