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PHOSPHORUS-CONTAINING ANALOGUES OF HYDROCARBON LIGANDS. MOLECULAR ORBITAL STUDY OF STRUCTURE AND BONDING IN POTENTIAL TRANSITION-METAL COMPLEXES CONTAINING PHOSPHORANIUM IONS AS π LIGANDS

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Summary

Structures of phosphoranium ions $C(PR_3)_3^{2+}$ and $CR(PR_3)_2^+$ reveal partial π character of the P–C bonds and molecular orbital calculations confirm that. These two ions are structurally and orbitally similar to well-known trimethylenemethane and allyl species, respectively. We cautiously suggest that possibility of π coordination of phosphoranium ions to transition metals be explored. We carried out molecular orbital calculations on various conformations of two hypothetical complexes, $(CO)_3Co[C(PH_3)_3]^+$ and $(PH_3)_2Pd[CH(PH_3)_2]^+$. In the former molecule, $Co(CO)_3^-$ and $C(PH_3)_3^{2+}$ groups tend to be staggered, and the P atoms tend to bend toward the Co atom. In the latter molecule, the $Pd(PH_3)_2$ group tends to slip toward the phosphoranium P atoms and to stay perpendicular to the mirror plane of $CH(PH_3)_2^+$; the ligand plane tends to tilt so that the CH group moves away from the Pd atom. In both molecules, the substituents at the phosphoranium P atoms tend to bend away from the metal atom. These predictions agree with structures of various known complexes of transition metals with unsaturated organic ligands.

Introduction

Knowledge about transition-metal complexes containing unsaturated hydrocarbons and their derivatives as ligands has revolutionized the thinking of chemists about bonding, structures and reactivity and has lead to various new industrial catalytic processes. Several properties of unsaturated hydrocarbons render them versatile π ligands: low polarity permits extensive delocalization of π molecular orbitals and absence of lone electron pairs makes *monohapto* (η^1) coordination

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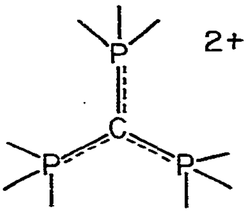
atypical. Introduction of heteroatoms into the carbon skeleton usually brings some polarity to the molecule, restricting delocalization of orbitals and furnishing the molecule with one or more lone pairs. Such a molecule may be expected to become less suitable than its all-carbon parent for delocalized bonding with the metal atom and more prone to coordination via the heteroatom.

Much has recently been learned about synthesis and reactivity of phosphaalkenes and phosphaalkynes, which contain double and triple P–C bonds, respectively [1]. Nixon and his co-workers have succeeded in coordinating a phosphaalkyne as π ligand in a transition-metal complex [2a], thus easing the aforementioned concerns. Phosphorins contain delocalized P–C bonds and also form π complexes [3]. But "inorganic" analogues of hydrocarbons that would have delocalized π molecular orbitals and yet not contain coordinatively unsaturated heteroatoms and the resulting lone pairs seem to be rare. The only examples known to us are phosphoranium ions of types **1** and **2**, which are structurally similar to well-known hydrocarbon ligands trimethylenemethane and allyl, respectively. This analogy is shown below. Ion **1** would be not only similar, but isoelectronic with the dication of trimethylenemethane.



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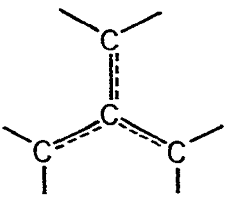

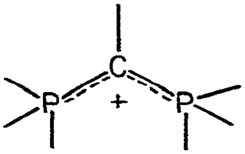

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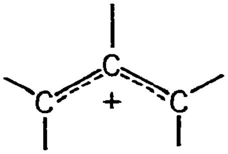
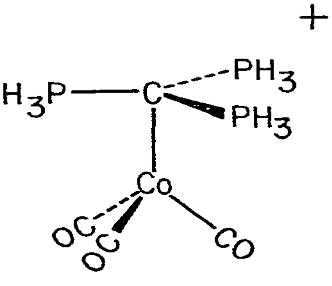


