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Molecular Orbital Study of Dinuclear Palladium Carbonyl Chlorides. Choice of the Bridging Ligand (CO vs. Cl) and the Question of Metal-Metal Bonding

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We carried out nonparameterized molecular orbital calculations on five conceivable isomers of the anionic Pd(I) compound $[Pd_2Cl_4(CO)_2]^{2-}$ and of the neutral Pd(II) compound $[Pd_2Cl_4(CO)_2]$. The former is known to contain CO bridging ligands, and the latter, Cl bridging ligands between the two Pd atoms. The choice of the bridging ligands seems to depend on the relative energies of those orbitals of the bridging ligands and of the Pd atoms that interact to form the molecular orbital that is the HOMO in the Pd(I) compound and the LUMO in the same isomer of the Pd(II) compound. In the isomer containing two CO bridges, this crucial molecular orbital lies *below* the high-lying carbonyl orbital and the palladium orbital and represents their *bonding* interaction in the bridging region. The Pd(I) compound is stabilized by occupation of this molecular orbital, whereas the Pd(II) compound would lack this stabilization because this molecular orbital in it would be empty. In the isomer containing two Cl bridges, this crucial molecular orbital lies *above* the low-lying chlorine orbital and the palladium orbital and represents their *antibonding* interaction in the bridging region. The Pd(I) compound would be destabilized by occupation of this molecular orbital, whereas the Pd(II) compound lacks this destabilization because this molecular orbital in it is empty. The calculations indicate that two formally d^9 Pd atoms in the Pd(I) compound do not interact appreciably through space to form a direct metal-metal bond. This molecule is diamagnetic apparently because it has an even number of electrons and a nondegenerate HOMO, so that all electrons are paired. The relatively short Pd-Pd distance seems to be caused by strong, multicenter bonding in the bridging region. The compound $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$ is one of several bridged, dinuclear transition-metal complexes that appear not to contain genuine metal-metal bonds although such bonds are commonly assigned to them on the basis of formal rules of electron counting. We emphasize conceptual advantages of molecular orbital theory over valence bond theory and show how the former theory explains net bonding that can arise from interactions between filled and between vacant orbitals.

Introduction

Polynuclear transition-metal complexes attract the attention of many inorganic and organometallic chemists today. Knowledge of the structures of these molecules and of their chemical bonds is needed for understanding of their reactions and possible catalytic activity. The simplest such molecules contain two transition-metal atoms and are well-suited for quantum-chemical, as well as experimental, studies.

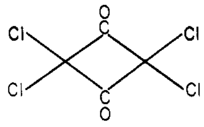
Our interest in dinuclear transition-metal compounds (often called dimers) was roused by recent reports about two dipalladium carbonyl chlorides. Goggin et al. showed spectroscopically[2a] and crystallographically[2b] that the anion $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$ is planar and that two Pd(I) atoms in it are bridged by two CO ligands. On the basis of diamagnetism,[2a] the Pd-Pd distance of 2.70 Å, and a qualitative molecular orbital argument,[2b] they concluded that the two d^9 Pd(I) atoms are linked by a metal-metal single bond. Calderazzo and Dell'Amico showed spectroscopically that the neutral molecule $[Pd_2Cl_4(CO)_2]$ is also planar and that two Pd(II) atoms in it are bridged by two Cl ligands.[3] The structure of the Pd(II) dimer is consistent with the rule that di- or polynuclear metal carbonyl halides invariably contain halogen rather than carbonyl bridges,[4,5] but the structure of the Pd(I) dimer violates this rule.[2] The presence of a metal-metal bond in the Pd(I) dimer is inferred from its diamagnetism and the relatively short intermetallic distance, which are commonly accepted as evidence for such bonding.

We became interested in these two dipalladium complexes because they differ by two electrons, and yet their structures differ radically. We examined bonding in them in an attempt to understand why they contain different bridging ligands and why the Pd(I) dimer is diamagnetic. These problems are interesting by themselves but may also be relevant to studies of many industrial and other synthetic reactions, some of them involving CO, that are catalyzed by various palladium compounds.[6-8]

Details of the Calculations

An approximation to the Hartree-Fock-Roothaan technique, the Fenske-Hall method, has been described elsewhere.[9] The method is devoid of adjustable or empirical parameters, so that results of a calculation (eigenvalues and eigenvectors) are determined completely by molecular geometry and the basis functions.

