

(CH), 53.66 (CO<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>18</sub>H<sub>18</sub>NO<sub>4</sub>RuPF<sub>6</sub>: C, 39.5; H, 3.31. Found: C, 38.33; H, 3.12.

**Decomplexation Reactions.** A 463-mg (1.0<sup>-</sup>mmol) sample of complex **3g** was dissolved in acetone and transferred to a vacuum sublimator. The solution was dried to a thin film using a N<sub>2</sub> stream. The sample was heated under vacuum (10 mm) at 165–170 °C (oil bath) for 2 h. The material from the cold finger was dissolved in chloroform. After removal of chloroform, the solid residue (135 mg, 89%) was identified on the basis of <sup>1</sup>H NMR spectral analysis and melting point to be 5-chloroindole.

In another experiment, 463 mg (1.0 mmol) of complex **3g** in 30 mL of CH<sub>3</sub>CN was photolyzed for 12 h. After evaporation of the acetonitrile by rotary evaporation, the solid residue was washed with ether (3 × 30 mL). The combined ether extracts were dried over MgSO<sub>4</sub>, and the solvent was removed to give a solid residue (139 mg, 92%) that was identified on the basis of <sup>1</sup>H NMR spectral

analysis and melting point to be 5-chloroindole.

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**Registry No.** 1, 80049-61-2; **3a**, 112398-42-2; **3b**, 112398-44-4; **3c**, 112398-46-6; **3d**, 112398-48-8; **3e**, 112398-50-2; **3f**, 112398-52-4; **3g**, 112398-54-6; **4a**, 112398-56-8; **4b**, 112398-60-4; **4c**, 112398-68-2; **4d**, 112398-72-8; **4e**, 112398-64-8; **4f**, 112398-70-6; **5a**, 112398-58-0; **5b**, 112398-62-6; **5c**, 112398-66-0; **6**, 112398-74-0; NaCH(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, 18424-76-5; indole, 120-72-9; 1-methylindole, 603-76-9; 1,5-dimethylindole, 27816-53-1; 5-bromoindole, 10075-50-0; 5-chloro-1-methylindole, 112398-75-1; 4-chloro-1-methylindole, 77801-91-3; 5-chloroindole, 17422-32-1; sodium mercaptoacetate, 16023-01-1; dimethyl malonate, 108-59-8; diethyl malonate, 105-53-3.

## Molecular Orbital Study of Bimetallic Complexes Containing Conjugated and Aromatic Hydrocarbons as Bridging Ligands

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Nonparametrized molecular orbital calculations were carried out on 14 compounds of the type Pd<sub>2</sub>L<sub>2</sub>(μ-A)(μ-B) containing PH<sub>3</sub> or Cl<sup>-</sup> as terminal ligands L and Br<sup>-</sup>, C<sub>3</sub>H<sub>5</sub><sup>-</sup>, C<sub>4</sub>H<sub>6</sub>, C<sub>5</sub>H<sub>5</sub><sup>-</sup>, and C<sub>6</sub>H<sub>6</sub> as bridging ligands A and B. These compounds provide the first examples of coordination of two metal atoms to the same side of planar, conjugated organic ligands. Since Pd<sub>2</sub>L<sub>2</sub>(μ-A) fragment has only two low-lying vacant molecular orbitals, it acts as a four-electron acceptor even toward C<sub>5</sub>H<sub>5</sub><sup>-</sup> and C<sub>6</sub>H<sub>6</sub>, ligands that usually are six-electron donors. Coordination of these rings in the bimetallic complexes results in partial localization of the π electrons, i.e., in diminution of the π conjugation. This effect of bridging coordination is especially prominent in the C<sub>5</sub>H<sub>5</sub><sup>-</sup> ring, which becomes akin to a composite of a coordinated allyl ligand (a four-electron donor) and an uncoordinated olefin fragment. If such partial localization of π electrons occurs in aromatic molecules chemisorbed on the metal surface, as it does in the molecules coordinated in the bimetallic complex, this effect may perhaps be related to the high efficiency with which palladium metal catalyzes hydrogenation of arenes.

