On the Transition Metal Complexation (Fischer-Type) of Phosphanylcarbenes

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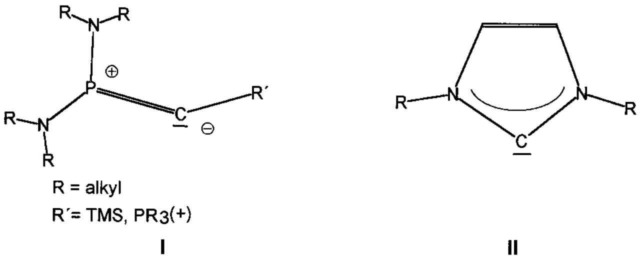
Abstract: The formation of a Fischer-type transition metal complex with a $W(CO)_5$ fragment is evaluated for the phosphanylcarbenes, Arduengo-type carbenes, and Bertrand-type carbenes by means of quantum chemical investigations at a density functional level with effective core potential methods. Accordingly, the stabilities of the complexes depend strongly on the substitution pattern of the carbenic unit. Amino-substituted carbenes as well as the Arduengo-type carbene form stable transition metal complexes. The stabilities of the complexes decrease for the phosphanylcarbenes and are at a minimum for the hitherto unknown transition metal complexes of the push−pull-type carbene of Bertrand. The matter is analyzed in terms of distortion energies required to bring the carbene units into the geometrical standard state for complexation with the transition metal fragment. The arguments evaluated for the phosphanylcarbenes should hold equally well for other carbenes substituted with electropositive ligands. For the mono-phosphanylcarbenes, η^1 as well as η^2 structures are investigated. For the diphosphanylcarbenes, a new structural type of metal complexes is predicted in which the transition metal fragment is strongly bound to a cyclic structural valence isomer of the carbene.

Introduction

The first syntheses of isolable phosphanylcarbenes, **I**, was recorded some time ago by Bertrand and co-workers in a series of pioneering studies.[1−7] The stability of this type of carbenes was attributed to the amino groups at phosphorus and simultaneously electron-withdrawing groups (SiR_3, $PR_3(+)$, R = alkyl, aryl) at the carbon atom. At the same time, another representative of a stable carbene, the imidazol-2-ylidene, **II**, was reported by Arduengo and co-workers.[8−11] In this type of structure, the electron-deficient divalent carbon center is π-conjugated with two amino groups. Recently, a "mixed" carbene which contains a phosphanyl and an amino group was characterized[12] (Scheme 1).

Regarding transition metal coordination, the two types of stable carbenes, **I** vs **II**, reveal a strikingly different behavior. The N-heterocyclic carbenes form very stable transition metal complexes with various early and late transition metal fragments.[13−18] An analysis of the peculiar bonds in these complexes shows only little metal → carbene π-back-donation, and yet the calculated bond strengths might be large (e.g., in $ClAu-C_{carbene}$[19]). Thus, the experimental investigations indicate that the Arduengo carbene bears bonding properties similar to those of the related Fischer carbene.[20] In contrast to **II**, transition metal complex formation of the Bertrand-type carbene **I** is

Scheme 1



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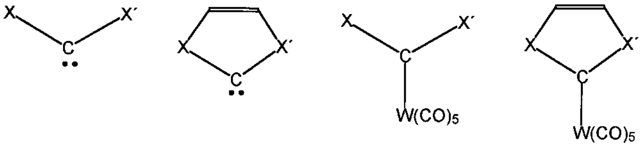
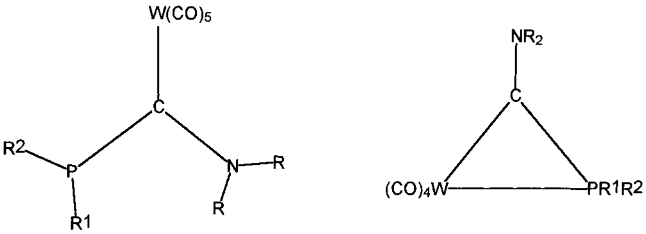


1 - 7 **8, 9** **1C - 7C** **8C, 9C**

Figure 1. Numbering of carbenes and transition metal complexes.