We carried out calculations on five isomers of $[Pd_2Cl_2(CO)_2]^{2-}$ and $[Pd_2Cl_4(CO)_2]$ each, ten species altogether. The constitutions of these five isomers are shown schematically in **1**-**5**; the Pd atoms are not shown explicitly, and the net charges are omitted. We will refer to these isomers using their numbers and palladium oxidation states in parentheses. For example, **2**(I) represents isomer **2** of the Pd(I) dimer, and 3(II) represents isomer **3** of the Pd(II) dimer; their total charges,



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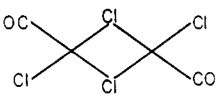

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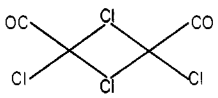

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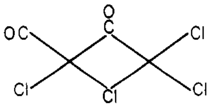

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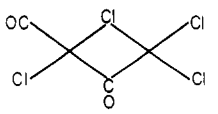

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(2) (a) Goggin, P. L.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1974**, 534-540. (b) Goggin, P. L.; Goodfellow, R. J.; Herbert, I. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1981**, 1077-1078.

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2- for the former and 0 for the latter, are not indicated explicitly. The geometry of **1** was taken from the crystal structure of the Pd(I) dimer,[2b] and the Pd–Pd distance and bond angles from it were used for other isomers as well; all structures were planar.

We divided each bridged dinuclear species into two closed-shell fragments: one containing two Pd atoms and four terminal ligands and the other containing two bridging ligands. For example, the species designated **2**(I), whose charge is 2–, consists of *trans*-$Pd_2Cl_2(CO)_2$ and $(Cl^-)_2$ as fragments. Such partitioning allows the inspection of important interactions among the metal atoms and the bridging ligands. We first carried out separate calculations on fragments and then on complete molecules. After the iterations on a complete dimer would converge in the atomic basis set, molecular orbitals of the dimer would be 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 do not affect the numerical results of the calculation 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 dimers. These energies reflect the influences of the molecular environment upon the fragments "ready for bonding" and therefore vary from one isomer to another. The basis functions were the same as in our previous studies.[10–15] The *z* axis of each Pd atom points toward another Pd atom.

Bonding Abilities of the Fragments

When discussing fragments, we will emphasize orbitals that are essential for bonding between the fragments in the complete dimers, that is, for bonding in the bridging region. A fragment orbital is classified as σ, π, or δ according to its character within the fragment; its bonding ability with respect to another fragment may be different from that.

Unbridged Dipalladium Fragments, Pd_2L_2. The important orbitals of the metal-containing fragments are composed chiefly of palladium 4d orbitals. A fragment orbital containing the bonding combination of 4d orbitals of the two Pd atoms invariably lies below the corresponding fragment orbital containing the antibonding combination of 4d orbitals. The strengths of various 4d–4d interactions can be estimated from the energy gaps between the corresponding bonding and antibonding fragment orbitals. The gaps caused by the σ (z^2–z^2), π (xz–xz or yz–yz), and δ (xy–xy or $x^2 - y^2$–$x^2 - y^2$) interactions in the $Pd_2Cl_4^{2-}$ fragment are about 2, 0.7, and 0.02 eV, respectively. Clearly, δ interactions across the distance of 2.70 Å are negligible, and therefore the δ-type orbitals are not appreciably localized between the metal atoms or in the region of the (missing) bridging ligands. We will focus our attention upon orbitals whose character within the dipalladium fragments is σ or π. (Their character with respect to the bridging ligands may be different.) These fragment orbitals are considerably localized between the palladium atoms and in the bridging region.

The general conclusion from comparisons among the ten dipalladium fragments (**1**–**5** with Pd(I) and Pd(II)) is that the nature and sequence of their frontier orbitals do not change significantly as the terminal ligands are varied (Cl or CO) and rearranged with respect to one another (cis or trans). Each fragment essentially consists of two fused PdL_2 units, and the exact nature of ligands L is not decisive. The Pd(I) fragment contains two electrons more than the Pd(II) fragment of the same constitution, and the HOMO of the Pd(I) fragment corresponds to the LUMO of Pd(II) fragment. Three crucial orbitals of the dipalladium fragments, designated π, π^*, and σ, are depicted schematically in Figure 1; these same symbols were used by Dedieu and Hoffmann in their study of Pt(0) dimers[16] and adopted by Goggin et al. in their qualitative discussion of bonding in dipalladium carbonyl halides.[2b] These three orbitals lie in the plane of the dimetal fragments. The ones designated σ and π are bonding, and the one designated π^* is antibonding, between the metal atoms. Orbitals π and π^* are predominantly palladium 4d in character, whereas orbital σ is composed of palladium 5s–5p hybrids and lies at considerably higher energy than π and π^*. As we will show later, the filled orbitals designated σ_{z^2} (shown in **6**) and δ (shown in **7**) are not important for bonding with the bridging ligands.

