compounds are too stabilized for oxidation to be observable. This is a further indication of the strong π-acceptor behavior of Azpy.

Only in some compounds where the coligands are not π-acceptors, and total π-stabilization is through the two Azpy ligands, is oxidation observed. The range of values lends confidence to the conclusion that it is a ruthenium-centered oxidation we are observing and not ligand oxidation.

Many workers have attributed increasing $Ru^{3+/2+}$ potentials to ML π bonding;[25] Dose and Wilson[26] have used potential measurements to rank the π-acceptor behavior of ligands. However, other factors such as σ effects and solvation energies are also important, as noted by Cloninger and Callahan.[27] Thus, in $[Ru(Azpy)_2en]^{2+}$ ruthenium(II) is greatly stabilized in spite of the fact that all π interaction must be with the two Azpy ligands. In this series of compounds, the potential data are not a quantitative probe for π bonding.

A far more interesting situation arises in the reduction potential data, for reduction of the ruthenium(II) complexes. All are reduced at potentials more positive than −0.6 V (vs. SCE). In fact, $Ru(Azpy)_3^{2+}$ is reduced to "$Ru(Azpy)_3^{+}$" at the highest potential yet observed for a ruthenium(II) complex; aqueous $SnCl_4^{2-}$ easily reduces the compound (this chemistry will be reported later).

It is well-known that $Ru(bpy)_3^{2+}$ undergoes reduction; Baxendale and Fiti first observed the formation of reactive, transient $Ru(bpy)_3^{+}$.[28] Using the stronger π-acceptor ligand 2,2′-bipyrazyl, Crutchley and Lever[29] observed the ruthenium(II) tris complex to be reduced at a much more positive potential (−0.86 V) than $Ru(bpy)_3^{2+}$. We feel the high reduction potentials we observe for Ru(Azpy) complexes are further verification of the very strong π-acceptor behavior of the ligand Azpy.

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Registry No. $Ru(Azpy)_2(NO_2)_2$, 80697-51-4; $Ru(Azpy)_2(CN)_2$, 80697-52-5; $[Ru(Azpy)_3](PF_6)_2$, 80697-54-7; $[Ru(Azpy)_2bpy](ClO_4)_2$, 80697-56-9; $[Ru(Azpy)_2Btz](ClO_4)_2$, 80697-58-1; $Ru(Azpy)_2Br_2$, 80735-95-1; $[Ru(Azpy)_2en](ClO_4)_2$, 80697-60-5; $Ru(Azpy)_2(N_3)_2$, 80697-61-6; $[Ru(Azpy)_2(tu)_2](ClO_4)_2$, 80697-63-8; $[Ru(Azpy)_2(acac)](ClO_4)$, 80697-65-0; $Ru(Azpy)_2Cl_2$, 80735-96-2; $Ru(bpy)_2(NO_2)_2$, 29241-01-8.

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Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27650

The Role of d Orbitals on Phosphorus in the Bonding of $P(CH_3)_3$ and $P(CF_3)_3$

M.-H. WHANGBO* and K. R. STEWART

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The optimum P–C bond lengths of $P(CH_3)_nH_{3-n}$ and $P(CF_3)_nH_{3-n}$ (n = 1–3) were determined by ab initio SCF MO calculations with STO-3G and STO-3G* basis sets. Our study shows that the P–C bond of $P(CF_3)_nH_{3-n}$ is longer than that of $P(CH_3)_nH_{3-n}$ regardless of whether d orbitals are present on phosphorus or not and that the role of phosphorus d orbitals in the bonding with carbon orbitals is not counterintuitive but normal.

Instances of anomalous orbital interactions have been observed in extended Hückel and ab initio SCF MO calculations[1–4] and have been discussed under the name of either altruistic covalent interaction[1] or counterintuitive orbital mixing.[2–4] An experimentally observable consequence of counterintuitive orbital mixing might be an unusual bond lengthening that occurs when a bond between electropositive atoms is surrounded by electronegative ligands.[1,4] Marsden and Bartell[1] observed that the P–C bond in $P(CF_3)_3$ is substantially longer than that in $P(CH_3)_3$ and suggested from their extended Hückel calculations that the unusually long P–C bond in $P(CF_3)_3$ arises in part from a counterintuitive interaction of d orbitals on phosphorus with carbon orbitals. Thus, d orbitals on phosphorus are regarded to play the role of bond lengthening.

It was recently shown by Collins et al.[5] that, in the accurate description of molecules with second-row atoms, d orbitals on second-row atoms play an important role. They found that geometries of molecules containing second-row atoms are well reproduced by a minimal basis set, when supplemented with d orbitals on second-row atoms. For example, two-heavy-atom bond lengths calculated by STO-3G* basis sets are generally shorter than those calculated by STO-3G basis sets and are in better agreement with experimental values. Thus, d orbitals on second-row atoms play the role of bond shortening.