### Introduction

Transition metals form myriad of monometallic complexes with allyl, butadiene, cyclopentadienyl, and benzene ligands and with various derivatives of these hydrocarbons. Although bimetallic compounds with conjugated hydrocarbons as bridging ligands are still rare,<sup>1</sup> triple-decker sandwiches<sup>2,3</sup> and pentadienyl complexes<sup>4-6</sup> being perhaps the best-known examples, the interest in them is growing. The subject of this theoretical study are dipalladium complexes in which the metal atoms are coordinated to the same face of the π ligand, as shown in Chart I. The actual compounds can be half-sandwiches, containing one π ligand, or sandwiches, containing two similar or dissimilar π ligands.

These noteworthy compounds are of recent vintage. Although Pd<sub>2</sub>(Al<sub>2</sub>Cl<sub>7</sub>)<sub>2</sub>(μ-C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> was reported in 1965<sup>7</sup> and the homologous Pd<sub>2</sub>(AlCl<sub>4</sub>)<sub>2</sub>(μ-C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> was reported in 1970,<sup>8</sup> systematic investigation of such complexes con-

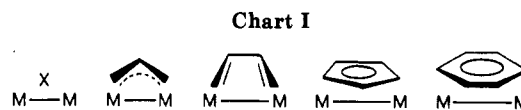


Table I. Complexes of the Type H<sub>3</sub>P-(A)Pd-Pd(B)-PH<sub>3</sub> That Are Examined by Molecular Orbital Calculations<sup>a,b</sup>

B	A			
	Br <sup>-</sup>	C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	C <sub>6</sub> H <sub>6</sub>
Br <sup>-</sup>	O	O		
C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	X <sup>c</sup>	X	X	O
C <sub>4</sub> H <sub>6</sub>	O	O	O	O <sup>d</sup>
C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	X	X	X	
C <sub>6</sub> H <sub>6</sub>	O	O	O	X <sup>d</sup>

<sup>a</sup>The molecules are constructed from the fragments Pd<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub>(μ-A) and B. <sup>b</sup>O, complex included in the study. X, existing complex with the given bridging ligands A and B, although with other terminal ligands than PH<sub>3</sub>. <sup>c</sup>Existing with Cl<sup>-</sup> and I<sup>-</sup> as A. <sup>d</sup>Also calculated with Cl<sup>-</sup> in the place of PH<sub>3</sub>.

taining bridging multihapto hydrocarbon ligands did not begin until mid-1970s.<sup>9</sup> Similar complexes of nickel have recently been discovered.<sup>10</sup> The new compounds are significant not only because of their novelty but also be-

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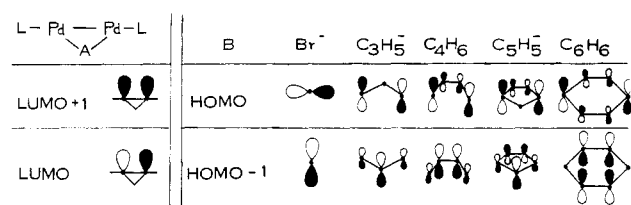
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**Figure 1.** Nodal properties of the frontier orbitals in the  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})^+$  fragment and in the bridging ligands B. The  $\pi$  donation can occur from the HOMO to the LUMO and from the HOMO-1 to the LUMO+1.

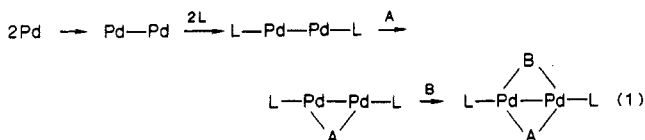
cause of their possible relevance to the activation of organic ligands in cluster compounds and on the surfaces of metals and of other heterogeneous catalysts. Indeed, palladium is one of the best heterogeneous catalysts for the hydrogenation of arenes.

Electronic structure and bonding in the new bimetallic complexes were examined by the iterative Fenske-Hall method,<sup>11</sup> which is rather rigorous. Presented here are the general findings from molecular orbital calculations on 14 compounds shown in Table I and on their fragments. The bonding in the complexes is related to their reactions with nucleophiles.

### Bonding in Dipalladium Complexes

**The Molecules.** The complexes studied, twelve of the type  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-A})(\mu\text{-B})$  and two of the type  $\text{Pd}_2\text{Cl}_2(\mu\text{-A})(\mu\text{-B})$ , contain similar or different bridging ligands A and B. In the last two complexes, models for the prototypical ones mentioned in the Introduction,  $\text{Cl}^-$  stands for the  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_4^-$  ligands, which are coordinated through the Cl atoms. Six of the molecules shown in Table I exist, and the other ones, included for the sake of completeness, are homologous to them.