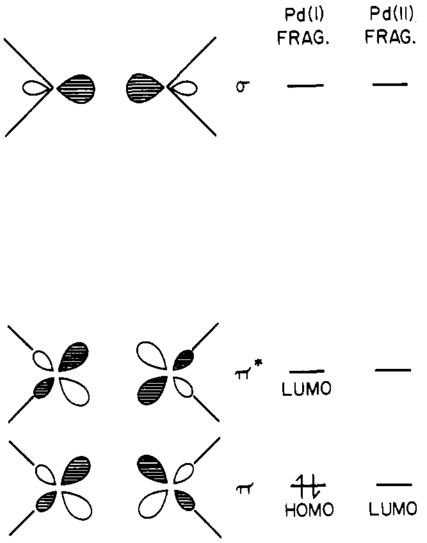
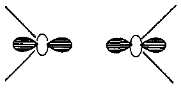


Figure 1. Important orbitals of dipalladium fragments and their occupations.


σ_{z^2}

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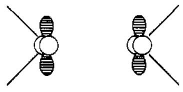
δ

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The calculated overlap populations between the Pd(I) atoms in various dimetal fragments are about 0.22 e, which indicates some accumulation of electron density between the metal atoms and their attraction in the absence of the bridging ligands. This attraction is due in part to substantial interaction between the two metal atoms in orbital π, which is the HOMO in each Pd(I) dimetal fragment. When this orbital is emptied, the intermetallic attraction weakens, and calculated overlap populations between the Pd(II) atoms in various dimetal fragments decrease to the values between 0.12 and 0.15 e.

Bridging Ligands, L_2. The electronic structures of isolated Cl^- and CO ligands are well-known and do not need to be discussed in detail. The Cl^- anion has all its valence orbitals filled. The CO molecule has a carbon lone pair, designated 5σ, as its HOMO and a degenerate pair of π-antibonding orbitals, designated 2π, as its LUMO level. Since the distances between the two bridging ligands are 3 Å or more, their orbitals perturb one another weakly.

Only those orbitals of the bridging fragments that lie in the plane of the complete dinuclear molecule can interact with orbitals of the dipalladium fragments that are shown in Figure 1 and in **6** and **7**. These important orbitals of the bridging fragments are shown in Figure 2 and designated according to their character within the fragments. The π-type orbitals shown in Figure 2 have counterparts perpendicular to the plane of the complete dinuclear molecule; these orbitals are not

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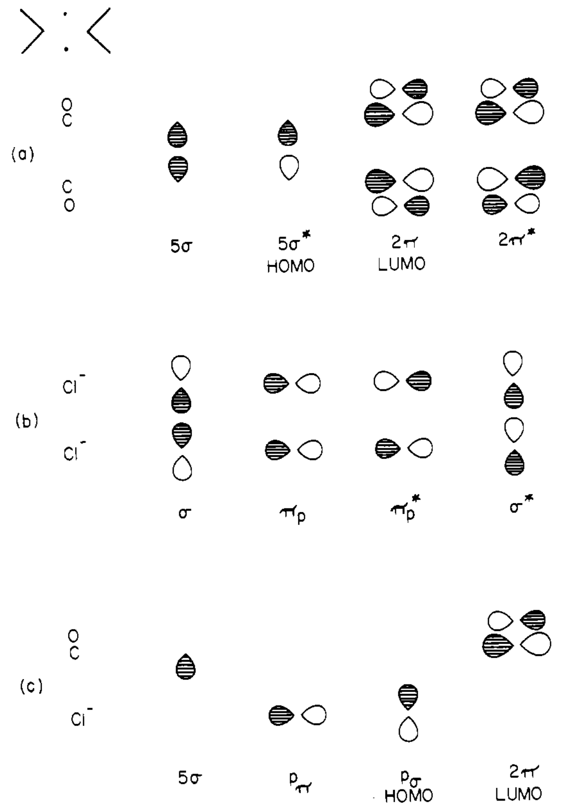


Figure 2. Important orbitals of bridging fragments: (a) $(CO)_2$; (b) $(Cl^-)_2$; (c) $(CO)Cl^-$. Orbital energies increase from left to right.

