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Notes

Character of the Direct M−M Bond in $M_2(CO)_8(\mu\text{-}PR_2)_2$ Complexes (M = V, Cr, Mn)

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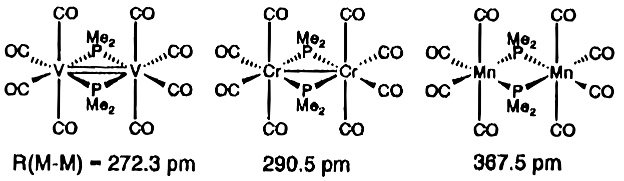
Summary: The first ab-initio calculations of phosphido-bridged binuclear organometallic compounds are reported. By analysis of the influence of electron correlation on the complex molecular structure, conclusions can be drawn about the nature of the direct bonding interaction between the two metal centers. The formal M−M bond order overestimates the direct M−M bonding interaction in the V case but underestimates it in the Cr and Mn cases.

Introduction

Phosphido-bridged transition metal carbonyls of the type $M_2(CO)_n(\mu\text{-}PR_2)_2$ (n = 4, 5, 6, 8) represent an interesting class of binuclear organometallic compounds. Much is known about their synthesis, structure, and reactivity. Only a few studies, however, exist about their bonding properties. They are concerned with qualitative molecular orbital discussions based on extended Hueckel, Fenske−Hall, or X_α calculations. Well-known is the paper of Teo et al. about the bent bond in the puckered diiron complex $(CO)_3Fe(\mu\text{-}PR_2)_2Fe(CO)_3$.[1] The bonding properties of the complex systems with n = 4, n = 5/6, and n = 8 are discussed in refs 2−4, respectively.

No investigations at a higher level of sophistication have been published up to now. In the present paper the results of the first ab-initio calculations of phosphido-bridged binuclear coordination compounds are reported. We concentrate on the systems $(CO)_4M(\mu\text{-}PR_2)_2M(CO)_4$ (M = V, Cr, Mn) (Chart 1) with planar M_2P_2 bridging unit. Complexes of this type were first prepared in the sixties[5] and were extensively studied by Vahrenkamp.[6] The R(M−M) bond length increases significantly in the order R(V−V) < R(Cr−Cr) < R(Mn−Mn). This corresponds to the assumption of a double, a single, or no direct bond, respectively, between the two metal centers as a consequence of the 18-electron rule.

Chart 1



However, the experimental R(M−M) bond length in a bridged moiety is not only determined by the formal M−M bond order. There are other influences that have to be considered.[4] The geometrical structure of the bridging unit is determined by the total of metal−metal as well as all the metal−bridge and even bridge−bridge interactions. Theoretical analyses are necessary if these interactions shall be distinguished, especially those metal−metal interactions that result from the formation of metal−bridge bonds (through-bond) and the direct metal−metal interactions (through-space). Only the latter can be related to the formal M−M bond order concluded from the 18-electron rule (see e.g. ref 7).

In this paper the results of ab-initio calculations for the three complexes are presented. Complete geometry optimization yields the minimum structures at the Hartree−Fock SCF level. The influence of the correlation energy is estimated by perturbation theory (MP2) and by considering substituted electronic configurations, the importance of which in relation to the reference configuration is discussed. A more detailed insight into the bonding situation in the planar M_2P_2 bridging unit results.

Computational Details

Complete SCF geometry optimizations were carried out for the complex systems $(CO)_4M(\mu\text{-}PH_2)_2M(CO)_4$ (M = V, Cr, Mn).

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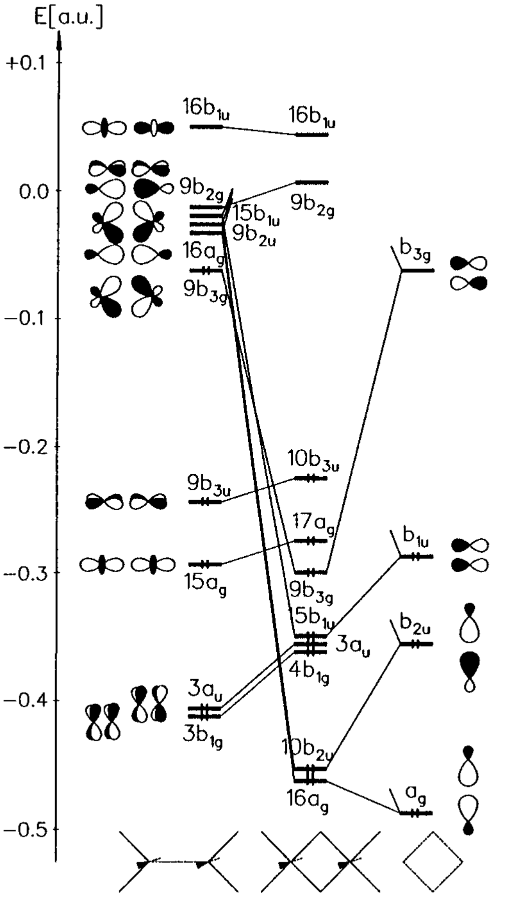

