Raman to become stronger when tryptophan is in a hydrophobic region.[10]

It seems quite likely that the highly resolved RR spectra of these chromophores will reveal additional spectroscopic signatures of the local environment of the chromophores. We have observed, for example, that the tyrosine doublet at 1610 cm^{-1} shifts to lower frequency upon deprotonation.

Acknowledgment. This work was supported by NSF Grant CHE-8106984 and NIH Grant GM25158. R.P.R. is the recipient of a postdoctoral research fellowship NIH 5 F32 GM 09104-02.

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(10) Kitagawa, T.; Azuma, T.; Hamaguchi, K. *Biopolymers* **1979**, *18*, 451.

π-Accepting Abilities of Phosphines in Transition-Metal Complexes

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A recent paper[1] described in some detail the nature of the frontier orbitals in PX_3 systems, with X = H, CH_3, or F. The authors concluded that "the π-acceptor orbital on phosphorus mostly consists of phosphorus 3p character".[2] Their conclusions were based on Xα calculations on the free ligands. Here, we use approximate[3] and ab initio molecular orbital theory to demonstrate π accepting in phosphine ligands *without involving d orbitals on phosphorus* in actual transition-metal complexes.

Our own interest in this subject arose from a study of cis–trans isomerization energies in systems such as $Cr(NH_3)_4(CO)_2$ and $Cr(PH_3)_4(CO)_2$.[4] Simple π-bonding arguments lead one to predict that $Cr(NH_3)_4(CO)_2$ should exist in the cis conformation, since only that conformation allows π back-bonding to the carbonyls from all three occupied t_{2g} orbitals[5] (assuming NH_3 cannot act as a π acceptor).[6] Indeed, the cis complex is calculated by the PRDDO method[3] to be 13.4 kcal/mol more stable than the trans isomer,[7] and its enhanced stability can be traced directly to greater π back-bonding.[8] A similar PRDDO calculation on *cis*- and *trans*-$Cr(PH_3)_4(CO)_2$ without d orbitals on phosphorus predicts the cis isomer to be only 0.3 kcal/mol more stable than the trans arrangement.[9] Analysis of the wave functions shows that the enhanced stability of *trans*-$Cr(PH_3)_4(CO)_2$ relative to the cis isomer is due to the fact that *the phosphine ligands are acting as π acceptors even though no d orbitals are included in the phosphorus basis set.* Thus, all three t_{2g} orbitals are stabilized by π back-bonding in both conformations of the phosphine complex,[10] reducing the energy difference between the two isomers.

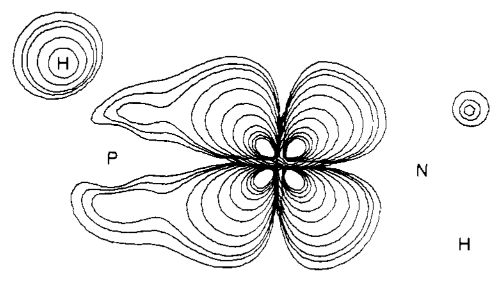

Figure 1. Electron density plot of one of the two π-donating d orbitals in $Cr(NH_3)_5(PH_3)$ without d orbitals on phosphorus. The contour levels are 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.0035, and 0.002 e/au^3.

To further quantify the π-accepting ability of phosphine without d orbitals a PRDDO calculation on the model complex $Cr(NH_3)_5(PH_3)$ was performed, with the phosphine on the z axis. No d orbitals were included in the phosphorus basis set. The resultant d-orbital populations on Cr were 1.80 e (d_{xz} and d_{yz}) and 1.97 e (d_{xy}). Examination of the phase relationships among the hydrogen, phosphorus, and chromium orbitals shows that the π-accepting orbital on phosphine has local σ^* symmetry with respect to the P–H bond axis.[11] An electron density plot of one of the two d_π orbitals is presented in Figure 1. Additional evidence for σ^* participation comes from the P–H overlap populations. Substantial population of the P–H σ^* orbital in the complex should lower the P–H overlap population relative to free phosphine. Indeed, the P–H overlap populations of the free and complexed ligand are 0.61 and 0.51, respectively.