This similarity has gone unnoticed in the literature. We constructed two transition-metal complexes containing these ligands, **3** and **4**, and examined their bonding



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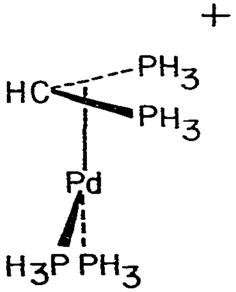


(4)

and structures (conformations) by molecular orbital calculations. Since $Co(CO)_3^-$ and $Pd(PR_3)_2$ form π complexes with allyl cation, a two-electron donor like **1** and **2**, we cautiously suggest that compounds like **3** and **4** might be realistic although they probably would not be as stable as their counterparts containing hydrocarbon ligands.

This paper is the seventh part of a study of transition-metal complexes whose bonding, structure and reactivity depend greatly upon the metal-ligand π interactions [4–9].

Details of the calculations

An approximation to the Hartree-Fock-Roothaan technique, the Fenske-Hall method has been described elsewhere [10]. The method is devoid of adjustable or empirical parameters so that results of a calculation (eigenvalues and eigenvectors) are completely determined by molecular geometry and the basis functions.

We partitioned both complex molecules, **3** and **4**, into two closed-shell fragments: the metal-containing group and the phosphoranium ligand. Such "cleavage" allows inspection of crucial interactions that affect the structures. After the iterative calculation would converge in the atomic basis set, the molecular orbitals of the complex were transformed into a basis set of the fragment orbitals. The redistribution of electrons between the fragments to make them closed shells and the basis-set transformation have no effect upon the numerical results of the calculations, but make them easier to interpret. The energies of the fragment orbitals in the molecular orbital diagrams are diagonal elements of the Fock matrices from the calculations on the complete molecules. These energies depend a little on conformation because they reflect the influences of the molecular environment upon the moieties "ready for bonding". We estimated relative stabilities of conformations by comparing summed eigenvalues of those occupied molecular orbitals that are affected by conformational changes.

The basis funtions were the same as in our previous studies [4–8]. The palladium $4d$ function [11] was fit to double-ξ form. When the single-ξ $3d$ function of phosphorus was included into the basis set, it had exponent 1.30.

We tock structures of phosphoranium ligands $C(PH_3)_3^{2+}$ (**1**) and $CH(PH_3)_2^+$ (**2**) from the crystallographic data for $[C(PMe_3)_3]I_2$ [12] and $[CH(PPh_3)_2]Br$ [13], respectively. Bond lengths in $Co(CO)_3^-$ [14] and $Pd(PH_3)_2$ [15] groups were taken from the appropriate crystal structures. The metal atom lay 2.00 Å beneath its projection onto the ligand plane.

Phosphoranium ligands

Chemistry of the phosphoranium species has been reviewed [16]. These molecules can be envisioned as resonance hybrids of phosphorane, phosphonium and carbanion canonical forms, but the delocalized representations **1** and **2** agree best with their properties, chemical behavior and structures [16]. Several derivatives of **1**, with different groups attached to the phosphorus atoms, are known [12,16–18]. Because of the charge 2+, a molecule of **1** must contain two π electrons. The calculation showed them to occupy the HOMO. Compound $[C(PMe_3)_3]I_2$ contains a planar CP_3 skeleton with P–C distances of 1.75 Å, which are about 0.10 Å shorter than P–C single bonds in a related compound [13,19] and slightly longer than P–C double bonds in phosphaalkenes [1]. Planarity and bond lengths both indicate that the P–C bonds in **1** have partial double character. Various derivatives of **2** are known

[13,16,20–29]. Because of the charge 1+, a molecule of **2** also must contain two π electrons; they occupy the HOMO. Compound $[CH(PPh_3)_2]Br$ contains planar CHP_2 skeleton with P–C distances of 1.70 Å, which are by 0.14 Å shorter than P–C single bonds [13,19] and similar to P–C double bonds in phosphaalkenes [1].