Figure 1. Molecular orbital scheme of $(CO)_4V(\mu\text{-}PH_2)_2V(CO)_4$, resulting from the SCF calculation (configuration I), built up from a $(CO)_4V\cdots V(CO)_4$ fragment and two bridging PH_2 ligands.

All systems are considered to have D_{2h} symmetry. PH_2 was used instead of the real PR_2 ligands not only to reduce the computational effort but also to equalize the systems, thus avoiding differences not crucial for bonding in the bridging unit. At the MP2 level the optimizations had to be restricted to the central M_2P_2 unit keeping the experimental or the SCF-optimized structure for the terminal ligand coordination.

The calculations were performed using the TURBOMOLE program system.[8] The core electrons of P and of the metal atoms were replaced by the effective core potentials of Hay and Wadt.[9] For the transition metals a Ne core was considered, thus including the outermost core orbitals into the SCF procedure. For the atoms C, O, and H, not directly involved into the metal−bridge bonds, the simple 3-21G basis set was employed.

Results and Discussion

In Figure 1 the resulting molecular orbital scheme of the system $(CO)_4V(\mu\text{-}PH_2)_2V(CO)_4$ is presented. This scheme will be used later on to denote substituted electronic configurations. Above four complex MOs ($16a_g$, $10b_{2u}$, $15b_{1u}$, $9b_{3g}$), which can be considered to describe four phosphido → vanadium(I) donor bonds, and two V−V nonbonding orbitals of δ/δ^* type ($4b_{1g}$, $3a_u$) there are two direct V−V bonding orbitals, the σ-bonding MO $17a_g$ and the out-of-plane π-bonding MO $10b_{3u}$.

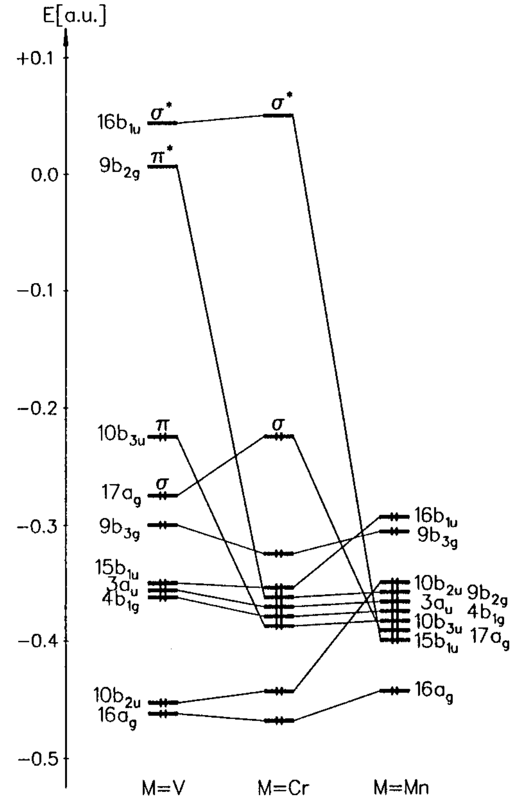

Figure 2. Complex molecular orbitals of $(CO)_4M(\mu\text{-}PH_2)_2M(CO)_4$ (M = V, Cr, Mn).