Table I. Energies and Percent Compositions of Important MO's in $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$

	$Pd_2Cl_4^{2-}$					$(\mu\text{-}CO)_2$		
ε, eV	σ_{z^2}	δ	π	π*	σ	5σ	5σ*	2π*
−2.86 (HOMO)				59				29
−2.91	40	36			15	7		
−10.78			17				46	
−10.97	8					58		

shown. The same designations, e.g., 5σ or 2π, are sometimes used for orbitals in different bridging fragments, but it should be clear from the context which fragment is meant. Out-of-phase combinations are labeled with asterisks, and this notation requires clarification. Orbital 2π of a single CO ligand is antibonding within that ligand, but two such orbitals in a $(CO)_2$ fragment can be combined in phase (2π) or out of phase (2π*). All valence orbitals of $(Cl^-)_2$ are filled, whereas some valence orbitals of $(CO)_2$ and of $(CO)Cl^-$ are vacant.

Bonding in the Bridged Molecules, Pd_2L_6, and Their Structures

In the preceding discussion we stated that bonding abilities of the various dipalladium fragments are fairly similar but that bonding abilities of the three bridging fragments are different. Next, we will examine the interactions between these two kinds of fragments in an attempt to understand why the Pd(I) dimer adopts structure **1**(I), whereas the Pd(II) dimer adopts structure **2**(II). We studied all five isomers, **1–5**, of both dimers but will emphasize the existing isomers **1** and **2**. Comparisons of **1** with **2** or **3** contribute most to the understanding of the structural preferences because bridges in them differ most: $(CO)_2$ in **1** vs. $(Cl^-)_2$ in **2** and **3**. Throughout the following discussion, we will refer frequently to the important orbitals of the fragments, depicted in Figures 1 and 2.

Pd(I) Dimer, $[Pd_2Cl_4(CO)_2]^{2-}$. This compound has configuration **1**(I). Its electronic structure is summarized in Figure 3 and Table I. Two interactions are essential for bonding in the molecule. One, shown in **8**, is strong a π interaction between the vacant orbital π* of the $Pd_2Cl_4^{2-}$ fragment and the vacant orbital 2π* of the bridging $(CO)_2$ fragment; these orbitals are mixed extensively in the HOMO, which lies *below* them in energy and represents their *bonding* combination. To attribute covalent bonding to the mixing of two *empty* fragment orbitals may be surprising because covalent bonds usually are envisioned as arising from the sharing of electrons (interaction between two half-filled orbitals) or donation–acceptance of electrons (interaction between a filled and a vacant orbital). But in a molecular orbital analysis, molecular orbitals are filled with the available electrons regardless of the "atomic origin" of these electrons. This is emphasized in **9**. The molecule **1**(I) contains enough electrons to fill the molecular orbitals through the one depicted in **8**. A number of molecular orbitals below this HOMO, including the one at −2.91 eV immediately below it, are essentially localized in the dipalladium fragment and do not contribute appreciably to formation of the bridges. Nineteen such orbitals between −2.99 and −7.77 eV are not included in Table I and are marked as two blocks in Figure 1.

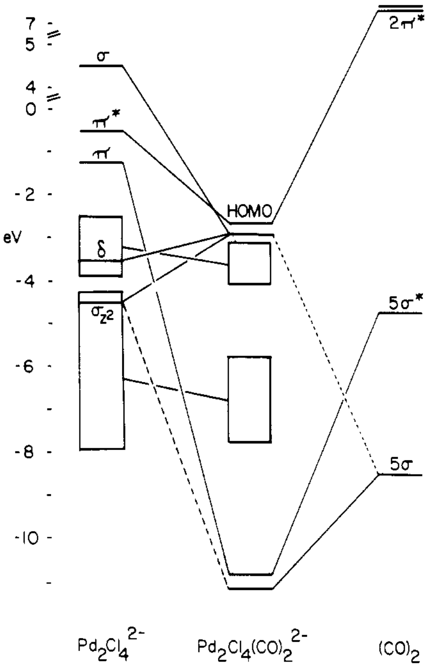
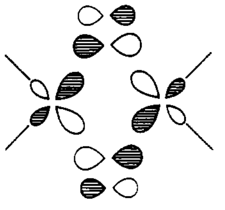


Figure 3. Molecular orbital diagram for $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$ (isomer **1**(I)).