Scheme 2



III **IV**

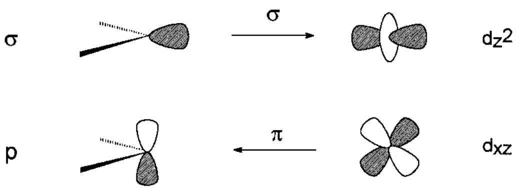
completely unknown. A pertinent example of a transition metal complexes of a phosphanylcarbene of Fischer type (d^6 transition metal) is the amino-substituted derivative, **III** (R = Et, R^1 = Me, R^2 = Ph).[21,22] It is η^1-coordinated (at the carbon), but on gentle heating the η^2-coordinated metallaphosphirene derivatives, **IV**, is obtained (Scheme 2). Recently, a chromium complex of a cyclic diphosphanylcarbene was reported.[23] An interesting discussion on the present status of the chemical findings on carbenes[24,25] and transition metal complexes of phosphanylcarbenes,[26] which also includes a discussion on other coordination compounds, was presented recently.

In the current paper, we report quantum chemical calculations which have a bearing on the transition metal complex formation of **I** and **II**, in comparison with various related phosphanyl- and aminocarbenes, **1(C)**−**9(C)** (X, X′ = PH, NH) (Figure 1). It will be shown that the stabilities of the complexes are largely determined by the distortion energies which are required to form bent carbene geometries (for coordination) from their metal-free equilibrium structures.

Theoretical Section

All calculations were performed with the Gaussian 98 set of programs.[27] The various structures were fully optimized at B3LYP level. This functional is built with Becke's three-parameter exchange functional[28] and the Lee−Yang−Parr correlation functional.[29] The

Scheme 3



effective relativistically corrected core potential basis sets of Stevens, Basch, and Krauss[30] with a double-ζ basis expansion for the valence space were used (B3LYP/SBK(d)). All heavy main group atoms were augmented by a single set of polarization functions as provided by Schmidt et al.[31] The energy optimizations were conducted by analytically determined nuclear gradients. All of the investigated structures were characterized by vibrational analysis within the harmonic approximation. The force constants were derived from analytically computed gradients. The population analyses at the given optimized geometries were carried out according to the Weinhold−Reed partitioning scheme.[32]

Results and Discussion

(a) Metal Complexation of Carbenes. The metal−carbon bond of a Fischer-type complex is usually discussed[33] in terms of the Dewar−Chatt−Duncanson model.[34,35] The dominant bonding interactions are considered to arise from ligand (carbene) → metal σ-donation and simultaneously from metal → ligand π back-donation. The matter is schematically illustrated in Scheme 3. In the case of a singlet carbene as a ligand, the most important contributions stem from transfer of electron density of the occupied a_1 orbital (σ) at the carbene into the empty d_{z^2} metal orbital and back-donation of electron density from the d_{xz} metal atomic orbital into the empty π(p) carbon orbital at the carbene. Following the pioneering concept of Taylor and Hall,[36] the metal−carbon bond is constituted by mutual donor−acceptor interaction of two closed-shell (singlet) fragments. This view may be contrasted to the Schrock-type transition metal−carbenes complexes, in which the metal−carbon bond is covalent in nature and constituted from coupling of two triplet fragments.[36] A variety of subsequent theoretical investigations[37−43] deepened this pioneering concept. Further-

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Table 1. Bonding Properties (Bond Lengths in Angstroms, Bond Angles in Degrees) of Compounds **1(C)**−**9(C)**, Wiberg Bond Orders (BO, in Parentheses), and Σ∠(P,N), the Sum of the Valence Angles at Phosphorus or Nitrogen