This corresponds to what is expected from qualitative molecular orbital arguments and from the 18-electron rule. The LUMO is the V−V π-antibonding MO $9b_{2g}$ followed by the V−V σ-antibonding MO $16b_{1u}$. If we turn to the chromium system, the π^* MO $9b_{2g}$ has to be occupied thus canceling the π-bond. In the resulting MO scheme (see Figure 2) one now has four Cr−Cr nonbonding orbitals of δ/δ^* and π/π^* type ($4b_{1g}$, $3a_u$, $10b_{3u}$, $9b_{2g}$), the σ-bonding HOMO $17a_g$ and the σ-antibonding LUMO $16b_{1u}$. This corresponds to a direct metal−metal single bond. Consequently, in the manganese system the orbital $16b_{1u}$ has to be occupied resulting in two further M−M nonbonding orbitals of σ/σ^* type ($17a_g$, $16b_{1u}$). No direct metal−metal interaction remains.

Selected structural parameters resulting from the geometry optimizations are collected in Table 1 and compared to the experimental values. For the individual systems the standard or reference configuration represented by the occupation schemes in Figure 2 is designated as configuration I. The energies of the complex molecular orbitals in the figures refer to the SCF-optimized geometries for these reference configurations.

The SCF level is not sufficient to reproduce the experimental geometries. For the reference configurations I the calculated bond lengths are significantly too long which is quite usual for transition metal compounds. The only exception is the R(V−V) value that comes out too short. Here we have a remarkable difference between the V case and the two others.

Rizzi et al. discussed the reasons for the structural differences between the three complexes in more detail.[4d] Their arguments, based on careful inspection of the molecular orbital pictures, can be confirmed and supple-

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Table 1. Selected Structural Parameters for $(CO)_4M(\mu\text{-}PR_2)_2M(CO)_4$ (M = V, Cr, Mn)[a–c]

	R(M−M)	R(M−P)	R(P−P)	∠M−P−M
		M = V		
expt	272.3	236.0	385.0	70.7
SCF conf I	262.5	246.3	416.8	64.4
SCF conf II	293.2	248.0	400.0	72.5
MP2 conf I	281	242	394	71
		M = Cr		
expt	290.5	231.8	361.3	77.6
SCF conf I	309.5	244.9	379.6	78.4
SCF conf II	268.4	239.0	395.6	68.3
SCF conf III	225.6	238.9	421.1	56.4
MP2 conf I	303	237	366	79
		M = Mn		
expt	367.5	234.6	291.8	103.1
SCF conf I	396.2	263.8	348.2	97.4
SCF conf II	363.3	249.6	342.0	93.5
MP2 conf I	384	246	310	102

[a] Bond lengths in pm, angles in degree. [b] Experimental values for R = Me,[6] calculated values for R = H. [c] Conf I denotes the reference configuration, conf II and III denote substituted configurations (see text).

mented by comparing the various results of the SCF optimizations (configuration I). Stepwise addition of electrons leads to characteristic changes in the forces between the atoms which for its part results in certain differences in the optimized structures. Going from the V to the Cr complex the π^* MO $9b_{2g}$ will be occupied. Thus the direct π-bond between the two metal centers vanishes and the bond length increases (from 262.5 to 309.5 pm). The M−M antibonding MO $9b_{2g}$ has no contribution from the bridging phosphorus; i.e., none of the four MOs representing the P→M donation has b_{2g} symmetry. Therefore, the M−P bond length remains essentially unchanged. As a consequence of both effects, the M−P−M bond angle increases and the P−P distance decreases.

In the next step the σ^* MO $16b_{1u}$ will be occupied. Now the M−M bond length increases drasticly (from 309.5 to 396.2 pm) in comparison with the previous step because it is more striking to omit a σ-bonding instead of a π-bonding interaction. However, as Rizzi et al. have pointed out, the MO $16b_{1u}$ is not only M−M antibonding but also has contributions from the bridging phosphorus because there is a P donor orbital combination of the same symmetry. Actually, the MO $16b_{1u}$ should be M−P antibonding as indicated by the high orbital energy. Indeed, the optimizations show that the occupation of this orbital significantly increases the M−P bond length (from 244.9 to 263.8 pm). However, the increase in the M−M distance is more apparent, thus causing a strong increase in the M−P−M angle and, therefore, a further decrease in the P−P distance.

Rizzi et al. gave theoretical and experimental arguments for a through-space P−P bonding interaction in the Mn complex. Indeed, the relatively large separation between the P→M donor orbitals $16a_g$ and $10b_{2u}$ that are formally P−P bonding and antibonding, respectively, could be confirmed (see Figure 2). However, we prefer to call this a through-bond-induced P−P interaction because it is a consequence of the formation of the metal-bridge bonds. We conclude from the optimizations that this P−P bonding interaction is no reason for but a consequence of the relatively short P−P distance in the Mn complex.