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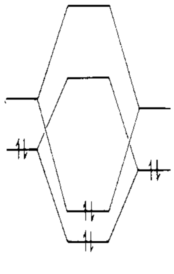

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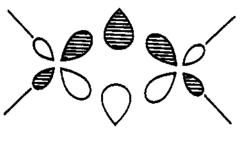
The other essential interaction occurs in the molecular orbital at −10.78 eV and is depicted in **10**. Orbital π of the $Pd_2Cl_4^{2-}$ fragment has π symmetry within this fragment but σ symmetry with respect to the bridging $(CO)_2$ fragment. A σ interaction exists between the filled orbitals π and 5σ*. One is not used to ascribing bonding to the mixing of filled orbitals although **9** shows that it is conceivable. In this molecule the overlap between π and 5σ* is large (calculated 0.40) and these



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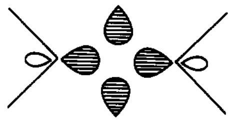
fragment orbitals are rather close in energy, so that they interact strongly. The antibonding counterpart of **10** is pushed to high energy (not shown in Figure 3) and is vacant, so that the contribution of **10** to interfragment bonding is not reduced. In the more usual case of a weaker interaction the antibonding molecular orbital would be pushed to a less high energy, where it might still be low enough to be filled with electrons. This could reduce or cancel the effect of the bonding molecular orbital.

These were the two strong interactions between the fragments in **1**(I). Considerably weaker is the interaction shown in **11**, between the vacant dipalladium orbital σ and the filled

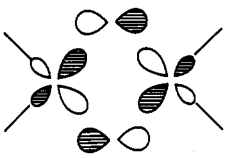


11

dicarbonyl orbital 5σ. The overlap **11** is large, but the orbitals involved differ greatly in energy, so that they do not mix much. Table I shows that **10** is only a minor component (22%) of the molecular orbital at −2.91 eV. Its major components are σ_{z^2} and δ, which are localized in the dipalladium fragment. The interaction between σ_{z^2} and 5σ does not contribute to bonding in the bridging region because the molecular orbitals that contain bonding (at −10.97 eV) and antibonding (at −2.91 eV) combinations of these two fragment orbitals are both filled. The interactions between δ and 5σ are negligible because their overlap is minute.

In summary, the calculations reveal strong, delocalized bonding in the bridging region of **1**(I). Because of the relatively high overall symmetry of this configuration, electron density in the molecule is distributed symmetrically; i.e., equivalent atoms bear equal charges, and equivalent bonds have equal overlap populations. Strong bridging bonds and symmetrical electron density both contribute to the stability of the observed structure of the Pd(I) dimer, **1**(I).

The molecular orbital diagram of the fictitious isomer **2**(I) is shown in Figure 4. Its HOMO, drawn schematically in **12**, has *higher* energy than orbitals π^*_p and π^* do and represents their *antibonding* combination; it would *weaken* the bonding in the bridges. The σ interactions, analogous to **10**, between the metal-based orbital π and the bridge-based orbital σ^* is relatively weak because of the large energy gap between them. The electronic structure of isomer **3**(I) is similar to that of the isomer **2**(I). In both these chloride-bridged structures the Pd–Cl bridging bonds are relatively weak (overlap populations between 0.05 and 0.22 e), unlike the strong Pd–CO bridging bonds (overlap populations 0.47 e) in the actual structure, **1**(I).



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Bonding in isomers **4**(I) and **5**(I) is intermediate between that found in **1**(I) and in **2**(I) and **3**(I) above. The HOMO in either **4**(I) or **5**(I) is bonding between the metal fragment and the CO bridging ligand but antibonding between the metal fragment and the Cl^- bridging ligand. The calculations show that, because of this contrast, the Pd–C(O)–Pd system has much higher overlap populations than the Pd–Cl–Pd system. Since isomers **4**(I) and **5**(I) have low symmetry (C_s), the two Pd atoms in each of them would bear different charges. All these factors make configurations **4**(I) and **5**(I) less favorable than the actual configuration **1**(I).