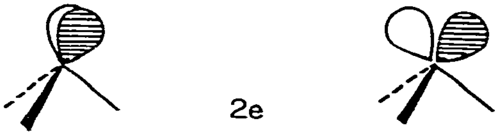
Partial multiple character of bonds to a tetracoordinate P atom is usually attributed to involvement of its 3*d* orbitals [30]. This question remains somewhat controversial because the PH_3 group has vacant hyperconjugative molecular orbitals of π symmetry, designated σ_π^*, which are composed of P–H σ bonds and largely localized on the P atom [31]. Like 3*d* orbitals, the σ_π^* orbitals can participate in π bonding within the ligands and in back-bonding with the transition-metal atom. Indeed, our calculations show that the P–C partial double bonds in **1** and **2** are composed of the carbon *p* orbital perpendicular to the ligand plane and the P–H σ bonds.

The most important orbitals for potential bonding with the metal fragment are the low-lying, vacant orbitals that protrude out of the ligand plane. In **1**, crucial is the doubly degenerate LUMO level (two molecular orbitals of equal energies and characters). In **2**, crucial is the non-degenerate LUMO, but the next lowest unoccupied orbital (above the LUMO) also becomes involved in bonding with the Pd atom in some conformations of **4**. Because phosphorus is less electronegative than carbon, the orbitals of **1** and **2** in the complexes **3** and **4** probably have higher energies than do the corresponding orbitals of trimethylenemethane and allyl ligands in similar complexes. Consequently, phosphoranium ligands **1** and **2** should be weaker π acceptors than their hydrocarbon counterparts.

Metal fragments

The electronic structures of $M(CO)_3$ [32–38] and ML_2 [37–40b] groups have been examined in detail elsewhere and their frontier orbitals drawn out for easy reference. We shall briefly summarize their bonding abilities, emphasizing orbitals that would be crucial for bonding with the phosphoranium ligands. The overall charges of the two metal fragments in the complexes **3** and **4** are dictated by the actual charges of the ligands **1** and **2**.

High-lying orbitals of $Co(CO)_3^-$, ordered by their increasing energies, are: level 1*e*, $1a_1$, level 2*e* (the HOMO's) and $2a_1$ (the LUMO). Two degenerate molecular orbitals that constitute the 1*e* level are mainly d_{xy} and $d_{x^2-y^2}$ in character, with some d_{yz} mixed into the first orbital and some d_{xz} into the second; they have δ symmetry with respect to the phosphoranium ligand. Orbital $1a_1$ is composed mainly of the metal d_{z^2} orbital and has σ symmetry. These three fragment orbitals represent the Co–CO π interactions and play minor role in bonding with other ligands. Two degenerate molecular orbitals that constitute the 2*e* level are mainly d_{xz} and d_{yz} in character, with some metal p_x mixed into the first orbital and some p_y into the second; there are also minor contributions from $d_{x^2-y^2}$ and d_{xy}, respectively. These fragment orbitals, crucial for the presumed bonding in the complexes, are shown schematically in **5**. Their partial *p* character causes them to point away from the



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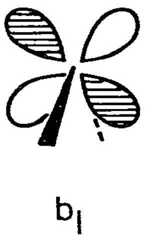
metal atom, which makes them suitable for potential π back-donation into the vacant orbitals of the phosphoranium ligand **1**. Vacant orbital $2a_1$ is a σ-type hybrid of p_z, d_{z^2} and s metal orbitals; it also points away from the metal atom.

Frontier orbitals of $Pd(PH_3)_2$, in the order of increasing energies, are: σ-type $1a_1$, δ-type a_2, π-type b_1, δ-type $2a_1$, π-type b_2 (the HOMO) and σ-type $3a_1$ (the LUMO). They are classified as σ, π or δ according to their symmetry with respect to the missing ligand(s), in this case **2**. Crucial for the presumed bonding with **2** would be the filled π-type orbitals, b_1 and b_2. Orbital b_1 is practically pure d_{xz}, perpendicular to the PdP_2 plane; it is shown schematically in **6**. Orbital b_2 is essentially a hybrid of d_{yz} and p_y, with some contributions from the Pd–P σ-bonding orbitals: it is drawn out schematically in **7**. The partial p character makes b_2 potentially effective in interacting with the vacant orbitals of the phosphoranium ligand **2**. Vacant orbital $3a_1$ is analogous to $2a_1$ in $Co(CO)_3^-$.



