On the d^6-Transition Metal Complex Formation of Electron-Rich Methylenephosphanes, a Quantum Chemical Investigation

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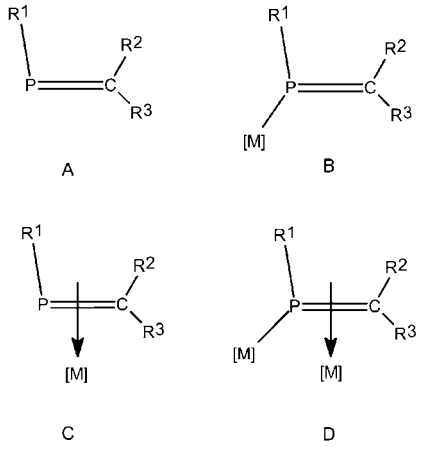
d^6-Transition metal fragments $M(CO)_5$ (M = Cr, Mo, W) form mono- and binuclear complexes with methylenephosphanes. In the mononuclear complexes the metal fragment adds to the lone pair at the phosphorus atom without considerable geometrical change of the original phosphaalkene moiety. Amino substitution at the phosphorus atom yields a slightly more stable complex than amino substitution at the carbon atom. The latter substitution pattern causes an *inverse polarization* of the P–C π-bond. As a further consequence, in the corresponding transition metal complexes, the phosphorus atom is slightly pyramidalized. In the binuclear complexes the transition metal atoms tend to adopt a distorted bipyramidal arrangement at the phosphorus atom with concomitant lengthening of the P–C bond. The stretching of the P–C π-bond is required to form a second lone pair for coordination at the phosphorus atom. However, the longest P–C bonds are achieved by *C*-diamino-substituted methylenephosphanes with overall bulky alkyl groups at the phosphorus and nitrogen atoms. It has the effect of not only extending the P–C bond but also widening the angle at the phosphorus atom.

Introduction

While the earliest reports of compounds containing a P=C double bond originated from Dimroth and Hoffmann,[1] its first stable acyclic species with a localized P=C bond was described in the pioneering work of Becker and co-workers,[2] type **A**. It opened an exciting chapter in modern phosphorus chemistry and is now documented in various review articles.[3−8] It has been stated that phosphorus is related to carbon by the diagonal relationship in the periodic table of elements[8] and typical reactions of organic chemistry may well be found also in organophosphorus chemistry[9] (Scheme 1).



Scheme 1

An archetypal reaction of phosphaalkenes **A** is the formation of transition metal complexes,[10] as η^1-complexes, type **B** {[M] = $Cr(CO)_5$,[11] $Fe(CO)_4$,[12] $Pt(PPh_3)_2$[13]}. The X-ray crystal structure of the solid indicated that for the latter, the ligand was η^1-bonded, whereas in solution η^2-coordination, type **C**, was favoured. A rationalization for this experimental observation was not given. It was also suggested that the ligation modes are a delicate balance of various effects.[14] Other η^2-bonded complexes with Ni, Rh, and W were subsequently reported.[15] A series of η^2-ligated nickel(0) species were prepared.[16] It has been shown that for an η^2-bonded ligand, the P−C bond is longer than it is in the comparable η^1-complexes or the free ligand systems.[17,18] An η^1,η^2-complex of a phosphaalkene with two coordinated transition metal atoms {[M] = $Fe(CO)_4$}, type **D**, was first recorded by Appel et al.[19] (see also ref.[15]). Phosphaalkenes acting as an η^1-(μ_2)-four-electron donor have also been reported {[M] = $Cr(CO)_5$,[20] $CpFe(CO)_2$[21]}. In these complexes the transition metal fragments are linked to the same phosphorus atom.

It is obvious that the experimental results obtained for transition metal coordination of phosphaalkenes is very rich. Besides the η^1- and η^2-mode of coordination, bridged metal centres in an η^1-(μ_2-P) or η^2-(μ_3) manner are also known. This material has been recorded in detail in reviews.[8,15] In the present publication we analyze the principal bonding features of transition metal coordination, i.e., the η^1- and η^2-modes, for methylenephosphanes. Particular attention is given to amino-substituted methylenephosphanes, since their coordination abilities are somewhat different and they can also be considered as electron rich π-systems. We considered mono- and binuclear transition metal complex formation at the phosphorus atom. The d^6-ML_5 (L = CO; M = Cr, Mo, W) species were chosen as the transition metal fragments. Our analysis is based on the results of quantum chemical investigations at a density functional level (DFT). We note that in this instance DFT calculations are the appropriate choice for the cases studied