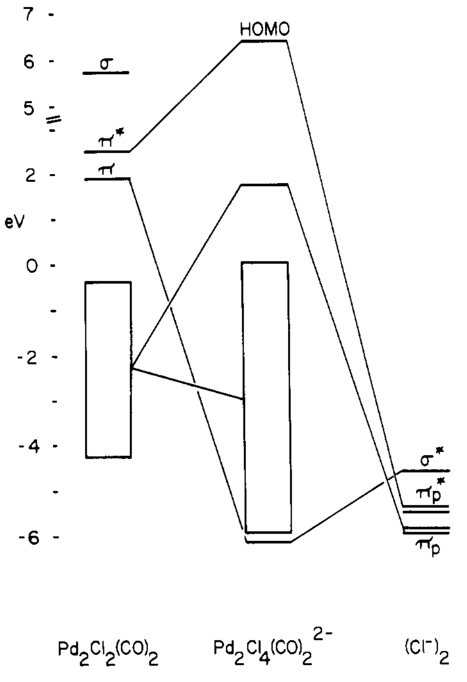

Figure 4. Molecular orbital diagram for *trans*(*CO*)-$[Pd_2Cl_2(CO)_2(\mu\text{-}Cl)_2]^{2-}$ (isomer **2**(I)).

Having examined and compared the bonding in five conceivable isomers of the Pd(I) dimer, we can now summarize the reasons that seem to determine its preference for the $(CO)_2$-bridged structure, **1**(I). Our calculations indicate that at least part of the answer lies in the energy of the bridging orbitals relative to that of the dipalladium orbitals. These relative energies of the interacting orbitals determine the nature of the HOMO in the complete bridged dimer. The $(CO)_2$ fragment has the *high-lying*, vacant π-type orbital $2\pi^*$, more localized on carbon than on oxygen atoms. Hence the HOMO in **1**(I), which lies *below* both $2\pi^*$ and the metal-based orbital π^*, is their *bonding* combination; its occupancy *stabilizes* the molecule. Since Cl is more electronegative than C, the $(Cl^-)_2$ fragment has the *low*-lying, filled π-type orbital π^*_p. Hence the HOMO in **2**(I) or **3**(I), which lies *above* both π^*_p and the metal-based orbital π^*, is their *antibonding* combination; its occupancy *destabilizes* the molecule.

Question of Direct Pd(I)–Pd(I) Bonding. Both palladium atoms in the anionic dimer **1**(I) have formal oxidation state +1 and electron configuration d^9. Their distance[2b] of 2.70 Å is slightly longer than most of the Pd(I)–Pd(I) distances in several other bridged dinuclear complexes.[17-23] The Pd(I)–

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Pd(I) distance in the only known *unbridged* dinuclear complex is considerably shorter than that, 2.53 Å, and represents the shortest Pd–Pd distance found to date.[24] All known Pd(I) dimers are diamagnetic.[2b,17–25] For most of these dimers, diamagnetism was attributed to direct bonding between the bridged Pd(I) atoms;[2b,17,18,20–23] naturally, such bonding was proposed for the unbridged Pd(I) atoms in the sole dinuclear compound that contains them.[24] The possibility of magnetic exchange was mentioned for only one bridged dimer.[25]

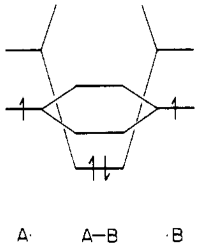
Our calculations indicate that direct metal–metal interaction in $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$ is practically negligible. Speaking qualitatively, we note that molecular orbital **8** is π antibonding between the Pd(I) atoms, whereas molecular orbital **10** is π bonding between them. Occupancy of *both* these orbitals and of the *pairs* of lower lying bonding and antibonding molecular orbitals that arise from lower lying fragment orbitals would mean that the net bond order between the metal atoms is close to zero. Population of the molecular orbital corresponding to **11**, which is σ bonding between the metal atoms, does not bring the net bond order to 1, as one may be tempted to conclude from a purely qualitative analysis. As we explained above, interaction **11** is weaker than interactions **8** and **10** and represents only a minor component of the delocalized molecular orbital at −2.91 eV. Interaction between the palladium d_{z^2} orbitals does not result in appreciable metal–metal bonding because the molecular orbitals containing the in-phase and out-of-phase combinations of d_{z^2} orbitals are both occupied.