The complexes were built systematically from chemically meaningful fragments and subfragments, which in turn were built from atoms, as shown in eq 1. (This equation



does not represent actual chemical reactions.) The oxidation state of Pd was +I, and the charges of the bridging ligands were as shown in Table I; the charges are omitted from the generic eq 1 for the sake of clarity. The most interesting interaction is the one corresponding to the last step, between the metal-containing fragment  $\text{Pd}_2\text{L}_2(\mu\text{-A})$  and the bridging ligand B. For five of the complexes this last step was carried out in two ways, with either of the bridging ligands, hence five entries above the diagonal in Table I.

**Bonding Abilities of the Fragments.** Orbital structures of halide ( $\text{X}^-$ ), allyl ( $\text{C}_3\text{H}_5^-$ ), butadiene ( $\text{C}_4\text{H}_6$ ), cyclopentadienyl ( $\text{C}_5\text{H}_5^-$ ), and benzene ( $\text{C}_6\text{H}_6$ ) ligands are known well and need not be detailed here; their principal frontier orbitals are shown schematically in Figure 1. Comparative calculations on the fragments  $\text{Pd}_2\text{L}_2(\mu\text{-A})$  containing  $\text{PH}_3$  or  $\text{Cl}^-$  as terminal ligands L and  $\text{Br}^-$ ,  $\text{C}_3\text{H}_5^-$ ,  $\text{C}_5\text{H}_5^-$ , or  $\text{C}_6\text{H}_6$  as the bridging ligand A revealed a homology of their frontier orbitals. Those of  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})^+$ , presented in Table II, are typical. The frontier orbitals evidently are localized on the Pd atoms and have no significant contribution from the terminal ligands (here  $\text{PH}_3$ )

**Table II.** Energies and Percent Compositions of the Important Molecular Orbitals in  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})^+$

$\epsilon$ , eV	designatn	$\text{Pd}_2$			$\text{Br}^-$ 4p
		4d	5s	5p	
-5.1 (LUMO+1)	$2a'_M$		44	46	4
-10.1 (LUMO)	$2a''_M$	76	6		15
-10.47 (HOMO)	$1a'_M$	74	6	4	13
-11.08 (HOMO-1)	$1a''_M$	90	8		1

because orbitals corresponding to the Pd-PH<sub>3</sub> bonds lie at lower energies. The fragment orbitals of  $\text{Pd}_2\text{L}_2(\mu\text{-A})$  and of  $\mu\text{-B}$  are designated  $a'$  or  $a''$ , corresponding to the  $C_s$  symmetry of the complete molecule, although the fragments themselves have higher symmetry. (To avoid confusion, the orbitals of the metal-containing fragment and of the bridging ligand are marked with subscripts M and L.) The most important property of the bimetallic fragments is that they contain only two low-lying vacant orbitals, designated  $2a''_M$  (mainly a  $\pi$ -antibonding combination of the two  $4d_{z^2}$  orbitals) and  $2a'_M$  (mainly a  $\pi$ -bonding combination of the  $5s$ - $5p$  hybrid orbitals). Contribution from the  $\mu\text{-A}$  orbitals causes the  $2a''_M$  and  $2a'_M$  orbitals to grow toward the bridging hydrocarbon ligand,  $\mu\text{-B}$ , and thus enhances their capacity for bonding with this ligand. With only two suitable vacant orbitals, the bimetallic fragments can formally accept only four electrons from the bridging ligands B. Total overlap population between the Pd atoms in all of the fragments is 0.10-0.13 e, consistent with a metal-metal bond; the relation between the overlap population and direct metal-metal interactions in binuclear complexes of Pt(I) and Pd(I) is discussed fully elsewhere.<sup>12</sup> The LUMO and the next lowest vacant orbital (designated LUMO+1) of the metal-containing fragment are matched in symmetry pairwise with the HOMO and the next highest filled orbital (designated HOMO-1) of the bridging ligand B, as Figure 1 shows.