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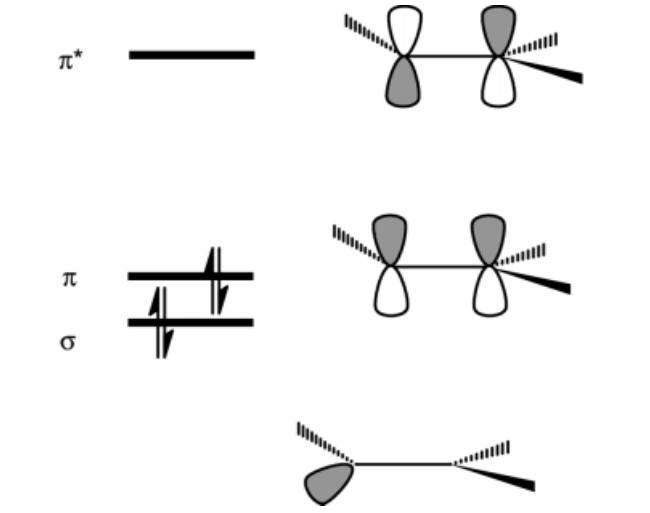
at hand, due to the large size of these structures. Recent investigations on a variety of transition metal complexes with phosphorus compounds were skilfully performed by Creve et al.[22,23] These studies show that the results of density functional calculations (at the B3LYP level) are comparable to those obtained at the more elaborate CCSD(t) level. Details of the used quantum chemical methodology are given in the Theoretical Section.

Results and Discussion

a. Various Modes of Complexation

We first discuss the qualitative bonding features of the P−C π-bond. The parent methylenephosphane possesses two closely spaced frontier orbitals,[24,25] shown schematically in Scheme 2.



Scheme 2

In general the HOMO is the π- and the LUMO the π*-orbital. Slightly below the HOMO is the σ-orbital, constituted from the nonbonding lone pair orbital at the phosphorus atom. On the contrary in the related iminophosphanes[26,27] the HOMO is the σ- and the HOMO-1 is the π-orbital, thus the orbital sequence is reversed. This gives rise to a different chemical behaviour of methylene- vs. iminophosphanes. The latter class of compounds reveals a pseudo-carbenic behavior.[24] The levelling of frontier orbitals in the methylene- and iminophosphanes is in agreement with detailed photoelectron-spectroscopic investigations[27,28−31] and the assignment of the orbital character (σ vs. π) is performed by supplementary investigations of the UV spectra.[26,27]

The P−C π-bond (in methylenephosphane) is essentially weaker than a C−C or an N−C π-bond,[32−34] thus it can be more easily distorted by other potential π-donors, e.g., an amino group at the carbon atom. It causes a polarization of the P−C π-bond, in terms of canonical valence bond structures best described as quasi-allylic resonance, under accumulation of negative charge at the phosphorus atom.[25] Since phosphorus and carbon atoms possess comparable electronegativities,[35] the P−C π-bond is unpolarized in the parent methylenephosphane. With this we mean the coefficient at the HOMO is almost the same for both the carbon and the phosphorus atom. However, substitution by an amino group at the carbon atom causes the formation of a strong N−C π-bond, with concomitant weakening of the P−C π-bond. As a consequence negative π-charge is accumulated at the phosphorus atom by allylic resonance. In terms of frontier orbital considerations the π-bond coefficient becomes enlarged at the phosphorus atom and diminished at the carbon atom. The effect is rather strong since an N−C π-bond is stronger than a P−C π-bond. This aspect was first noted some time ago[25] and was coined as *inverse π bond polarization*, in the studies on phosphatriafulvenes.[36−38] Thus, while parent methylenephosphane possesses an unpolarized π-bond (phosphorus and carbon have similar electronegativities), in *C*-amino-substituted species the π-bond is *inversely polarized*. This concept explains the large variation in the cycloaddition behavior of the P−C double bond[39,40] and was recently summarized in a review article.[41]

What effect does it have on transition metal complex formation? This is the aim of our present study. In order to reveal the effect of π-bond polarization we included in our work the transition metal complexes of (a) the parent compound and an amino group attached (b) to the phosphorus or (c) to the carbon atom. Thus, the DFT calculations probe the various alternatives. For mononuclear transition metal complexation with a d^6-$M(CO)_5$ (M = Cr, Mo, W) fragment the bonding parameters as shown in Figure 1 were obtained.