For a more quantitative analysis, results of the calculations are needed. The filled molecular orbitals corresponding to interactions **8**, **10**, and **11** differ in their metal–metal characters and therefore provide different amounts of electron density in the region between the metal atoms. Any filled molecular orbital contains two electrons, but this total charge can be divided differently among the participating orbitals. The calculated populations of the dipalladium orbitals π, π^*, and σ in the complete bridged molecule **1**(I) are 0.81, 1.4, and 0.59 e, respectively. The total population of the two orbitals that are bonding between the metals (π and σ) is 1.4 e, the same as the population of the one antibonding orbital (π^*). The bonding and antibonding Pd–Pd interactions in these three molecular orbitals apparently cancel each other out. The conclusion reached by considering only the three important molecular orbitals is not changed when one considers contributions from *all* molecular orbitals to the Pd(I)–Pd(I) interaction: the total overlap population between the two metal atoms is practically equal to zero (0.03 e), which means that the Pd(I) atoms are practically not bonded to each other. To make sure that this negligible overlap population is real and not an aritfact of our molecular orbital method, we carried out a calculation on $[Pd_2(CNMe)_6]^{2+}$ with the same basis functions that we used for $[Pd_2Cl_4(CO)_2]^{2-}$. Since the two Pd(I) atoms in $[Pd_2(CNMe)_6]^{2+}$ are not bridged by ligands, they must be linked by a direct metal–metal bond.[24] The calculation clearly showed that bond and, corresponding to it, the total overlap population of 0.39 e between the two Pd(I) atoms.

In conclusion, $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$ appears not to contain appreciable metal–metal interaction. The diamagnetism of this compound seems to be due to coupling of metal electrons indirectly (through the carbonyl bridges) rather than directly (through space). The relatively short Pd–Pd distance of 2.70 Å seems to reflect strong bonding in the bridges, rather than direct bonding between the metal atoms.

Early in the development of interest in metal–metal bonds it was realized that pairing of metal electrons may occur indirectly (through bridges, especially CO ligands) as well as directly (through space), so that diamagnetism or diminished paramagnetism of a polynuclear compound need not be due to direct metal–metal bonding.[26–28] Recent studies of superexchange interactions in dimetal complexes have confirmed this view.[29] It was also realized that bonds in polynuclear metal carbonyls are delocalized.[30,31] That orbitals (i.e., electrons) can interact through bonds as well as through space has been accepted among theoretical organic chemists for some time.[32,33] Particularly relevant to our study is the finding by Colton et al. that a molecule containing two Pd(I) atoms bridged by a CO ligand is diamagnetic even though the metal atoms are too far apart to be directly bonded.[28,34] Like **1**(I), this compound contains a CO rather than a Cl ligand in the bridging position and violates the rule about bridging in metal carbonyl halides.[4,5]

From the general viewpoint of molecular orbital theory, a dinuclear molecule with metal atoms in such oxidation states that they formally contain unpaired electrons may easily be diamagnetic and not contain a direct metal–metal bond. If the molecule has a singly degenerate HOMO that is sufficiently separated in energy from the LUMO, and if its number of electrons is even, it will most likely be diamagnetic. This is so in $[Pd_2Cl_4(\mu\text{-}CO)_2]^{2-}$. Unlike classical valence bond theory, in molecular orbital theory the "atomic origin" of molecular electrons is not crucial because they are delocalized anyway. These two theoretical approaches may be contrasted with each other by considering an interaction between two radicals, possibly open-shell metal fragments. The bond between them need not be formed from the half-occupied orbitals, as **13** shows schematically.



13

Several recent studies, experimental as well as theoretical, have challenged the notion of direct metal–metal bonds in a few bridged dinuclear compounds that are customarily represented as containing such bonds.[28,35–42] Some compounds

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are still controversial.[35b,43,44]

Pd(II) Dimer, $[Pd_2Cl_4(CO)_2]$. This neutral molecule is derived formally by removing two electrons from the anionic Pd(I) dimer. The reasons for the preferred structure of the Pd(II) dimer can be analyzed by considering the effects of such formal ionizations upon various isomers of the Pd(I) dimer. We carried out separate calculations on all five isomers of the Pd(II) dimer, **1**(II)–**5**(II), and confirmed that the nature and sequence of the molecular orbitals in the corresponding isomers of the Pd(I) and Pd(II) dimers are similar, so that consideration of formal ionizations may be useful. In particular, the HOMO in the Pd(I) dimer and the LUMO in the same isomer of the Pd(II) dimer correlate with each other.