The most striking result of the SCF optimizations (configuration I in Table 1) is that the V−V bond distance turns out to be too short, whereas the Cr−Cr as well as the Mn−Mn distances, as it could be expected, turn out to be too long. This means that the experimental structure of the bridging unit of the systems under study must be essentially determined by electron correlation. To investigate this influence the Møller−Plesset perturbation theory was applied. We optimized the bridging unit at the MP2 level getting the structural parameters given in Table 1. Now we have the fact that the too-short V−V distance increases and the too-long Cr−Cr and Mn−Mn distances both decrease. This corresponds to a weakening of the V−V bond but a strengthening of the Cr−Cr and the Mn−Mn bonding interactions due to the electron correlation.

The MP2 level is also not sufficient to reproduce the experimental geometries. Although the bond angles agree surprisingly well with the experimental angles, all the atomic distances within the bridging units turn out to be too long. A sufficiently good reproduction of the experimental bond lengths would require a higher-correlated level.

We use the following strategy to estimate the relative importance of substituted ("excited") electronic configurations in comparison to the reference configuration I. Selected configurations built up by exciting two electrons from a formerly occupied into a formerly empty orbital were optimized at the SCF level. From the differences between the resulting geometries and the reference SCF geometries (configuration I) as well as the experimental geometries, conclusions can be drawn about the contribution of the substituted configurations to the electronic ground state.

In the V case we consider the substitution $3a_u \rightarrow 9b_{2g}$ (configuration II), i.e. substitution from a V−V nonbonding orbital of δ^* type into the V−V π-antibonding LUMO. This, indeed, results in a larger V−V distance. Substitution into V−V bonding orbitals would have the opposite effect. Therefore, we conclude that, besides the reference configuration I, configuration II also contributes to the ground state. This means, that no formal double bond, as is expected from the 18-electron rule, arises between the two V centers, but only a weak partial π-bonding character is acting.

In the Cr case only substitutions into orbitals with Cr−Cr bonding character can give rise to shorter Cr−Cr distances. The lowest appropriate orbital is the MO $11b_{3u}$ with Cr−Cr π-bonding character. Substitution from the nonbonding MO $3a_u$ into this orbital (configuration II) has the expected effect of decreasing the Cr−Cr distance. It corresponds to the formal introduction of a π-bond. An unrealistic decreasing effect results for the substitution from the Cr−Cr π-antibonding MO $9b_{2g}$ into $11b_{3u}$ (configuration III), which would sum up to two π-bonds. From the comparison of the R(Cr−Cr) values in Table 1 we conclude that substituted configurations with π-bonding character have to contribute to a certain extent to the ground state. Consequently, some π-bonding interaction should exist in addition to the σ-bond between the two Cr centers.

Finally, in the Mn case the same substitution $3a_u \rightarrow 11b_{3u}$ of $\delta^* \rightarrow \pi$ type (configuration II) seems to play the most important role. Other substituted configurations that we optimized, $3a_u \rightarrow 18a_g$ ($\delta^* \rightarrow \sigma$), $16b_{1u} \rightarrow 11b_{3u}$ ($\sigma^* \rightarrow \pi$), and $16b_{1u} \rightarrow 18a_g$ ($\sigma^* \rightarrow \sigma$), lead to very short Mn−Mn distances connected with the cleavage of some of the terminal Mn−carbonyl bonds; i.e., the complex molecular structure is not retained in these cases. The conclusion is that at least some π-bonding but perhaps also some additional σ-bonding Mn−Mn interaction is present. This means that the bridging unit is essentially linked together by the metal−bridge bonds but for the realization of the experimental Mn−Mn distance some additional direct Mn−Mn interaction has to be assumed.

We remark that the double substitutions, for which a very strong geometrical influence turned out, were considered because of computational reasons. We intended to compare closed-shell configurations. The corresponding single substitutions should also or even more greatly contribute to the multiconfiguration ground-state wavefunction. Actually, for single substitutions a weaker geometrical influence can be expected resulting in more realistic metal−metal bond lengths. Nevertheless, the same conclusions concerning the bonding situations would result.

It is shown by this type of theoretical analysis that the 18-electron rule only roughly describes the molecular structure of the bridged complex systems. To reproduce the experimental structure of the bridging unit one has to consider static electron correlation, the influence of which leads to a refinement of the usual bonding picture given in the textbooks.

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