**Coordination of the Bridging Ligands.** Upon binding of B to the metal-containing fragments, the Pd-Pd bond remains and significant changes in the electronic structure occur only in the  $\text{Pd}_2(\mu\text{-B})$  region. The main bonding interactions in the complete molecules amount to donation from the two highest-lying filled orbitals of the ligand B into the two lowest-lying vacant orbitals of the dipalladium fragment  $\text{Pd}_2\text{L}_2(\mu\text{-A})$ . These two interactions belong to irreducible representations  $a'$  and  $a''$  under the  $C_s$  symmetry of the complete molecules. A weak four-electron repulsive interaction between the HOMO of  $\mu\text{-B}$  and the HOMO-1 of the metal fragment, although evident, is comparatively unimportant for bonding. The rudimentary molecular orbital diagram in Figure 2 depicts the essence of bonding in the complexes and explains some striking features of their geometric structures. Crystallographic studies<sup>8</sup> of  $\text{Pd}_2(\text{Al}_2\text{Cl}_7)_2(\mu\text{-C}_6\text{H}_6)_2$  and  $\text{Pd}_2(\text{AlCl}_4)_2(\mu\text{-C}_6\text{H}_6)_2$  showed the benzene rings to be coordinated as  $\eta^4$ -conjugated dienes rather than as  $\eta^6$ -arenes. Similarly, the cyclopentadienyl rings in  $\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-2-MeC}_3\text{H}_4)(\mu\text{-C}_5\text{H}_5)$ ,<sup>13,14</sup>  $\text{Pd}_2[\text{P}(\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{Me})_3]_2(\mu\text{-2-MeC}_3\text{H}_4)(\mu\text{-C}_5\text{H}_5)$ ,<sup>14</sup> and  $\text{Pd}_2(\text{P-}i\text{-Pr}_3)_2(\mu\text{-Br})(\mu\text{-C}_5\text{H}_5)$ <sup>15,16</sup> resemble the  $\eta^3$ -allyl ligands in  $\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-I})(\mu\text{-C}_3\text{H}_5)$ <sup>17</sup> and  $\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-I})(\mu\text{-C}_3\text{H}_5)$ <sup>17</sup>

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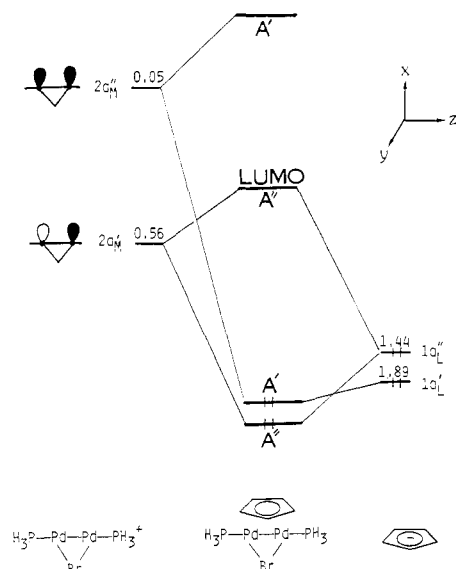
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**Figure 2.** The principal orbital interactions in  $\text{Pd}_2\text{L}_2(\mu\text{-A})(\mu\text{-B})$ . Fragment orbitals (lower-case symbols) as well as molecular orbitals (upper-case symbols) are designated according to the point group of the whole molecule,  $C_s$ . Populations of the fragment orbitals manifest  $\pi$  donation from the  $\mu\text{-C}_5\text{H}_5^-$  ligand to the  $\text{Pd}_2$  unit.

$\text{C}_3\text{H}_5$ ) $_2$  $^{18}$  rather the usual  $\eta^5$ -aromatic rings. The  $\eta^3$  coordination of  $\text{C}_5\text{H}_5$  remains in solution, as NMR spectroscopy shows. $^{9,14,19}$  The slippage from  $\eta^6$  to  $\eta^4$  in the case of  $\text{C}_6\text{H}_6$  and from  $\eta^5$  to  $\eta^3$  in the case of  $\text{C}_5\text{H}_5$  is easily understood from the quantum-chemical calculations. A six-electron aromatic ligand can donate (formally) only four electrons to a  $\text{Pd}_2\text{L}_2(\mu\text{-A})$  fragment because the latter contains only two suitable vacant orbitals of low energy, namely,  $2a''_M$  and  $2a'_M$ . Two C atoms, corresponding formally to a  $\text{C}=\text{C}$  fragment in the hydrocarbon ring, remain essentially uncoordinated.

