On the \( \pi \)-Donor Ability of Early Transition Metals: Evidence That Trialkylphosphines Can Engage in \( \pi \)-Back-Bonding and X-ray Structure of the Titanium(II) Phenoxide \( \text{Ti(O\text{OPh})}_2(\text{dmpe})_2 \)

We have recently proposed the idea that the early transition metals in their lower oxidation states are unusually strong \( \pi \)-donors and that this phenomenon to a large degree governs the characteristic chemistry of these elements.\(^{1-3}\) We now show how this effect can explain unexpected spin state changes in a series of titanium(II) phosphine complexes. We also describe the synthesis of the first well-characterized titanium(II) aryloxide and a description of its bonding.

**Interaction of trans-\( \text{TiCl}_2(\text{dmpe})_2 \)**\(^{4}\) (\( \text{dmpe} = 1,2\)-bis(di-methylphosphino)ethane) with sodium phenoxide in diethyl ether followed by filtration and cooling affords red crystals of the titanium(II) phenoxide complex \( \text{trans-Ti(O\text{OPh})Cl(dmpe)}_2 \).\(^{5}\) The monophenoxide complex is isolated even in the presence of excess NaOPh. However, treatment of the tetrahydroborate complex \( \text{Ti(BH}_4)_2(\text{dmpe})_2 \) with 2 equiv of NaOPh in tetrahydrofuran results in the replacement of both BH\(_4^+\) groups and formation of the bis(phenoxide) complex \( \text{trans-Ti(O\text{OPh})_2(dmpe)}_2 \).\(^{7}\)

\[
\text{TiCl}_2(\text{dmpe})_2 + 2\text{NaOPh} \rightarrow \text{Ti(O\text{OPh})Cl(dmpe)}_2 + \text{NaCl}
\]

Unlike \( \text{TiCl}_2(\text{dmpe})_2 \) and \( \text{Ti(BH}_4)_2(\text{dmpe})_2 \), which are paramagnetic \( d^0 \) species, the two phenoxide complexes are diamagnetic. Along with the previously reported methyl complex \( \text{trans-TiMe}_2(\text{dmpe})_2 \),\(^{6}\) which is also diamagnetic, these are the only examples of octahedral complexes of a first-row transition metal that exhibit spin pairing within the \( t_2g \) (or pseudo-\( t_{2g} \)) manifold.

The titanium center in \( \text{Ti(O\text{OPh})}_2(\text{dmpe})_2 \) adopts an octahedral coordination environment (Figure 1).\(^8\) The average Ti-P distance of 2.515 (2) Å is essentially identical with the Ti-P distance of 2.514 (1) Å in diamagnetic TiMe\(_2(\text{dmpe})_2 \)\(^{6}\), but is significantly shorter than the 2.586 (5)-2.626 (1) Å distances in the high-spin species TiCl\(_2(dmpe)_2 \)\(^4\) and Ti(BH\(_4\))\(_2(dmpe)_2 \).\(^6\) The average Ti-O distance in \( \text{Ti(O\text{OPh})}_2(dmpe)_2 \) of 1.911 (6) Å is somewhat longer than those of 1.807 (6) to 1.891 (7) Å in titanium(III) aryl-...
methods that can distinguish that are similar to those of trialkylamines9 and are therefore weak studies'b's suggest that trialkylphosphines have bonding properties evidence to support the idea that trialkylphosphines can engage in strong *-back-bonding with transition metals. Of the few physical our view of the bonding in trialkylphosphine complexes of the early oxides,"" as expected from the larger radius of Ti". The planes transition metals. To date, there has been little compelling evi-*dation of these studies yields direct evidence that the energies of metal-based orbitals of *-symmetry are strongly perturbed by bonding with trialkylphosphine ligands. The TiX(dmpe)2 compounds provide such evidence.

The TiX(dmpe) complexes can be divided into two classes according to their spin state: the two phenoxide complexes and TiMe(dmpe)2, are diamagnetic, while the chloride, bromide,10 iodide,10 and tetrahydroborate analogues are paramagnetic with two unpaired electrons. These spin states can be understood as follows. In a D4h ligand field, the degeneracy of the t2g orbitals will be broken to yield orbitals of eg (dxz, dyz) and b2g (dz2) symmetry. The energy difference between the eg and b2g orbitals will be small unless (1) the axial X groups are strong *-donors,12 or (2) the equatorial dmpe ligands are strong *-acceptors. Apparently, neither situation pertains in the TiX(dmpe)2 complexes with X = Cl, Br, I, or BH4 (Figure 2b), which must have small eg-b2g splittings to account for their paramagnetism. In contrast, the diamagnetism of the phenoxide complexes can be attributed to the first effect (Figure 2a), since aryloxides are better *-donors than halides. The orthogonal orientation of the two phenoxide groups in Ti(OPh)2(dmpe)2 also supports this view.13 However, this effect gauges only indirectly the degree of *-back-bonding. Finally, there are some theoretical studies of the *-accepting ability of phosphorus ligands.25 However, none of these studies yields direct evidence that the energies of metal-based orbitals of *-symmetry are strongly perturbed by bonding