Concerning the role of d orbitals on phosphorus, therefore, the conclusion of Marsden and Bartell is not consistent with that of Collins et al. To resolve this discrepancy, we have determined the optimum P–C bond lengths in $P(CH_3)_nH_{3-n}$

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Table I. P–C Bond Lengths (r_{P-C}), the P–C Overlap Populations (p_{P-C}), and the Total Energies (E_{tot}) of $P(CH_3)_nH_{3-n}$ and $P(CF_3)_nH_{3-n}$ Calculated by STO-3G and STO-3G* Basis Sets[a]

molecule	r_{P-C}, Å	p_{P-C}[d]	$-E_{tot}$, au
CH_3PH_2	1.8440	0.2883	377.2213
	1.8320	0.3302 (0.3278)	377.2734
CF_3PH_2	1.9056	0.2516	669.5971
	1.8835	0.2901 (0.2867)	669.6519
$(CH_3)_2PH$	1.8452	0.2854	415.8105
	1.8340	0.3293 (0.3272)	415.8660
$(CF_3)_2PH$	1.9135	0.2472	1000.5552
	1.8897	0.2873 (0.2830)	1000.6152
$P(CH_3)_3$[b]	1.8467	0.2817	454.4010
	1.8361	0.3278 (0.3257)	454.4595
$P(CF_3)_3$[c]	1.9216	0.2413	1331.5103
	1.8973	0.2832 (0.2785)	1331.5747

[a] For each molecule, the numbers obtained from the STO-3G and STO-3G* basis sets are respectively given in the first and the second rows. [b] The experimental P–C bond length is 1.846 Å. [c] The experimental P–C bond length is 1.904 Å. [d] The numbers in parentheses represent the P–C overlap population calculated by using the STO-3G* basis set on the molecular geometry determined from the STO-3G basis set.

and $P(CF_3)_nH_{3-n}$ (n = 1–3) by employing ab initio SCF MO calculations with STO-3G and STO-3G* basis sets.[7] In our calculations, all the geometrical parameters other than the P–C bond lengths were taken from the experimental values of $P(CH_3)_3$[6] and $P(CF_3)_3$.[1] For molecules $P(CH_3)_nH_{3-n}$ and $P(CF_3)_nH_{3-n}$ with n = 1 and 2, the P–H bond length of 1.378 Å[5] was adopted while the valence angles around phosphorus were taken from those of $P(CH_3)_3$ and $P(CF_3)_3$, respectively. Results of our calculations are summarized in Table I, which reveals the following trends that are independent of n: (a) the P–C bond length of $P(CF_3)_nH_{3-n}$ is longer than that of $P(CH_3)_nH_{3-n}$, regardless of whether d orbitals are present on phosphorus or not; (b) either in $P(CH_3)_nH_{3-n}$ or in $P(CF_3)_nH_{3-n}$, the P-C bond length becomes shorter upon including d orbitals on phosphorus; (c) in each molecule the P–C overlap population is not decreased but enhanced by phosphorus d orbitals.

Thus our study shows that the role of phosphorus d orbitals in $P(CH_3)_3$ and $P(CF_3)_3$ is not counterintuitive but normal, in agreement with the observation of Collins et al.[5] In accounting for the long P–C bond of $P(CF_3)_3$, the concept of counterintuitive orbital interaction remains valid since it provides a mechanism by which electron density shifts from the electropositive region of P–C bond to the electronegative region of C–F bond.[4] However, this electron shift is not due to phosphorus d orbitals as indicated by the extended Hückel calculations.[1] Use of the weighted H_{ij} formula is found to greatly reduce the extent of counterintuitive orbital interaction in extended Hückel calculations on $P(CF_3)_3$, as in the case of molecules containing transition-metal atoms.[2]

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Registry No. $P(CH_3)_3$, 594-09-2; $P(CH_3)_2H$, 676-59-5; $P(CH_3)H_2$, 593-54-4; $P(CF_3)_3$, 432-04-2; $P(CF_3)_2H$, 460-96-8; $P(CF_3)H_2$, 420-52-0.

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Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27650

Importance of the Out-of-Plane Niobium Displacement for the Semiconducting Property of $NbOX_2$ Net

M.-H. WHANGBO

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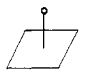
Tight-binding band calculations were performed on $NbOCl_2$ net to examine the effect of Nb–Nb···Nb and Nb–O···Nb alternations on the electronic structure of $NbOCl_2$ net. The out-of-plane Nb displacement is found as crucial as the pairing distortion of Nb atoms for the semiconducting property of $NbOX_2$ net.

The crystal structure of two-dimensional $NbOX_2$ net[1–3] can be conveniently described in terms of a hypothetical $NbOX_4$ square pyramid **1**, in which the Nb atom is located at the center of the X_4 plane. A one-dimensional $NbOX_2$ chain **2** is obtained when $NbOX_4$ pyramids are linked together by sharing their opposite edges. A two-dimensional $NbOX_2$ net **3** is derived when $NbOX_2$ chains are joined together by sharing their oxygen atoms. The real structure of $NbOX_2$ net differs from the ideal structure **3** in two important aspects: (a) there occurs a pairing distortion of Nb atoms in each $NbOX_2$ chain of **3**, leading to an alternation of two unequal Nb–Nb distances along the x axis (i.e., Nb–Nb···Nb alternation); (b) each Nb atom of **3** is displaced from the center of X_4 plane as depicted in **4a**, giving rise to an alternation of two unequal Nb–O bonds along the z axis (i.e., Nb–O···Nb alternation).[3]

1


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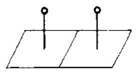
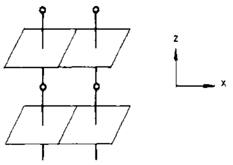


3


Each $NbOX_2$ chain of **3** consists of Nb^{4+} (d^1) ions, so the occurrence of Nb–Nb···Nb alternation is an expected result just as in the case of NbX_4 chains.[4–7] Thus the semicon-

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