In a series of calculations the  $\text{C}_5\text{H}_5^-$  ring was translated over the  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})^+$  fragment with the  $C_s$  symmetry maintained. $^{20}$  The sum of the eigenvalues of the two filled molecular orbitals shown in Figure 2, which correspond to two  $\text{Pd}_2\text{-C}_5\text{H}_5$  bonds, reaches minimum at the allylic  $\eta^3$  configuration, the structure actually found in the complexes. A small tilt of the  $\text{C}_5\text{H}_5$  ring away from perpendicularity to the  $\text{Pd}_2(\mu\text{-Br})$  plane improves the overlap between the metal and ring orbitals and strengthens the Pd-C covalent interactions. In this respect, too, the cyclopentadienyl ligand resembles the allyl ligand. $^{21,22}$

**New Isolobality.** Similarity of the frontier orbitals, evident in Figure 1, indicates that the seemingly disparate bridging ligands perhaps form an isolobal series. In monometallic complexes, among which isolobal relationships were originally recognized, $^{23,24}$  ligands such as halide and cyclopentadienyl are not considered isolobal, but in bimetallic complexes they apparently become such. Isolobality of several metal complexes and fragments with  $\text{Cp}^-$  as bridging ligands in  $\text{Pd}_2\text{L}_2(\mu\text{-A})(\mu\text{-B})$  has been discovered. $^{25-28}$  It would be interesting to extend this useful

**Table III.** Effect on the Carbon-Carbon  $\pi$ -Overlap Populations (in Electrons) of Bridging Coordination of Ligands B in  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-B})$

ligand B	free <sup>a</sup>	coordinated <sup>b</sup>	limiting case
$\text{C}_3\text{H}_5^-$	0.300	0.241	
$\text{C}_4\text{H}_6$	0.091 0.477	0.172 0.341	
$\text{C}_5\text{H}_5^-$	0.267	0.466 0.116 0.205	
$\text{C}_6\text{H}_6$	0.292	0.300 0.241 0.227 0.334	

<sup>a</sup> With  $\text{sp}^2$ -hybridized C atoms. <sup>b</sup> With actual dimensions.

concept to polymetallic clusters and to use it in planning syntheses and in elucidating structures.

Although the qualitative diagram in Figure 2 applies to all of the bridging ligands B, there are some quantitative differences among them, arising primarily from their different charges (as free species): anionic  $\text{Br}^-$ ,  $\text{C}_3\text{H}_5^-$ , and  $\text{C}_5\text{H}_5^-$  versus the neutral  $\text{C}_4\text{H}_6$  and  $\text{C}_6\text{H}_6$ . Although the calculated electronic structure of a composite molecule is independent of the initial charges of its fragments, the charges in this case are realistic and the following discussion, although somewhat formalistic, is meaningful. Since orbital energies depend greatly on charge, the  $\pi$  donor orbitals in the anionic ligands lie higher than such orbitals in the neutral ligands. Even the energies of the  $\pi$  acceptor orbitals in  $\text{Pd}_2\text{L}_2(\mu\text{-A})$  are affected by the charge of B; the effect on them is qualitatively the same, but lesser because of the distance between the fragments. (In these calculations the fragments are not treated as isolated from each other; their orbital energies are not fixed but depend on the electrostatic fields of the neighboring atoms. See the last section, concerning calculational details.) The net result is that the energy gap between the donor and acceptor fragment orbitals is larger in the case of the neutral than in the case of the anionic bridging ligands. That the former ligands are weaker  $\pi$  donors than the latter ones is evident from the calculated electron charge removed from the two donor orbitals of each ligand B in the complete  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-B})$  molecules: 0.27, 0.35, 0.51, 0.67, and 0.79 e for  $\text{C}_6\text{H}_6$ ,  $\text{C}_4\text{H}_6$ ,  $\text{Br}^-$ ,  $\text{C}_5\text{H}_5^-$ , and  $\text{C}_3\text{H}_5^-$  as B, respectively. These numbers, although probably not accurate in the absolute sense, do show similarity between  $\text{C}_6\text{H}_6$  and  $\text{C}_4\text{H}_6$  and between  $\text{C}_5\text{H}_5^-$  and  $\text{C}_3\text{H}_5^-$ . They also remind us that electron counting is only a formalism; a ligand is considered a four-electron donor not because it can transfer four electrons but because it interacts with the metal fragment mainly via two orbitals. Back-donation of  $\delta$  symmetry, from  $\text{Pd}_2$  to the LUMO of the hydrocarbon ligands, is considerably weaker than donation of  $\pi$  symmetry.