For completeness we include the bonding parameters for the (substituted) methylenephosphanes. The transition metal fragment in our study refers to the d^6-$M(CO)_5$ fragment. In qualitative terms it possesses the frontier orbital system[42] as shown in Scheme 3.

Two doubly occupied orbitals at the transition metal centre (d_{xz}, d_{yz}) can provide electron density for the formation of a π-bond while the d_z^2-orbital can accept electrons. In more detail, on a qualitative basis this extends the common view on bonding in Fischer-type complexes[43] to the diagram in Scheme 4, with **II** referring to donation and **I** to back-donation of electron density. One expects that the amount of back-donation $\pi(ML_5)\rightarrow\pi^*(PC)$ is less compared to (phosphanyl)carbenes,[44] due to the energetically higher (antibonding) π*-orbital in methylenephosphane as compared with the corresponding empty (nonbonding) p-orbital in methylene.

The calculations indicate that the mononuclear transition metal coordination does in essence only slightly alter the geometry of the methylenephosphane. The transition metal variation insignificantly changes the bonding parameters of the (free) methylenephosphane moieties. It is in contrast to the phosphanylcarbene complexes in which complexation requires substantial changes in the geometries of the free

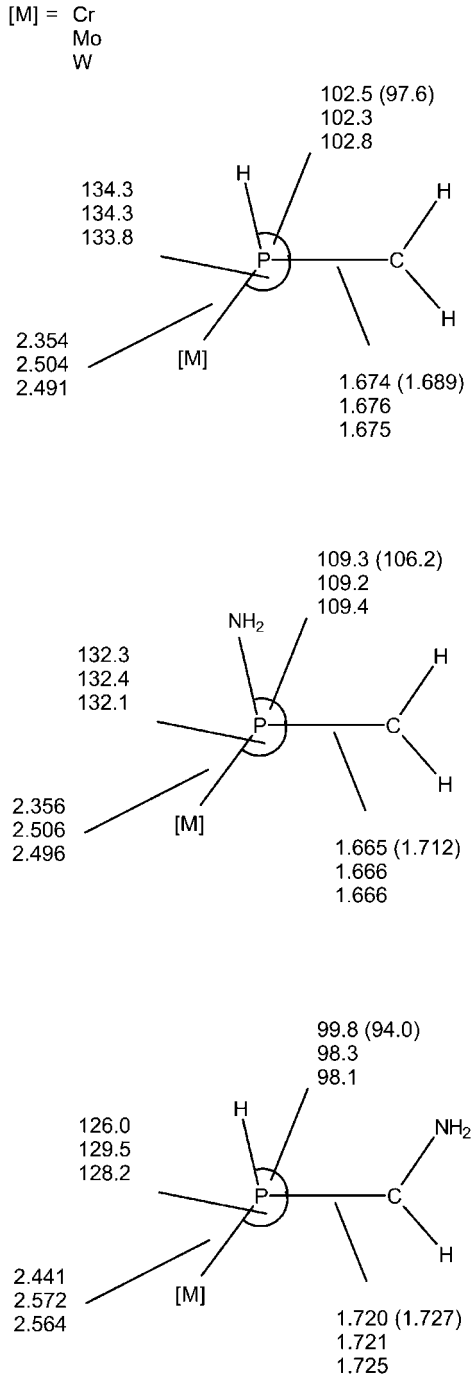
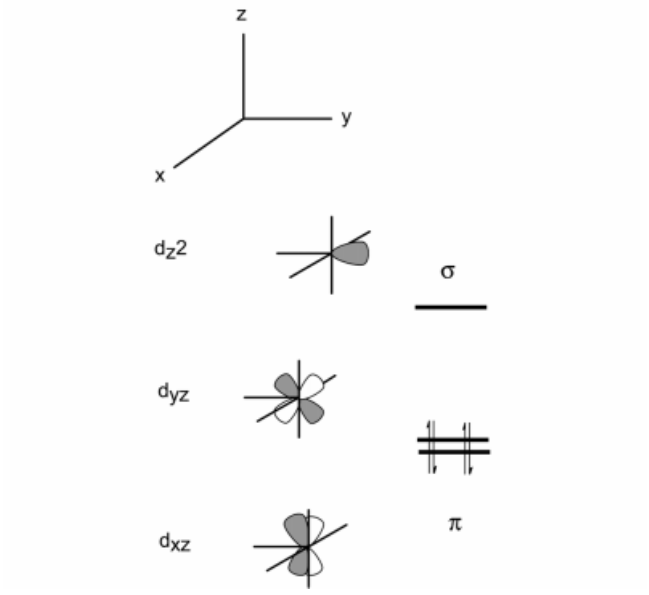