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$(CO)_3Co[C(PH_3)_3]^+$

From the preceding discussion of the fragments it is clear how the interfragment bonding in **3** might in principle be accomplished. As mentioned above, the distribution of electrons between the free fragments is dictated by the actual charge of the free ligand: it is not chosen arbitrarily. Donation from the HOMO of the ligand into the LUMO $2a_1$ of the metal fragment would be the σ component of bonding. The overlap intergral between these two orbitals is large (0.260), mainly because $2a_1$ has some p character. But the energy gap between them is also large (about 7 eV), which makes the metal–phosphoranium σ interaction relatively weak. As Fig. 1 shows, the corresponding molecular orbital σ is largely localized in the ligand. The overlap integral between the HOMO of the ligand and the orbital $1a_1$ of the metal fragment is small (0.049) because $1a_1$ does not have p character. Although these two orbitals are relatively close in energy, they interact very weakly, and $1a_1$ does not contribute significantly to the molecular orbital designated σ. Back-donation from the $2e$ level of the metal fragment into the LUMO level of the ligand would be the π component of bonding.

We examined three kinds of structural changes in **3**: bending of the substituents on phosphorus atoms away from the Co atom (**8** versus **9**); internal rotation about the Co–C axis (staggered, **10**, and eclipsed, **11**, conformations); and puckering of the ligand (**12**).

The substituents on phosphorus atoms are expected to deviate greatly from their tetrahedral arrangement (**8**) when the ligand becomes attached to the $Co(CO)_3^-$

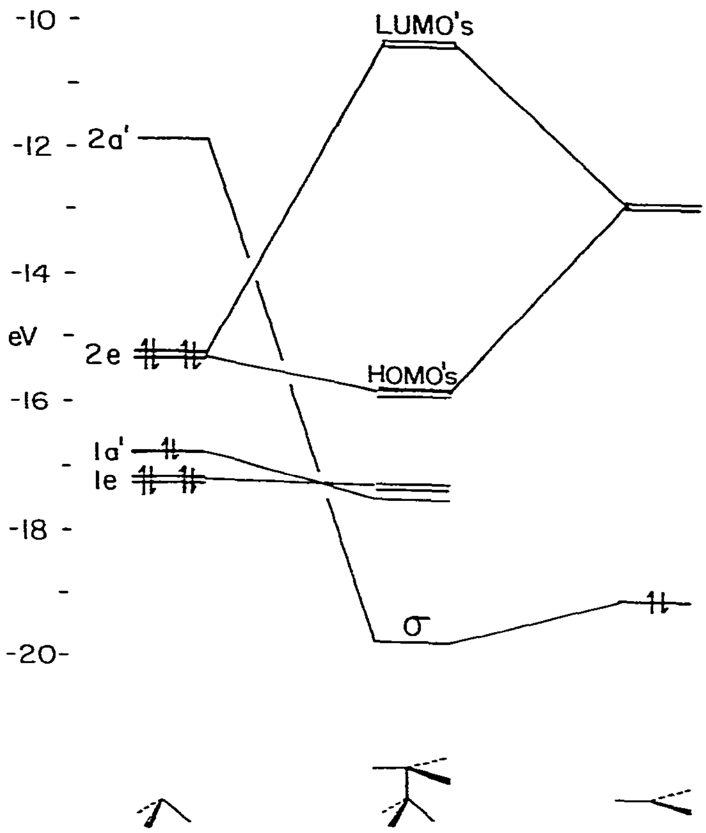
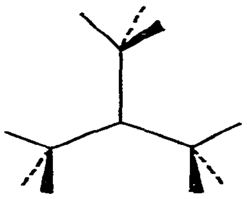


Fig. 1. Molecular orbital diagram for staggered form of (CO)$_3$Co[C(PH$_3$)$_3$]$^-$ containing planar phosphoranium ligand and H atoms bent away from the Co atom.