**Diminution of Conjugation.** The  $\pi$ -electron systems of the cyclic bridging ligands are altered in a remarkable way upon coordination of these ligands to the dipalladium fragment. This phenomenon, illustrated in Table III, is particularly evident in the case of the  $\text{C}_5\text{H}_5^-$  ring. Since the bridging ligand no longer has  $D_{5h}$  symmetry, the orbitals designated  $1a'_L$  and  $1a''_L$ , descended from the doubly degenerate  $e_1''$  level, have slightly different energies, as

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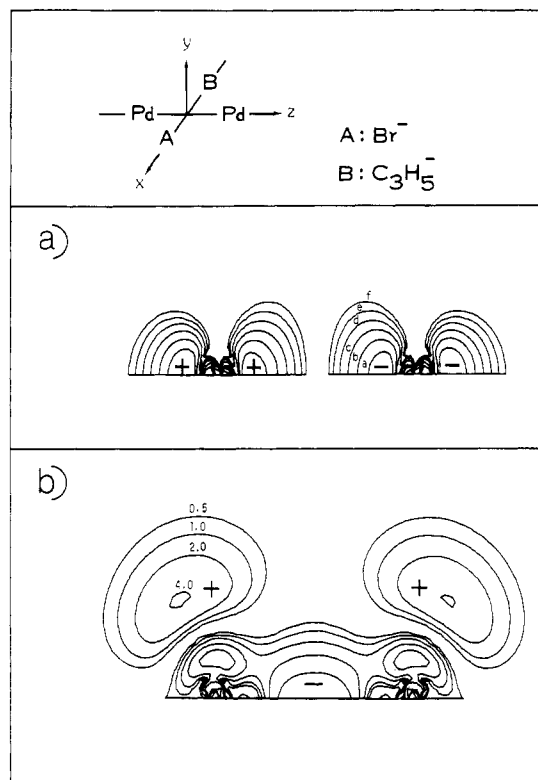
Figure 2 shows. Nodal properties of the ring  $\pi$  orbitals are such that greater donation from the  $1a''_L$  than from the  $1a'_L$  and partial back-donation into the  $2a'_L$  (the well-known LUMO of the ligand, shown in I but not in Figure



2), act concertedly to strengthen one C-C  $\pi$  bond and weaken the others. Consequently, the cyclopentadienyl ligand becomes akin to a composite of allyl and olefin ligands. The bridging  $\eta^3\text{-C}_5\text{H}_5$  ligand can even be substituted by the  $\eta^3\text{-C}_3\text{H}_5$  ligand.<sup>9,29</sup> Despite the appreciable disruption in  $\pi$  conjugation, the bridging  $\eta^3\text{-C}_5\text{H}_5$  ring remains planar, unlike the  $\eta^3\text{-C}_5\text{H}_5$  ring in  $(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2$ , which is folded.<sup>30</sup> This structural difference can perhaps be traced to a simple difference between the electronic configurations of the bimetallic and the monometallic complex. The interelectron repulsion between the olefinic  $\pi$  bond in the ring and the metal electrons is weaker in the case of the unsaturated, 30-electron  $\text{Pd}_2$  unit than in the case of the saturated, 18-electron W atom. Similarly, the bridging  $\eta^4\text{-C}_6\text{H}_6$  ring in the dipalladium complexes<sup>8</sup> is much closer to planarity than the  $\eta^4\text{-arene}$  rings in monometallic complexes.<sup>31-35</sup>

Although  $\pi$  electrons become partially localized, there should be no significant weakening of the C-C bonds because the dominant  $\sigma$  interactions (i.e., the corresponding overlap populations) are little affected by coordination. The diminution of the conjugation, however, may well be sufficient to facilitate addition across the C-C bonds. Indeed,  $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\eta^4\text{-C}_6\text{Me}_6)$  is a homogeneous catalyst for hydrogenation of arenes.<sup>36-38</sup> This theoretical study perhaps is germane to heterogeneous catalysis as well. Benzene, a prototypical arene, chemisorbs molecularly on low-index planes of palladium with its ring parallel to the surface.<sup>39-44</sup> Bonding to the metal surface is mainly through the ring  $\pi$  orbitals, as in these discrete dipalladium complexes. Moreover, chemisorption of benzene on metal surfaces can cause localization of the  $\pi$  electrons,<sup>45</sup> as in the coordinated molecules. In general, this electronic effect may perhaps be related to the high efficiency of palladium