Figure 1. Relevant bonding parameters (bond lengths [Å], bond angles [°]) of η^1-transition metal complexes of methylenephosphanes

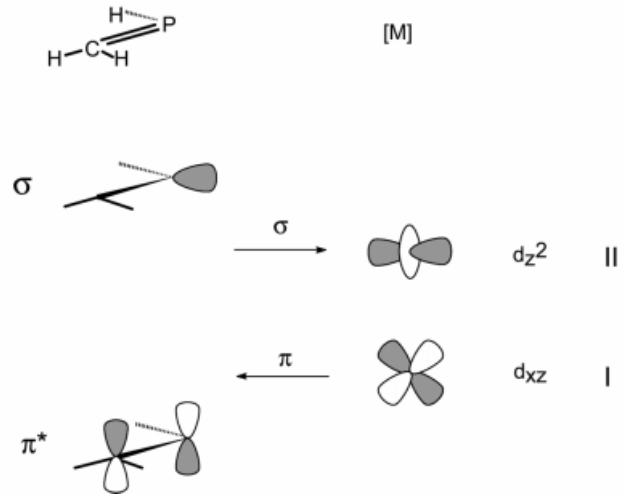
carbenes.[44] The situation for η^1-coordination is more deeply analyzed by an inspection of the energies for bonding of the transition metal fragments (Table 1). They are defined by the reactions according to Equations (1) and (2).

$$R^1P{=}CR^2R^3 \rightarrow [R^1P{=}CR^2R^3]^{\ddagger} \quad (1)$$

$$[R^1P{=}CR^2R^1]^{\ddagger} + ML_5 \rightarrow (ML_5)(R^1P{=}CR^2R^3 \quad (2)$$



Scheme 3



Scheme 4

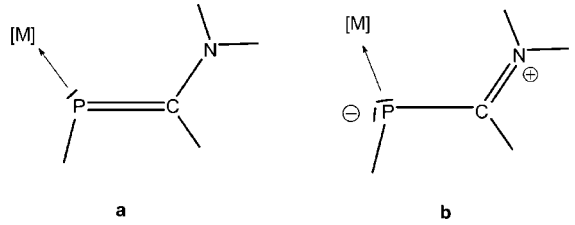
The first process [Equation (1)] refers to the energy (E_{prep}) needed to bring the free ligand (methylenephosphane) towards the structure for complexation.[45] Overall the preparation energies are in the range of 1−2 kcal/mol, thus fairly small. The second process [Equation (2)] corresponds to the energy gained in the formation of the transition metal complex from its standard state. The table includes the electronic energies (ΔE, with zero-point vibrational energy correction) and the free energies (ΔG, at room temperature) for complexation. The binding energies (as given by ΔE and ΔG) are throughout exothermic and strongly superimpose the (endothermic) preparation energies. We note here that the free energies also include the entropy contributions and were determined by standard thermodynamic formulae (see Theoretical Section). The bonding situation for transition-metal complexation contrasts that of the phosphanylcarbene complexes, where both

Table 1. Energies for η^1-coordination of d^6-$M(CO)_5$ fragments

Ligand	Metal	$-\Delta E$ [kcal/mol]	$-\Delta G$ [kcal/mol]	ΔE_{prep} [kcal/mol]
$HP{=}CH_2$	Cr	26.5	16.0	1.0
	Mo	27.7	17.5	0.9
	W	31.8	21.5	1.0
$H_2N{-}P{=}CH_2$	Cr	28.2	17.2	0.7
	Mo	29.4	18.8	0.7
	W	33.5	22.9	0.7
$HP{=}CH{-}NH_2$	Cr	25.3	15.1	1.4
	Mo	27.7	18.0	1.1
	W	30.8	21.6	1.4

quantities are comparable in magnitude.[44] Overall the free energies (ΔG) are smaller in magnitude than the electronic energies (ΔE + zero-point vibrational energy corrections). There is a continuous trend in that the binding energies increase slightly from Cr to W.