To test the relative importance of σ^* vs. 3d orbitals in π accepting, we have performed ab initio calculations on the model tetrahedral complex $Ni(NH_3)_3(PH_3)$ with a double-ζ basis set with and without d orbitals on the phosphorus.[12] PRDDO-optimized geometries were employed.[13] This complex is formally d^{10}, and if the phosphine is placed on the z axis, the d_{xz} and d_{yz} orbitals should be depopulated relative to d_{xy} and $d_{x^2-y^2}$.[14] Indeed, without d orbitals on phosphorus, the relevant d-orbital populations on Ni are d_{xz}, d_{yz} (1.60 e) and d_{xy}, $d_{x^2-y^2}$ (1.74 e). Significant delocalization is seen from the metal d's to the phosphine hydrogens (0.30 e) and the phosphorus (0.13 e), but not to the amine hydrogens or nitrogen (0.01 e).[15] Addition of a d orbital to the phosphorus changes the Ni d-orbital populations only very slightly: d_{xz}, d_{yz} (1.57 e), and d_{xy}, $d_{x^2-y^2}$ (1.76 e); however, the group charge on PH_3 (defined as the sum of the orbital populations of all orbitals on phosphine) is exactly the same in the polarized and unpolarized calculations.

It is well-known that PF_3 is a better π acceptor than PH_3. The textbook explanation[16] is that electronegative substituents lower the energy of the d orbitals on phosphorus and therefore make them more available for bonding; however, π accepting into σ^*

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(1) Xiao, S.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033.

(2) This conclusion was explicity stated for PF_3, but also holds for PH_3.

(3) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58*, 1569. Marynick, D. S.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1341.

(4) Marynick, D. S.; Askari, S.; Nickerson, D. F., manuscript in preparation.

(5) For convenience, we employ octahedral symmetry notation.

(6) Only two d orbitals are π bonding in the trans isomer.

(7) The basis sets for these calculations are given in: Marynick, D. S.; Kirkpatrick, C. M. *J. Phys. Chem.* **1983**, *87*, 3273. The geometries were optimized.

(8) For the cis isomer, with carbonyls on the z and y axes, the d-orbital populations are d_{xz} (1.80), d_{yz} (1.19), and d_{xy} (1.80). For the trans isomer, with carbonyls on the z axis, the corresponding populations are 1.45, 1.45, and 1.99.

(9) The phosphine complex is known to exist in the cis form: Hutter, G.; Schelle, S. J. *Cryst.* Mol. *Struct.* **1971**, *1*, 69.

(10) The d-orbital populations for the *cis*-phosphine complex are d_{xz} (1.69), d_{yz} (1.35), and d_{xy} (1.69). For the trans complex the corresponding values are 1.44, 1.44, and 1.87. The significant reduction of the d_{xy} population of the *trans*-phosphine complex relative to that of the *trans*-amine complex is a direct manifestation of the π-accepting ability of PH_3, even without d orbitals.

(11) In ref 1, the π-accepting orbitals are described as simply being dominately 3p, but the wave function plots clearly identify the orbitals as having local σ^* symmetry. Participation of σ^* orbitals in some organophosphorus systems has been discussed previously: Gray, G. A.; Albright, T. A. *J. Am. Chem. Soc.* **1977**, *99*, 3243. Earlier qualitative discussions of bonding in similar systems appear in: Hoffmann, R.; Boyd, D.; Goldberg, S. Z. *J. Am. Chem. Soc.* **1970**, *92*, 3929. The π-accepting utility of the lowest unoccupied orbital of e symmetry in calculations without d orbitals on phosphorus has been briefly noted by: Yarbrough, L. W.; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269.

(12) The basis set, which is minimal for the inner shells and double-ζ for the valence shells (including the metal 3d), will be fully described in ref 4. We have repeated these calculations with two d orbitals on phosphorus and find no significant differences.

(13) *R*(Ni–N) = 2.012 Å and *R*(Ni–P) = 1.981 Å, tetrahedral angles assumed. Note that the exceptionally short Ni–P distance is another manifestation of π back-bonding. The ab initio calculations were repeated with the Ni–P bond lengthened by 0.13 Å, with no significant differences.