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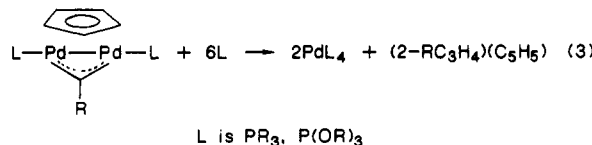
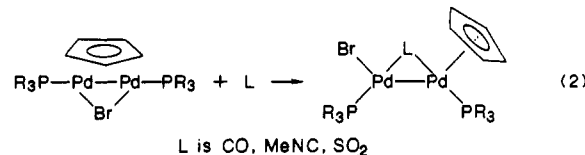


**Figure 3.** Contour plots in the  $yz$  plane of the two lowest vacant molecular orbitals in  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-C}_5\text{H}_5)$ : (a) the LUMO, of  $A''$  symmetry (the relative values of the contours designated a through f are 125, 63, 23, 12, 1.5, and 0.5); (b) the next lowest orbital, of  $A'$  symmetry.

metal as a catalyst for hydrogenation of arenes and unsaturated organic compounds. Our future studies will deal with conjugated and aromatic bridging ligands in cluster compounds and on metal surfaces.

### Nucleophilic Attack on Dipalladium Complexes

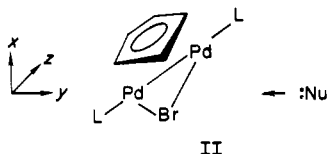
Experimental studies of reactivity have mostly been done with  $\text{Pd}_2\text{L}_2(\mu\text{-RC}_3\text{H}_4)(\mu\text{-C}_5\text{H}_5)$  and  $\text{Pd}_2\text{L}_2(\mu\text{-Br})(\mu\text{-C}_5\text{H}_5)$ , but other complexes behave similarly.<sup>9</sup> In the reactions with nucleophiles the metal-metal bond can be preserved (eq 2) or cleaved (eq 3).<sup>9,46,47</sup> Since the concept



of frontier control has proven useful in theoretical study of nucleophilic attack on various organometallic complexes,<sup>48-51</sup> we have examined the frontier orbitals of the

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complexes  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-C}_5\text{H}_5)$  and  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_3\text{H}_5)(\mu\text{-C}_5\text{H}_5)$  and of the nucleophiles CO, MeNC,  $\text{PMe}_3$ , and  $\text{P}(\text{OH})_3$ . Since the Pd atoms are bridged on both sides in the vertical direction ( $x$ ), the incoming nucleophile approaches in the horizontal plane ( $yz$ ), as shown in II.



II

The two lowest-lying vacant orbitals in a representative complex,  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-C}_5\text{H}_5)$ , are depicted in Figure 3. Although their calculated energies are not completely reliable (a shortcoming shared by the Hartree-Fock method and the methods approximating it), their localization and nodal properties can be trusted. The LUMO of  $a''$  symmetry, designated  $1a''_M$ , is localized mainly in the vertical ( $xz$ ) plane. Its small lobe in the horizontal ( $yz$ ) plane is orthogonal to (provides no net overlap with) the lone pair of the incoming bridging ligand, whose symmetry is  $a'$ . Thus the LUMO is not suited, by either localization or symmetry, to the interaction with a nucleophile.

The next lowest vacant orbital, designated  $2a'_M$ , is well-suited to this interaction on both accounts. This orbital is localized mainly in the horizontal ( $yz$ ) plane and has  $a'$  symmetry. Since it is virtually nonbonding between the Pd atoms, donation into it from the nucleophile should not affect the metal-metal bond. Indeed, the crystal structure of the  $\text{SO}_2$  adduct confirms that the Pd-Pd bond is retained.<sup>46</sup>

The nucleophiles that bridge the Pd-Pd bond and those that cleave it differ from each other in their capacity for  $\pi$  acceptance, but this difference does not seem to be the decisive one because the dipalladium complex lacks filled orbitals suitable for  $\pi$  back-donation. Although the nucleophiles have similar frontier orbitals<sup>51</sup> and every one of them has a lone pair available for donation, the greater capacity for  $\sigma$  donation on the part of the reagents that cleave the Pd-Pd bond may be significant. This lone pair and the Pd-Pd  $\sigma$ -bonding orbital give rise to a repulsive four-electron interaction, which, although weak, may contribute to the cleavage of the metal-metal bond. The contrast between the reactions shown in eq 2 and 3 probably is not due chiefly to a difference in electronic properties and in orbital interactions. It may be attributed largely to the different steric demands of the incoming ligands: the small ones can fit in a bimetallic complex (eq 2), whereas the bulky ones cannot (eq 3). Consideration of molecular models corroborates this conclusion in a qualitative way.