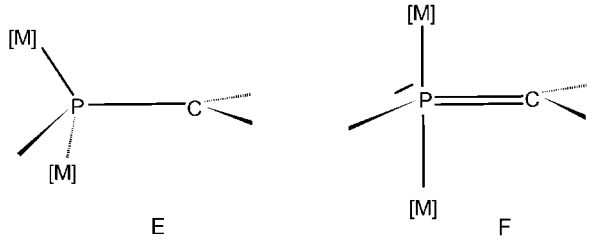
The structures of the methylenephosphanes are to a degree preserved by the coordination. Amino substitution at the phosphorus atom does not essentially alter the geometry of the parent compound, the P−C bond is only slightly elongated, as compared with the parent compound. In terms of π-conjugation, the amino group at the phosphorus atom acts only as a weak π-donor toward the P−C π-bond. The case is different for amino substitution at the carbon atom. Here the P−C bond is sizeably elongated, due to effects of *inverse* π *bond polarization*. In the coordinated compounds the phosphorus atom adopts for **a** the parent methylenephosphane and **b** for its $P{-}NH_2$-substituted congener a trigonal planar arrangement. The situation is different for the $C{-}NH_2$ substitution. After coordination, the phosphorus atom becomes slightly pyramidal, in agreement with the experiments.[31,41] The sum of valence angles for *C*-amino substitution are as follows: Cr 348.9°, Mo 353.9°, W 350.9°. This matter can be touched on in the limiting structures shown in Scheme 5.



Scheme 5

In **a** the transition metal centre coordinates to the lone pair at the phosphorus atom while in **b** the transition metal fragment occupies one lone pair of the phosphorus atom which is obtained by shifting electron density from the amino group towards the P−C π-bond. In this case one lone pair is available for complexation while the other becomes stereochemically active and causes pyramidalization at the phosphorus atom.

For the *binuclear coordination*, the various modes for complexation at the phosphorus as shown in Scheme 6 are possible.



Scheme 6

In **E** the phosphorus atom adopts a tetrahedral coordination with equal bond angles [M]−P−C. In **F** the phosphorus atom adopts a trigonal bipyramid with one lone pair in an equatorial position. In principle, the stereochemical activity of the phosphorus lone pair can lead to such conformations.[46] However, the electropositive transition metal fragment would occupy the axial rather than the equatorial positions. This would be uncommon for a trigonal bipyramid. In any case, one expects for all three alternatives, **D** to **F**, a longer P−C bond than for the mononuclear cases since the phosphorus atom has now to provide a second lone pair for coordination. It becomes only available by adopting the limiting structure **b**.

A binuclear chromium complex of $F_3CP{=}C(F)NMe_2$ has been reported recently.[20] The P−[M] distances are 2.459, 2.457 Å, with Cr−P−Cr = 127.5° and Cr−P−C = 113.5, 104.6°. Thus, this structures has been addressed as a (η^1-μ_2)-4e-complex. Concomitantly the P−C bond results in a value of 1.859 Å, which is in the range of the length of a P−C single bond (exp. 1.82−1.86 Å).[47]

We have studied the binuclear case for [M] = $Cr(CO)_5$ at (*C*-amino)methylenephosphane. A Molden plot[48] of the resulting equilibrium geometry is shown in Figure 2.

Only the case where the transition metal fragment was situated *trans* to the amino group at the carbon atom was studied, in order to mimic the situation with the least steric hindrance. The P−C bond here is sizeably longer (1.784 Å) than in the parent compound or in the mononuclear congener (see Figure 1), however also essentially shorter than in the experiment.[20] Interestingly, the angles [M]−P−C are

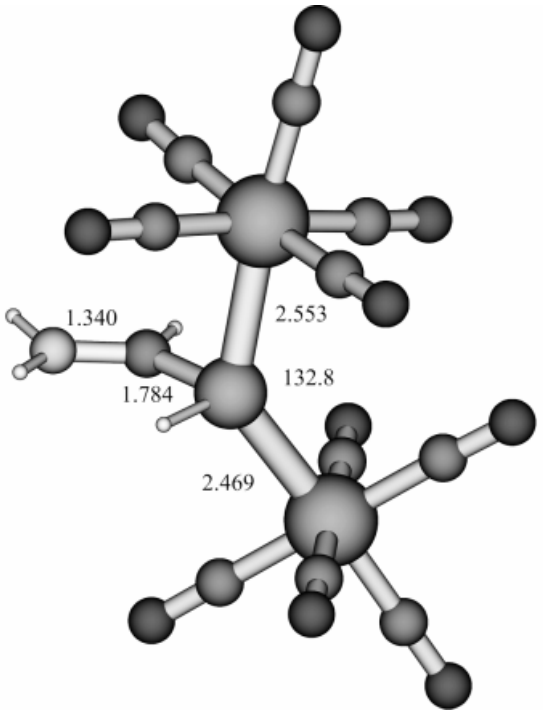


Figure 2. Molden plot of the chromium binuclear complex of *C*-aminomethylenephosphane

different (112.8, 88.2°), also the Cr−P distances are not equal (2.469, 2.553 Å) (see Figure 2). This indicates that the structure does not adopt type **D**, rather it prefers a bonding situation between **E** and **F**. In other words, the first transition metal fragment can easily coordinate to the lone pair of the phosphorus atom, however, the second transition metal fragment cannot bind strongly enough, such as to emphasise the limiting structure of **b** over **a**. It will be shown in the following section that steric effects also contribute to a further lengthening of the P−C bond in methylenephosphanes.

