not,[7] and questions have arisen concerning the necessity of including such orbitals.[6b,c,7a] We feel that the symmetry of the state in question often provides a good criterion for estimating the stereochemical, as opposed to merely numerical, importance of such basis functions.

If an occupied molecular orbital transforms according to an irreducible representation of the point group of the nuclear configuration for which the usual s and p functions do not provide a basis, it then becomes crucial to include orbitals of higher azimuthal quantum number in the description of the molecular bonding. Alternatively, if the s and p functions do provide such a basis, the energy lowering provided by the inclusion of higher orbitals is due to such factors as polarization and is therefore not of fundamental importance in the qualitative bonding picture. In the case of molecules involving second-row atoms, these higher orbitals will be principally the 3d functions.

As a simple example consider the pyramidal inversion of phosphine. In the pyramidal (C_{3v}) ground-state configuration, all occupied molecular orbitals have A_1- or E-type symmetry. Bases for these irreducible representations are provided by s- and p-type functions. Therefore, d functions are not qualitatively significant in the bonding of this state. On the other hand, for the maximum-potential, planar (D_{3h}) transition state, occupied molecular orbitals, especially in configuration interaction calculations, may have A_1', A_2'', E', or E'' symmetry. Of these, only the E'' irreducible representation does not have a basis in s- and p-type phosphorus orbitals. Therefore, for this state, the d functions are important if there is any occupied molecular orbital of E'' symmetry. Kari[8] has, in fact, reached more or less the same conclusion by means of a CI calculation on NH_3.

The simple question of whether d orbitals are qualitatively important in sulfur bonding becomes meaningless with respect to this symmetry criterion. For a molecule such as H_2S (C_{2v}), calculations have shown that d orbitals, while providing polarization effects, are unimportant in understanding the actual bonding scheme.[6b,e] In the octahedral case (O_h) of SF_6, however, there are occupied molecular orbitals of T_{2g} and E_g symmetries.[6c] These irreducible representations do not have a basis in the s- and p-type functions, and therefore d-type functions are qualitatively necessary for understanding their bonding structure.

The cases of H_2S and SF_6 are well-known extremes for the contribution of d orbitals and symmetry considerations. There are also many intermediate cases,[9] and these have been treated by a variety of methods. A survey of some representative calculations is given by Rauk, Wolfe, and Csizmadia,[10] and the role of d orbitals in various compounds is discussed. Recently, Maclagan[11] has discussed the symmetry criterion for d-orbital participation from a valence-bond point of view.

We feel that this symmetry criterion, used in conjunction with the usual overlap considerations,[12] should aid in evaluating the importance of higher orbitals in the description of molecular orbital bonding.

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Reactivity of Trialkylphosphine Complexes of Platinum(0)

Sir:

We find the reactivity of trialkylphosphine complexes of platinum(0) to be surprisingly greater than that of the established triarylphosphine analogs.[1] The exemplar is the facile cleavage of carbon–carbon bonds in aryl nitriles.

The new trialkylphosphine–platinum complexes were prepared through displacement of the π-borallyl ligand[2] from $PtB_3H_7(R_3P)_2$[4] by excess phosphine. In this fashion, we isolated colorless crystals of the tetrakis-triethylphosphine and -trimethylphosphine complexes.[5] The triethylphosphine complex dissolved in hydrocarbons with ligand dissociation to give red-orange solutions. On heating $Pt[P(C_2H_5)_3]_4$ at 50–60° *in vacuo*, $Pt[P(C_2H_5)_3]_3$ was isolated as a red-orange oil. In contrast, the tetrakis-trimethylphosphine complex did not dissociate up to 70–80°.

The ^{31}P nmr spectra of solutions of $Pt[P(C_2H_5)_3]_3$ and $Pt[P(C_2H_5)_3]_4$ at $-55°$ consist of singlets flanked by ^{31}P–^{195}Pt satellites. Chemical shifts and ^{31}P–^{195}Pt coupling constant data for these compounds and for $Pt[P(p\text{-}C_7H_7)_3]_3$ and $Pt[P(p\text{-}C_7H_7)_3]_4$ are set forth in Table I. The coupling constants for PtL_3 complexes are significantly larger than those for PtL_4 complexes. This is consistent with the presumed greater s character in Pt–P bonds of tris-phosphine complexes.[6] Ligand ex-

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(2) This reaction is strikingly similar to the displacement of the π-allyl ligand from $\{Pt(\pi\text{-}C_3H_5)[P(C_6H_5)_3]_2\}^+$ by excess triphenylphosphine[3] and is consistent with our formulation of the B_3H_7 ligand as a π-allyl analog.

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(5) Satisfactory elemental analyses were obtained for all new compounds. *E.g. Anal.* Calcd for $Pt[P(C_2H_5)_3]_4$: C, 43.2; H, 9.06; P, 18.5; Pt, 29.2. Found: C, 43.3; H, 9.28; P, 18.5; Pt, 29.2.