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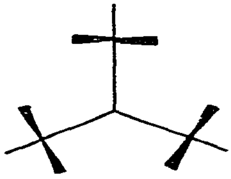

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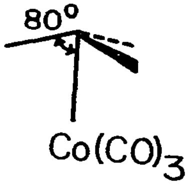


(12)

fragment [41]. Indeed, the calculations show that bending of the H atoms as in **9** greatly reduces the repulsion among the filled orbitals of the two fragments and strengthens the overlap between the 2*e* HOMO level of the metal fragment and the LUMO level of the ligand.

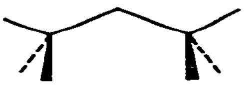
Since 2*e* orbitals of $Co(CO)_3^-$ are concentrated in the regions between the CO ligands, they largely "miss" the phosphorus-based vacant orbitals of **1** in the eclipsed conformation **11**. Staggering in **10** causes better π interaction and somewhat greater stabilization of the two highest occupied molecular orbitals in **3**, which are shown in Fig. 1. Albright et al. came to the same conclusion in their lucid analysis of conformations of $[C(CH_2)_3]Fe(CO)_3$ [35]. Structure **10** is calculated to be more stable than **11** by some 16 kcal mol^{-1}. This predicted barrier for interconversion of two identical conformers **10** via "transition state" **11** is only approximate because the energy of the internal rotation depends upon the extent of distortions shown in **9** and **12**.

Puckering in **12** shortens the Co–P distance and seems to strengthen the π interaction, somewhat lowering the HOMO level. In addition to this covalent effect, there appears to be an "ionic" effect, electrostatic attraction between the positively charged P atoms and the negatively charged Co atom, which somewhat stabilizes the three nonbonding, metal-based molecular orbitals below the HOMO level. Trimethylenemethane complex $[C(CH_2)_3]Fe(CO)_3$ [42a] and several others closely related to it indeed adopt staggered, puckered conformations. Substituents in cyclopolyene ligands also bend out of the ligand plane; this distortion, observed in numerous transition-metal complexes, has been explained in essentially the same way as here [42b].

We carried out exploratory calculations on **3** without the phosphorus 3*d* function in the basis set. The LUMO level of the ligand is raised in energy and its bonding interaction with the 2*e* HOMO level of $Co(CO)_3^-$ is considerably weakened although not destroyed. These observations indicate that phosphorus 3*d* orbitals may not be absolutely essential for bonding between ligand **1** and transition-metal atoms, but they seem to strengthen this bonding appreciably.

$(PH_3)_2Pd[CH(PH_3)_2]^+$

Various conformations of this hypothetical molecule (**4**) are conceivable. We examined distortion at phosphorus atoms (**13** versus **14**) and three kinds of movements of the metal fragment and the phosphoranium ligand with respect to each other: slippage, rotation and tilt. The degree of slippage is measured by the distance *s* between the C atom and the projection of the Pd atom on the ligand plane, as **15** shows; when *s* = 0.75 Å, the Pd atom is beneath the P–P edge of the ligand. The rotamers are shown in **16** and **17**, and in **18** and **19**; we examined both kinds of rotamers as the metal fragment slipped, Pd remaining equidistant from the two P atoms in the phosphoranium ligand. Structures **18** and **19** are formed from **16** and **17**, respectively, by allowing the ligand plane to tilt by 20° at various degrees of



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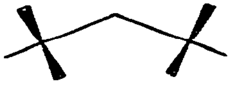

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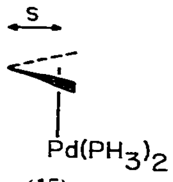

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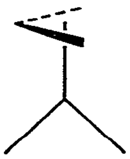

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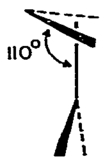

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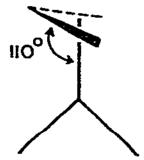


(19)

slippage (i.e., for various values of *s* in **15**) without moving the P atoms in the phosphoranium ligand. Because the Pd–P distance in corresponding tilted and untilted structures is the same, the effects of slippage and tilt can be examined separately.