Accordingly, an amino group at the phosphorus atom shortens the [M]−P bond. It can be attributed to an increase of the p-character of the lone pair. On this basis the phosphorus atom changes from p^3-hybridization[32,49] (R−P−C = 90°) to sp^2-hybridization (R−P−C = 120°). This is already witnessed in the structures of the transition metal free methylenephosphanes. The amino substitution at the phosphorus atom causes an opening of the angle at P, as compared with the parent methylenephosphane. In the experimentally reported structure of the binuclear chromium complex the M−Cr distances as well as the angles of the transition metal centres with the P−C bond are almost equal. Thus, our investigations make it likely that the crucial structural effect on bicoordination is exerted by the electron-withdrawing substituent at the phosphorus atom. The energy quantities for coordination of a second $Cr(CO)_5$ fragment in addition to the η^1-complex of *C*-aminomethylenephosphane are: $\Delta E = -20.8$, $\Delta G = -8.0$, $\Delta E_{prep} = 1.4$ kcal/mol. Hence the second metal coordination is essentially less favored than the first metal coordination. The preparation energy, i.e., the energy mainly required to stretch the P−C π-bond is rather small. It is evident that the η^1/η^2- or η^1/η^1-coordination will preferentially take place for inversely polarized methylenephosphanes, since the energy contributions ΔE_{prep}, i.e., the energy to stretch the P−C π-bond can be expected to be small. Our analysis is in agreement with the wealth of experimental data available on transition metal coordination of the P−C systems.[8]

There is a further aspect that must be considered here, that is the electron distribution in the various coordination compounds. In the η^1-complexes, the $M(CO)_5$ fragments are only weakly bound to the phosphorus atom. The Wiberg bond indices yield a result for the [M]−P bond of approximately 0.5 which indicate a rather weak bond. These values are almost independent on the nature of the transition metal (Cr, Mo, W). Overall −0.4 e flow from the ligand (methylenephosphane) into the $M(CO)_5$ fragment. In other words, the latter acts only as a poor electron acceptor. Again, it is not essentially effected by the nature of the transition metal, e.g., for η^1-coordination at the *C*-aminomethylenephosphane the following Wiberg bond orders and flow of electron densities result: Wiberg bond order (Δ charge) Cr 0.411 (−0.438), Mo 0.437 (−0.374), W 0.434 (−0.376). Thus, the $Cr(CO)_5$ fragment is the slightly stronger electron acceptor, although the $W(CO)_5$ fragment binds slightly stronger to the methylenephosphanes. With respect to the electron distribution in the transition metal complexes we will now report our results on the Laplacians (Figure 3).

Figure 3 (top) views the Laplacian of the electron density of Cr bound to the phosphorus atom as well as in plane with the carbon atom. The bond-critical point is at the phosphorus atom that indicates a bond of the lone pair at P towards the transition metal centre. In comparison to the coordination of the second transition metal fragment, an essentially different electronic structure results (Figure 3, bottom). The bond-critical point is located within the triangle spanned by the atoms C, P, and Cr. It indicates that the second transition metal fragment binds simultaneously to the phosphorus and the carbon atom. Whether the second transition metal fragment coordinates according to type **E** or **F** thus depends largely on the preparation energy required to stretch the P−C π-bond.

b. Steric Effects

While it seems clear that monocoordination does not effect the P−C bond length, this, however, is the case for the addition of a second transition metal fragment, since a second lone pair at the phosphorus atom has to be provided. Alternatively in the coordination **C** to **F** the P−C π-bond is weakened. In practise the methylenephosphanes are substituted by bulky groups in order to kinetically protect the central π-bond. It is well established that the "naked" methylenephosphanes tend to undergo immediate reactions after generation.[50] To further analyze this aspect we performed quantum chemical calculations on a variety of differently substituted methylenephosphanes, at times utilizing the B3LYP/6-31g* level of approximation (see following Theoretical Section). The most important bonding para-