As **8** shows, the HOMO in **1**(I) is strongly bonding between the metal fragment and the $(CO)_2$ fragment but antibonding between the metal atoms. Emptying of this orbital in **1**(II) causes weakening of the bridging bonds (decrease in the Pd–CO overlap population) and slight strengthening of the direct metal–metal interactions (small increase in the Pd–Pd overlap population). The only significant bridging bonds that remain in **1**(II) are those of the σ type, depicted in **10**.

Experimental evidence indicates that the Pd(II) dimer adopts structure **2**(II).[3] Its molecular orbital diagram is similar to that of **2**(I), shown in Figure 4, except that the HOMO of **2**(I) becomes the LUMO in **2**(II). As **12** shows, this orbital is antibonding between the dipalladium fragment and the bridging $(Cl^-)_2$ fragment, so that its emptying causes large strengthening of the bridging bonds. Whereas the two fragments in **2**(I) appear to be hardly bonded to each other, the fragments in **2**(II) seem to be bonded strongly to each other: the total overlap population between the fragments is calculated to be 0.14 e in **2**(I) and 0.81 e in **2**(II). The small negative overlap population (−0.05 e) between the Pd(II) atoms in **2**(II) indicates that they weakly repel each other at the distance of 2.70 Å. The actual distance in the Pd(II) dimer probably is longer than that, so that the repulsion is relieved.

The electronic structure of the cis isomer **3**(II) is quite similar to that of the trans isomer **2**(II) but less favorable because the low symmetry of **3**(II) causes uneven distribution of electron density in the molecule and uneven strengths of bonds linking similar atoms. These differences in bond strengths, particularly the bridging ones, could cause distortions of the molecule. Goggin et al. have concluded,[2b] as we do, that the structure containing chloride bridges (**2** or **3**) should be unfavorable for the Pd(I) dimer but favorable for the Pd(II) dimer.

Isomers **4**(II) and **5**(II) are less realistic, and their electronic structures are less important than the ones discussed above.

Concluding Remarks

One advantage of molecular orbital calculations over qualitative arguments about electronic structure is that calculations provide better insight into the relative energies of orbitals. We emphasized the energies of orbitals in the bridging fragments relative to the orbitals in the dipalladium fragment in our explanation why $[Pd_2Cl_4(CO)_2]^{2-}$ contains CO, rather than Cl, bridging ligands. These relative energies determine whether the HOMO will have bonding or antibonding character between the fragments, which affects the stability of the molecule. The structural preference cannot be understood easily when orbital overlaps or orbital populations are considered. We also tried to understand these structural preferences on the basis of the distribution of atomic charges in the molecules and the fact that Cl is more electronegative than C in CO, but the analysis proved inconclusive. Calculations on the Pd(I) dimer do not reveal any significant metal–metal interactions through space. Apparently the compound is diamagnetic simply because it contains an even number of electrons; the Pd–Pd distance is relatively short because the multicenter bridging bonds are relatively strong. Many di- and polynuclear metal compounds undoubtedly contain direct metal–metal bonds,[45] but even in some of them these interactions may not be the only cause of diamagnetism or short metal–metal distances.

Controversy about direct bonding between the bridged metal atoms exposes a fundamental difference between two approaches to the study of electronic structure. Valence bond theory, upon which chemical intuition is still largely based, attributes covalent bonding to the pairing of odd electrons or to the donation–acceptance of electron pairs; bonds are envisioned as more or less localized over the atoms that contribute these odd electrons or electron pairs. According to such a view, two Pd(I) centers with d^9 formal configurations should be bonded directly if the dimer is to be diamagnetic. Molecular orbital theory attributes bonding among atoms to an excess of electrons in the molecular orbitals that are significantly bonding among these atoms over the molecular orbitals that are significantly antibonding among them. Since the molecular orbitals are delocalized, the "atomic origin" of electrons that populate them is not crucial for the description of bonding. The molecular orbital approach permits us to understand how net bonding can result from interactions between filled and between vacant orbitals.

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Registry No. $[Pd_2Cl_4(CO)_2]^{2-}$, 52653-91-5; $[Pd_2Cl_4(CO)_2]$, 43062-39-1.

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