(6) Formally sp^2 and sp^3 hybridization may be assumed for the tris and tetrakis complexes, as was done for the analogous AgL_3^+ and AgL_4^+

Table I. ^{31}P Nmr Data of ML_3 and ML_4 Complexes

Complex	Chemical shift,[a] ppm	$J_{^{31}P-^{195}Pt}$, Hz
$Pt[P(C_2H_5)_3]_3$	−42	4220
$Pt[P(p\text{-}C_7H_7)_3]_3$	−51	4340
$Pt[P(C_2H_5)_3]_4$	+17	3740
$Pt[P(p\text{-}C_7H_7)_3]_4$	−11	3780
$Ni[P(C_2H_5)_3]_4$	−3	

[a] Relative to external 85% H_3PO_4.

change is rapid in solutions of PtL_4 at room temperature, and no Pt–P coupling is observed.

Tris(triethylphosphine)platinum(0) is an extraordinarily strong nucleophile and undergoes a wide range of oxidative-addition reactions. For example, addition of benzonitrile to a refluxing toluene solution of the tris complex gives within 15 min a high yield of *trans*-$C_6H_5Pt(CN)[P(C_2H_5)_3]_2$. Under similar conditions, the carbon–chlorine bond in chlorobenzene is cleaved with concomitant formation of *trans*-$C_6H_5PtCl[P(C_2H_5)_3]_2$. In contrast, the tris-triphenylphosphine complex does not react with benzonitrile or chlorobenzene under these conditions.[8] These comparisons demonstrate the qualitatively different reactivities of aryl- and alkylphosphine complexes of platinum(0). Like the arylphosphine complexes, the alkyl analogs react with alkyl and allyl halides. We found that tris(triethylphosphine)platinum(0) reacts vigorously with allyl chloride at 25° to give $\{(\pi\text{-}C_3H_5)Pt[P(C_2H_5)_3]_2\}^+$, which was isolated as the tetrafluoroborate salt.

Hydrogen adds readily to the alkylphosphine–platinum complexes to give five-coordinate hydrides. For example, the tris(triethylphosphine)platinum complex, in hydrocarbon solution, absorbed hydrogen at 25° to give $H_2Pt[P(C_2H_5)_3]_3$. This novel hydride is thermally unstable and decomposes within several days on standing in hydrocarbon solvent at −40°. In solution this hydride shows a single platinum–hydrogen infrared stretching frequency at 1766 cm^{-1}. The 220-MHz proton nmr spectrum of the hydride region at −50° consists of a quartet at τ 23.37 (J_{PH} = 18 Hz) with ^{195}Pt satellites (J_{PtH} = 635 Hz). The spectrum is temperature dependent. On warming, the platinum–hydrogen coupling is lost above ~−30°, and the spectrum consists of three broad resonances with chemical shifts and platinum–hydrogen coupling constants substantially unchanged from those found at −50°. With increasing temperature, the three lines sharpen and remain sharp to 80°. The ligand-proton-decoupled ^{31}P nmr spectrum at −60° consists of a triplet (J_{PH} = 18 Hz) with ^{195}Pt satellites (J_{PtP} = 3060 Hz). These spectral data are consistent with, but do not define, a trigonal-bipyramidal structure with the hydrogen nuclei at axial positions. The temperature dependence of the hydride spectrum indicates that above −30° ligand dissociation is rapid through a four-coordinate complex, $H_2Pt[P(C_2H_5)_3]_2$, present at very low concentrations. For this dissociation process, the free energy of activation is ~12 kcal/mol.

The marked basicity of $Pt[P(C_2H_5)_3]_3$ is well delineated by its interaction with ethanol and water. The tris complex dissolves in both solvents to form the previously reported[10,11] cationic hydride, $HPt[P(C_2H_5)_3]_3^+$ which was isolated as the hexafluorophosphate salt by addition of ammonium hexafluorophosphate to the aqueous reaction mixture. The reaction of the tris complex with water is reversible; the tris complex was recovered by simple evaporation of the water.

We find some parallel to the reactivity of $Pt[P(C_2H_5)_3]_4$ in the chemistry of $Ni[P(C_2H_5)_3]_4$.[12] This complex, an off-white crystalline compound, was formed almost quantitatively by reaction of bis(1,5-cyclooctadiene)nickel(0) with triethylphosphine. It dissolved in hydrocarbon solvents with ligand dissociation to give intensely purple solutions of $Ni[P(C_2H_5)_3]_3$. This tris complex reacted smoothly with chlorobenzene and with benzonitrile *at room temperature* to give the corresponding *trans*-$C_6H_5NiX[P(C_2H_5)_3]_2$ compounds.[13] Work is in progress to examine other aspects of reactive d^{10} complexes of Ni, Pd, and Pt.

species.[7] In the silver system, the ratio of metal–phosphorus coupling constants in the tris and tetrakis complexes was about 3:4. This ratio in the platinum series is substantially larger.

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Structure of Bilobalide, a Rare *tert*-Butyl Containing Sesquiterpenoid Related to the C_{20}-Ginkgolides

Sir:

Extraction of a sesquiterpene closely related to the diterpenoid ginkgolides[1,2] from leaves of *Ginkgo biloba* ("fossil tree") was first reported in 1967[3] and then in 1969 (bilobalide).[4] Structure **1** deduced for this bilobalide shows that it is a unique trilactone sesquiterpene having a *tert*-Bu group, which so far has been encountered only in the ginkgolides (*cf.* **10**).

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