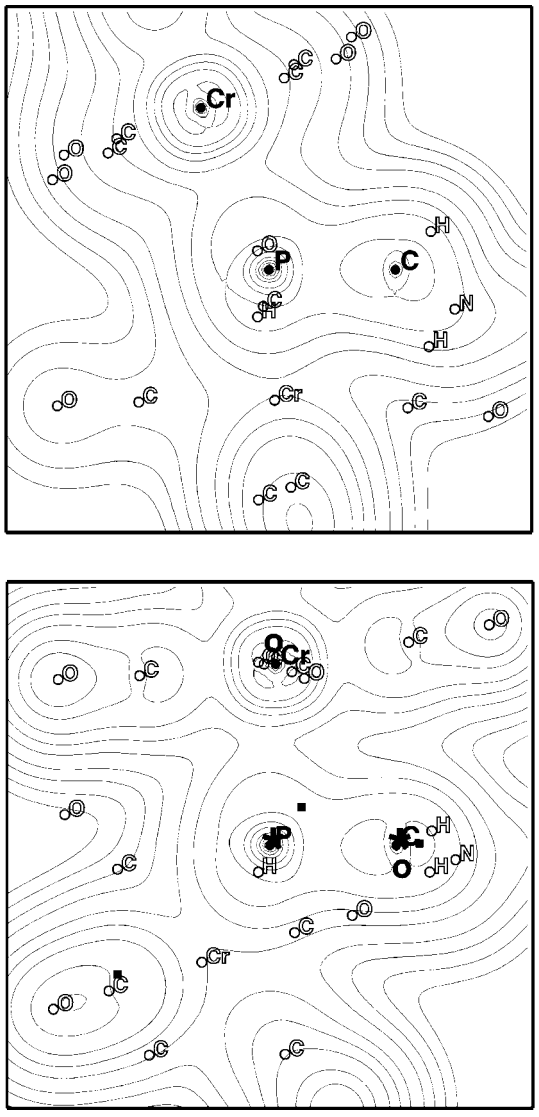


Figure 3. Laplacian of the electron density distribution for $Cr(CO)_5$ complex formation with *C*-aminomethylenephosphane; top: first transition metal fragment (with a large angle bound to the phosphorus atom); bottom: second transition metal fragment (with a small angle bound to the phosphorus atom)

meters are the P−C bond lengths and the R−P−C angles; these are collected in Table 2.

The amino groups at the carbon atom sizeably extend the P−C bond lengths. The effect is largely electronic. Two amino groups increase the P−C distance to 1.742 Å, but the further substitution by sterically demanding isopropyl groups does not essentially continue this tendency. Still the resulting equilibrium bond lengths are shorter than the largest value (1.805 Å) obtained for the binuclear metal complex.[20] According to our investigations the stretching of the P−C bond does not require much energy. Consequently the actual P−C bond lengths are determined by the bonding state in the crystal.

The alkyl substitution in the phosphaalkenes has a further effect, it induces a twisting of the π-bond. The matter is illustrated for the case R^1 = *i*Pr and $R^2 = R^3 = NiPr_2$ in a Molden plot of the computed equilibrium geometry

Table 2. Relevant bonding parameters of various alkyl-substituted phosphaalkenes (bond lengths [Å], bond angles [°]), computed at B3LYP/6-31 g(d) level

R^1(P)	R^2(C)[a]	R^3(C)[b]	P−C	R−P−C
H	H	H	1.674	97.7
H	NH_2	H	1.715	95.5
H	H	NH_2	1.721	93.8
H	NH_2	NH_2	1.742	94.5
H	NMe_2	NMe_2	1.749	96.0
Me	NMe_2	NMe_2	1.744	103.0
Me	$NiPr_2$	$NiPr_2$	1.752	103.2
*i*Pr	$NiPr_2$	$NiPr_2$	1.751	104.8
Me	H	NH_2	1.728	97.2
SiF_3	H	NH_2	1.735	94.7
CF_3	H	NH_2	1.716	97.2
F	H	NH_2	1.701	99.1

[a] *cis* to R^1(P). − [b] *trans* to R^1(P).

(Figure 4). The substituents at the phosphorus and carbon atoms exert considerable mutual steric hindrance, such as to induce rotation at the amino groups (Figure 4, top). As a further consequence, the P−C π-bond starts rotating (Figure 4, bottom).

Conclusion

The results of our investigations can be summarized as follows:

(1) For π-conjugation of an amino group with the π-bond in methylenephosphane an essential lengthening of the P−C bond is observed for the case of substitution of an amino group at the carbon atom. It is due to the stronger N−C π-bond compared with the P−C π-bond that makes the stronger N−C π-conjugation feasible. This refers to the case of *inverse polarized* PC π-bonds.