The main features of bonding in various conformations of this presumed complex are shown in Fig. 2. Molecular orbital diagrams in Fig. 2a and 2b indicate that the main interaction between the fragments in **16** and **18** should be π donation from the b_2 HOMO of $Pd(PH_3)_2$ into the LUMO of $CH(PH_3)_2{}^+$; this interaction occurs in the HOMO of the complex molecule and is shown schematically in **20**. Four metal-based orbitals below b_2 seem not to contribute appreciably to the interfragment bonding. Despite the sizable σ overlap between the phosphoranium HOMO and the metal LUMO ($3a_1$), these two orbitals perturb each other weakly because

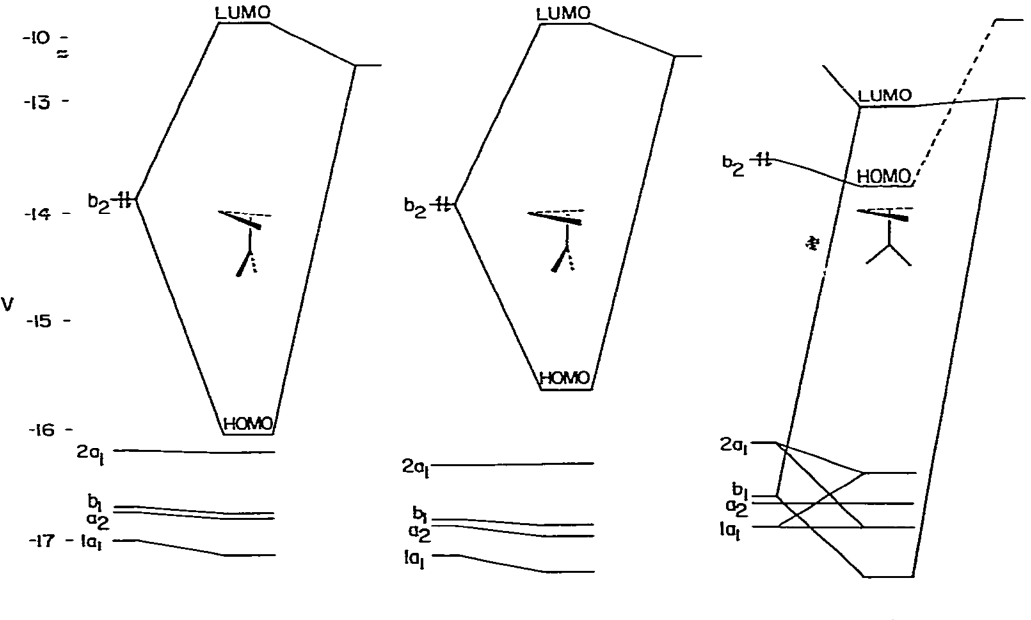
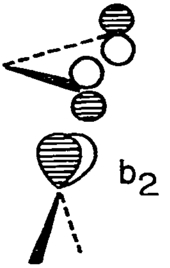


Fig. 2. Molecular orbital diagrams of $(PH_3)_2Pd[CH(PH_3)_2]^+$ in which the H atoms in the phosphoranium ligand are bent away from the Pd atom and the metal fragment is slipped by 0.7 Å. (a) Tilted phosphoranium ligand in the more stable rotamer; (b) untilted phosphoranium ligand in the more stable rotamer; (c) untilted phosphoranium ligand in the less stable rotamer. Shown are the five uppermost filled orbitals of $Pd(PH_3)_2$ and the lowest vacant orbital of $[CH(PH_3)_2]^+$; in (c), the next lowest vacant orbital of the phosphoranium ligand is also shown.

their energies differ greatly; this interaction is not shown in Fig. 2. In conformations **16** and **18**, orbital b_1 points between the P atoms so that its interaction with the phosphoranium LUMO is practically negligible, as **21** shows.