(14) With respect to the phosphine, the d_{xz} and d_{yz} orbitals are π bonding, while the d_{xy} and $d_{x^2-y^2}$ orbitals have local δ symmetry.

(15) The orbital populations quoted here represent the electron delocalization from the four MO's which are dominately d_{xy}, $d_{x^2-y^2}$, d_{xz}, and d_{yz}. The phase relationships among the phosphine orbitals are clearly consistent with σ^* π acceptance.

(16) See, for instance: Huheey, J. E. "Inorganic Chemistry"; Harper and Row: New York, 1983; pp 832–833.

orbitals is also consistent with the strong π-accepting character of PF_3. PRDDO calculations on the model complex $Cr(NH_3)_5(PF_3)$ yield Cr d-orbital populations of 1.74 e for d_{xz} and d_{yz} and 1.98 e for d_{xy}. The enhanced depopulation of the d_π orbitals in this complex relative to $Cr(NH_3)_5(PH_3)$ demonstrates the greater π-accepting ability of PF_3 relative to PH_3 even without d orbitals on phosphorus. There are several reasons for the enhanced π-accepting ability via σ^* orbitals of PF_3 compared to PH_3 and PH_3 relative to NH_3. First, highly polar bonds, such as those between phosphorus and fluorine, characteristically have low-lying σ^* orbitals and are thus better π acceptors. Similarly, the P-H σ^* orbitals in PH_3 lie at lower energies than those of NH_3.[17] Second, because the σ P-F bond is highly polar toward F, the σ^* orbital must necessarily be highly polar toward P, therefore increasing the σ^*-metal d_π overlap. The second argument also holds to a lesser extent for P-H as compared to N-H bonds: e.g., the N-H σ^* orbital will be polar toward H and therefore not overlap well with the metal. Finally, the phosphine σ^* orbitals are composed of 3s and 3p orbitals, which overlap more effectively with metal 3d orbitals than the 2s and 2p orbitals utilized by amines. Of course, a quantitative calculation of the π-accepting ability of ligands such as PF_3 will probably require d orbitals, but our results show that *d orbitals on phosphorus are not necessary for a qualitative understanding of π back-bonding effects in these systems.*

Acknowledgment. This work was supported by the Robert A. Welch Foundation (Grant Y-743), the Research Corporation, and the Organized Research Fund of The University of Texas at Arlington.

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(17) When a polarized double-ζ basis set is used, the eigenvalues and symmetries of the three LUMO's of free PH_3 are 0.177 au(e) and 0.250 au(a). For NH_3, the corresponding values are 0.236 au(e) and 0.357 au(a).

Bond Energy-Bond Order Relations in Transition-Metal Bonds: Vanadium

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One of the strengths of organic chemistry has been the extensive tabulation and correlation of bond strengths, bond lengths, and bond orders. This enables the prediction of the stability of unknown species and the estimation of the thermochemistry of postulated reaction mechanisms. Presently, transition-metal chemistry does not enjoy a similar power. While bond lengths are often known and bond orders can be estimated, bond strengths, particularly of individual bonds, are virtually unknown. Consequently, the energetics of even a simple series of single, double, and triple bonds between a metal and a ligand remain undocumented. In this paper, we present the first such results for the bond energies of vanadium ions to hydrogen, oxygen, and a number of carbon ligands.

The technique employed to determine bond energies is guided ion beam mass spectrometry. In this method, a mass- and energy-selected ion beam, here V^+, is reacted with a neutral gas. The interaction occurs inside an octopole ion trap[1] which "guides" the ion beam and product ions into the analyzer and detector. The trap eliminates many of the experimental difficulties common to conventional ion beam experiments and dramatically increases the sensitivity. The data are analyzed to yield reaction cross sections as a function of kinetic energy. Details of the technique and methods of analysis can be found elsewhere.[2,3] In this study, the vanadium ions are produced by surface ionization of $VOCl_3$ (Puratronic, 99.995% pure, used as received except for multiple freeze-pump-thaw cycles) on a resistively heated rhenium filament. At the filament temperature used, ~2200 K, the V^+ ions are calculated to be primarily in the ^5D ($(3d)^4$) ground state, >81%, and the first excited state, ^5F ($(4s)^1(3d)^3$), <19%.[4] The presence of the ^5F state is estimated to influence the bond energies cited here by no more than 0.06 eV (1.5 kcal/mol).[5]