(2) The mononuclear transition metal coordination causes only slight changes in the equilibrium geometries of the free ligands, resulting in small preparation energies required for coordination. The phosphorus atom remains essentially planar. However, for the case of amino substitution at the carbon atom, the phosphorus atom accumulates negative charge. As a consequence the latter are slightly pyramidal in the coordinated compounds and [M]−P is also slightly longer compared to the other cases.

(3) For the binuclear complexes the first transition metal fragment is coordinated to the phosphorus lone pair and the second fragment to the P−C π-bond. Consequently, the second fragment is weaker bound than the first fragment. The second fragment can easily slip from η^1- to η^2-coordination.

(4) Sterically demanding alkyl groups cause a further lengthening of the P−C π-bond. Concomitantly a twisting of the P−C π-bond is induced.

Theoretical Section

All structures were fully optimized at the B3LYP[51,52] level. For the description of the metal complexes the effect-

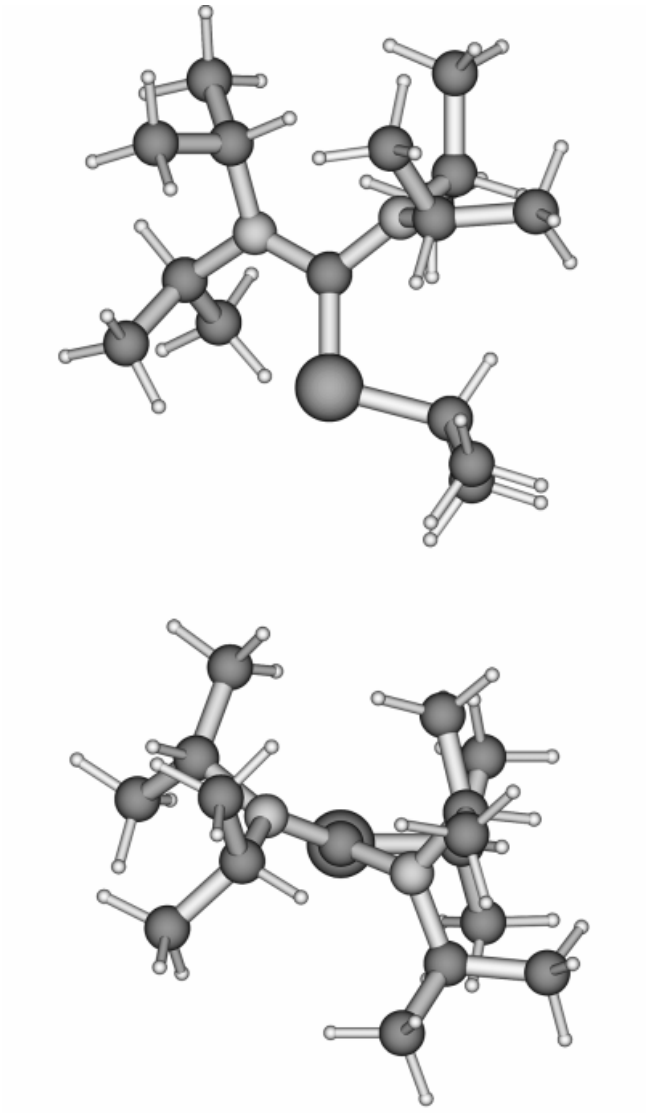


Figure 4. Molden plot of a substituted phosphaalkene (R^1 = *i*Pr; $R^2 = R^3$ = N*i*Pr$_2$)

ive core potential basis sets of Stevens, Basch, and Krauss,[53,54] were augmented by one set of polarization functions (of d-type) for the heavy (non-hydrogen) main group elements [SBK(d) basis]. The use of polarization functions is imperative to obtain a correct description of the polar [M]−P bond. All stationary points were characterized as local minima by inspection of the eigenvalues of the corresponding Hessian matrices calculated at the DFT level. The free energy contributions were evaluated using standard thermodynamic formulae and refer to contributions at 25° C (room temperature). For the cases of the uncomplexed methylenephosphanes which are substituted by bulky substituents [see Section (b)] we employed the 6-31g(d) basis set.[55] For the population analyses the NBO partitioning scheme[56] was used. Further investigations of the electron density distributions were performed with the method of "atoms in molecules".[57] All calculations were performed using the Gaussian 98 package of programs.[58]

Acknowledgments

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