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The previously reported titanium(II) aryloxide Ti(0-2.6-(i-Pr)2C6H4)2(bpy)12 may actually be a titanium(III) aryloxide containing reduced ligands like the pyridine analogue Ti(O-2.6-(i-Pr)2C6H4)2(py)13 since bipyridine should be reduced by Ti11 more readily than pyridine.

The d2 complexes of TiX(dmpe)2 have forced us to reconsider our view of the bonding in trialkylphosphine complexes of the early transition metals. To date, there has been little compelling evidence to support the idea that trialkylphosphines can engage in strong *-back-bonding with transition metals. Of the few physical methods that can distinguish *- from x-bonding effects, PES studies14-18 suggest that trialkylphosphines have bonding properties that are similar to those of trialkylamines19 and are therefore weak *-acceptors at best.20,21 Other evidence that trialkylphosphines can serve as *-acceptors is that metal-phosphorus bond lengths often increase slightly upon oxidation of the metal center.22-27

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(21) In contrast, many studies clearly provide convincing evidence that aryloxophenes can serve as strong *-acceptors.9-20
(22) Orpen, A. G.; Connolly, N. J. Organometallics 1990, 9, 1206-1210.
is possible in part because the low effective nuclear charges $Z_{eff}$ of the early transition elements make the d orbitals unusually high in energy. The energies of the d orbitals are raised even higher in TiMe$_2$(dmpe)$_2$ (but not in the halide or BH$_4^-$ complexes) by the inductive effect of the strongly σ-donating Ti-Me groups. In other words, by acting as strong σ-donors, the methyl groups put electron density into the d orbitals. This effect is further enhanced by the fact that the d orbitals is preferentially stabilized (Figure 2c). The amount of π-overlap must be large, since the splitting between the $b_2$ and $e_g$ orbitals is sufficient to cause pairing of the two d electrons of TiMe$_2$(dmpe)$_2$ in the $b_2$ orbital.

These results add strength to the contention that early transition metals in their lower oxidation states are exceedingly strong σ-donors, and can engage in strong σ-back-bonding even with normally poor σ-acceptors such as trialkylphosphines. This suggests that the diffuse nature of the d orbitals and the resulting delocalization of charge is responsible for the lack of luminescence, recent work in our laboratory and elsewhere indicates that the perturbation of the π* orbital on the bridging ligand is of prime importance in determining the photophysical properties of such complexes. Tapolsky et al. have exploited this effect to achieve an "electron-energy-transfer cascade" in the binuclear complex $[(bpy)\text{CO}_3\text{Re}(4,4'-\text{bpy})\text{Re(CO)}_3(\text{bpy})]^{2+}$, where 4,4'-bpy represents 4,4'-bipyrindine and bpy = 2,2'-bipyridine. In this complex, the proximity of the Re → bpy and Re → 4,4'-bpy MLCT levels allows for control of the excited-state properties by variation of the oxidation state of the Re atoms.

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**Supplementary Material Available:** Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for Ti(OPh)$_2$(dmpe) (4 pages); a table of final observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(35) We are currently investigating the optical spectra of the TiX$_2$(dmpe)$_2$ complexes, which should allow us to determine the $b_2$-$e_g$ splitting directly.


(40) Frerichs, R. S.; Ellis, J. E. J. Organomet. Chem. 1989, 359, C41-C44.

(41) Ellis, J. E. Polyhedron 1989, 8, 1611-1616.


(43) Note added in proof: Detailed ab initio calculations have recently confirmed the importance of the low $Z_{eff}$ and the inductive shielding effect of the Ti-Me groups in TiMe$_2$(dmpe)$_2$. However, the results suggest that the diffuse nature of the d orbitals and the resulting decreased electron-electron repulsions are largely responsible for the diamagnetism (Simpson, C. Q.; Hall, M. B.; Guest, M. F. Submitted for publication). We thank Professor Hall for sharing his results with us before publication.

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