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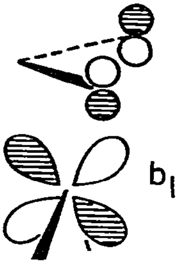
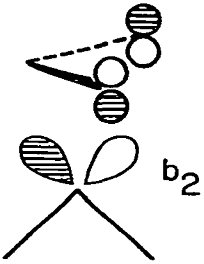


(21)

As the metal fragment slips toward the P atoms of the phosphoranium ligand, overlap **20** increases and the HOMO of the complex molecule is lowered in energy. Another cause of stabilization by slippage appears to be electrostatic attraction between the positively charged P atoms in the phosphoranium ligand and the negatively charged d^{10} Pd atom. This attraction somewhat stabilizes the set of nonbonding, metal-based molecular orbitals below the HOMO. Because of these two stabilizing interactions, covalent and "ionic", the $Pd(PH_3)_2$ group seems to favor almost a *dihapto* (η^2) coordination to phosphoranium ion **2**.

Comparison between Fig. 2a and 2b indicates that electronic structures of **16** and **18** are very similar, i.e., that tilting of the phosphoranium ligand should not affect substantially the nature of its bonding with $Pd(PH_3)_2$. Tilt, like slippage, seems to permit better Pd–P overlap. When the Pd atom is almost beneath the P atoms of the ligand (nearly η^2 coordination), the tendency for tilting seems to be weak because interaction **20** is already strong and is little strengthened by tilting. As in complex **3**, bending of the phosphoranium substituents away from the Pd atom in complex **4**, which is shown schematically in **14**, appears to be essential for interfragment bonding. This bending strengthens the Pd–P interaction, mainly by relieving the repulsions among the filled orbitals in the fragments. It is diffucult to predict which combination of slippage, tilt, and bending, which all affect interfragment bonding similarly, should be optimal in a molecule as complex as **4** is.

Comparisons between Figures 2b and 2c and also between pictures **20**, **21** and **22**, **23** show the calculated effect of rotating the metal fragment by 90°, from **16** to **17**



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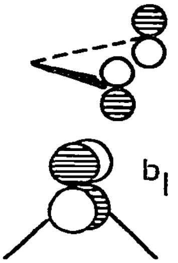

(23)

and from **18** to **19**. This rotation practically destroys the interaction between b_2 and the ligand LUMO, as **22** shows, and replaces it by a far weaker interaction between b_2 and the next lowest unoccupied molecular orbital of the phosphoranium ligand. The newly established interaction between b_1 and the ligand LUMO, shown in **23**, does not seem to compensate for the lost interaction **20** because b_1 has lower energy than b_2 and lacks partial p character (hybridization) of b_2, as can be seen by comparing **6** and **7**. We expect structures **16** and **18** to be more stable than **17** and **19**, respectively. The reasoning about slippage and tilt in **16** and **18** can be applied to **17** and **19** as well. Slippage and tilt that we predict for hypothetical complex **4** have been observed in real complexes of d^{10} ML_2 fragments with polyene [40b], π-allyl [43], trimethylenemethane [44,45] and cyclopropenium [15] ligands.

Concluding remarks

In our opinion, molecular orbital calculations cannot be used to prove or disprove that unknown complex molecules should exist. The present study is not an exception to this general view, nor is it meant to be. Although the ultimate answer to such question lies in thermodynamics and kinetics, which only in part depend on bonding, molecular orbital theory can predict and explain orbital interactions in a hypothetical molecule and liken them suggestively to the patterns established for known similar compounds. Of course, even inherently stable substances may be difficult to synthesize. The structures of compounds are more amenable to calculations, but the finer details of geometry may depend on crystal packing forces and nonbonding interactions as much as upon the intramolecular bonding. Mindful of these inherent limitations of our study, we present its results.

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