## Details of the Calculations

An approximation to the Hartree-Fock-Roothaan technique, the Fenske-Hall method, has been described elsewhere.<sup>11</sup> This iterative SCF method is devoid of empirical or adjustable parameters, so that results of a calculation—eigenvalues, eigenvectors, and the derived quantities—are determined fully by the molecular geometry and by the basis functions. The small but significant effects of the intramolecular electrostatic interactions are taken into account in the computation of the Fock matrix elements. Consequently, the energies of the fragment orbitals (diagonal elements in the Fock matrix) reflect the influences of the molecular environment on the fragments "ready for bonding", and the energies of the molecular orbitals depend somewhat on the overall distribution of charges in a molecule. Each molecule or a larger fragment was divided into two closed-shell subfragments bearing chemically meaningful charges; the gradual buildup of complex molecules is shown in eq 1. The transformations of basis sets and partitioning of fragment charges do not affect the results of the calculations but make them more readily interpretable.

The structures of the molecules studied were taken from those of the actual compounds  $\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-I})(\mu\text{-C}_3\text{H}_5)$ ,<sup>17</sup>  $\text{Pd}_2(\text{P-}i\text{-Pr}_3)_2(\mu\text{-Br})(\mu\text{-C}_5\text{H}_5)$ ,<sup>15,16</sup>  $\text{Pd}_2(\text{PPh}_3)_2(\mu\text{-MeC}_3\text{H}_4)(\mu\text{-C}_5\text{H}_5)$ ,<sup>13,14</sup>  $\text{Pd}_2(\text{AlCl}_4)_2(\mu\text{-C}_6\text{H}_6)_2$ ,<sup>8</sup> and  $\text{Pd}_2(\text{Al}_2\text{Cl}_7)(\mu\text{-C}_6\text{H}_6)_2$ .<sup>8</sup> The usual basis functions were used for the metal,<sup>52</sup> non-metal,<sup>53</sup> and hydrogen<sup>54</sup> atoms. Occupations of the fragment orbitals, overlap populations, and atomic charges were calculated by the Mulliken population analysis.

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**Registry No.**  $\text{Pd}_2(\text{Ph}_3)_2(\mu\text{-Br})_2$ , 111848-33-0;  $\text{Pd}_2(\text{Ph}_3)_2(\mu\text{-C}_3\text{H}_5)(\mu\text{-Br})$ , 111848-34-1;  $\text{Pd}(\text{PH}_3)_2(\mu\text{-I})(\mu\text{-C}_3\text{H}_5)$ , 111848-35-2;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_3\text{H}_5)_2$ , 111848-36-3;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_5\text{H}_5)(\mu\text{-C}_3\text{H}_5)$ , 111868-88-3;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_6\text{H}_6)(\mu\text{-C}_3\text{H}_5)^+$ , 111848-37-4;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-C}_4\text{H}_6)^+$ , 111848-38-5;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_3\text{H}_5)(\mu\text{-C}_4\text{H}_6)^+$ , 111868-89-4;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_6\text{H}_5)(\mu\text{-C}_4\text{H}_6)^+$ , 111848-39-6;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_6\text{H}_6)(\mu\text{-C}_4\text{H}_6)^{2+}$ , 111848-42-1;  $\text{Pd}_2(\text{Cl})_2(\mu\text{-C}_6\text{H}_6)(\mu\text{-C}_4\text{H}_6)$ , 111848-46-5;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-C}_6\text{H}_5)$ , 111848-40-9;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_5\text{H}_5)_2$ , 111848-41-0;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})(\mu\text{-C}_6\text{H}_6)^+$ , 111848-43-2;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_5\text{H}_5)(\mu\text{-C}_6\text{H}_6)^+$ , 111848-44-3;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-C}_6\text{H}_6)_2^{2+}$ , 111848-45-4;  $\text{Pd}_2(\text{Cl})_2(\mu\text{-C}_6\text{H}_6)_2$ , 111848-47-6;  $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-Br})^+$ , 111848-48-7; Pd, 7440-05-3.

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