Table I. Vanadium Ion-Ligand Bond Energies Derived from Reaction 1 and the Carbon Bond Used for Comparison in Figure 1

			correlation for Figure 1	
A	$D°(V^+-A)$, kcal/mol[a]	AB	H_nC-A	$D°(H_nC-A)$, kcal/mol[b]
H	50.0 (2)[c]	H_2	CH_3-H	104
C	88 (5)	CO	C-C	145
CH	115 (5)	C_2H_6	HC-CH	230
CH_2	80 (8)	C_2H_4	H_2C-CH_2	173
CH_3	50.5 (3)	C_2H_6	H_3C-CH_3	90
O	131 (5)[d]	CO	C-O	257
C_2	140 (12)	C_2H_2		
C_2H	109 (12)	C_2H_2, C_2H_4		
C_2H_2	>42	C_2H_4		
C_2H_3	75 (12)	C_2H_4		
C_2H_4	>33	C_2H_6		

[a] All values from this work except as noted. Uncertainties in parentheses. [b] Wagman, D. D. et al. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. [c] Elkind, J. L.; Aristov, N.; Ervin, K. M.; Armentrout, P. B., unpublished work. [d] This value agrees with that derived from appearance potential measurements on $VOCl_3$, 129 ± 5 kcal/mol (Flesch, G. D.; Svec, H. J. *Inorg. Chem.* **1975**, *14*, 1817) as well as unpublished studies of the reactions of V^+ and VO^+ with other oxygen-containing species.

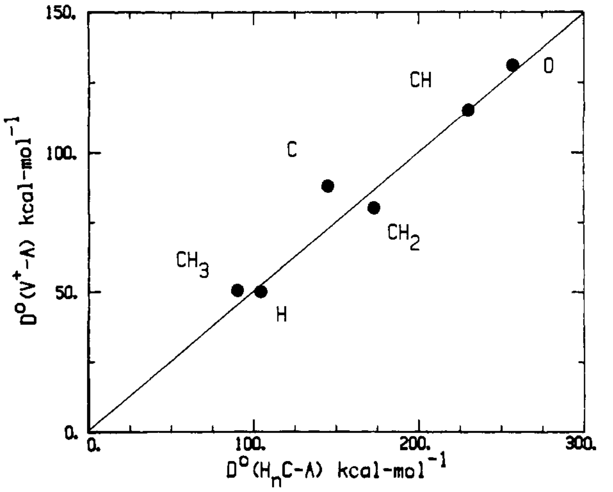

Figure 1. Bond dissociation energies from Table I for V^+-A vs. H_nC-A where A is the group indicated. The line is the least-squares best fit to the data.

Bond dissociation energies (BDEs) are derived from the cross-section data by measuring the endothermicity, E_0, of reaction 1, which is taken to equal the difference in energy of the bond

$$V^+ + AB \rightarrow VA^+ + B \qquad (1)$$

broken, $D°(AB)$, which is generally known, and the bond formed, $D°(V^+-A)$, the quantity of interest. Full details of the reactions of V^+ with H_2, CO, and the C_2 hydrocarbons and the analysis of these results will be published elsewhere.[6] Table I lists these

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(1) Teloy, E.; Gerlich, D. *Chem. Phys.* **1974**, *4*, 417.

(2) Ervin, K. M.; Aristov, N.; Loh, S. K.; Armentrout, P. B. *J. Phys. Chem.* **1983**, *87*, 3593. Ervin, K. M.; Armentrout, P. B., *J. Chem. Phys.*, submitted for publication.

(3) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

(4) Moore, C. E. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, *34*.

(5) This is 19% of the excitation energy of the ^5F state, 0.32 eV.[4]

(6) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.*, submitted for publication.

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