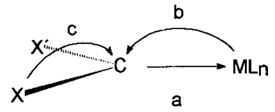
structure	X	X′	C−W (BO)	C−X	C−X′	∠XCX′	Σ∠(P,N)
1	H	H		1.142	1.142	99.7	
1C	H	H	2.062 (1.096)	1.118	1.118	108.0	
2	PH_2	H		1.641	1.121	113.9	360.0[a]
2C	PH_2	H	2.113 (0.884)	1.789	1.119	107.0	306.8[a]
3	PH_2	PH_2		1.713	1.713	130.9	322.3[a]
3C	PH_2	PH_2	2.166 (0.733)	1.809	1.809	113.7	304.3[a]
4	$P(NH_2)_2$	SiH_3		1.590	1.837	133.1	360.0[a]
4C	$P(NH_2)_2$	SiH_3	2.224 (0.589)	1.713	1.900	113.9	336.6[a]
5	$P(NH_2)_2$	PH_3^+		1.556	1.673	175.6	360.0[a]
5C	$P(NH_2)_2$	PH_3^+	2.086 (1.037)	1.828	1.832	105.7	308.5[a]
6	NH_2	H		1.338	1.135	104.8	360.0[b]
6C	NH_2	H	2.171 (0.644)	1.341	1.117	107.9	360.0[b]
7	NH_2	NH_2		1.362	1.362	111.9	360.0[b]
7C	NH_2	NH_2	2.256 (0.474)	1.359	1.359	113.6	360.0[b]
8	NH	NH		1.383	1.383	100.2	360.0[b]
8C	NH	NH	2.241 (0.475)	1.376	1.376	102.1	360.0[b]
9	PH	PH		1.740	1.740	101.2	332.4[a]
9C	PH	PH	2.164 (0.710)	1.805	1.805	107.6	310.7[a]

[a] Sum of angles at phosphorus. [b] At nitrogen.

more, a detailed qualitative discussion of the various types of transition metal fragments was given.[44]

We first evaluated for a selected variety of phosphanylcarbenes their Fischer-type complexes and compared them with the corresponding lowest energy (singlet) free carbene structures. A detailed discussion of singlet and triplet states of phosphanyl-, amino-, and nitrido-substituted carbenes was given recently,[45] based on the results of quantum chemical investigations with all-valence electron basis sets at a density functional level of theory. For the cases at hand, effective core potential methods were employed throughout. For all cases, the $W(CO)_5$ unit was chosen as a transition metal fragment. The resulting equilibrium geometries obtained by energy optimization of the carbenes as well as those for the corresponding transition metal complexes are summarized in Table 1. The relevant structures are numbered according to Figure 1. For comparison, we included in our considerations the Arduengo carbene,[8−11] **8** (X, X′ = NH), its corresponding phosphorus analogue, **9** (X, X′ = PH), and the corresponding transition metal complexes, **8C** and **9C**. The phosphorus analogue of the Arduengo carbene, **9**, is experimentally unknown, but quantum chemical calculations predicted for this species a sizable singlet−triplet energy separation (17.3 kcal/mol at the B3LYP/6-31 g(d,p) level).[45] In addition, we also considered the monoamino-, **6C** (X = H, X′ = NH_2), and the diamino-substituted carbene complexes, **7C** (X, X′ = NH_2). As noted previously,[45] the alicyclic phosphanylcarbenes possessed singlet ground states. However, the energy differences between singlets and triplets were essentially smaller than those for the Arduengo carbene[46] as well as for the aminocarbenes.[40,47,48] In general, the phosphanylcarbenes bear much smaller singlet−triplet energy separations,[45] due to the reduced ability of the phosphanyl group to donate electron density into the empty p-orbital at carbon (in comparison with the amino group).

Scheme 4



The quantum chemical investigations have shown that the equilibrium geometries reveal an essential difference between the phosphanyl- and aminocarbenes (see also ref. 45). The former adopt larger ∠XCX′ angles than the latter. The widening of the valence angle at the central carbon atom is most strongly pronounced for the push−pull-substituted Bertrand-type carbenes, **4** (X = $P(NH_2)_2$, X′ = SiH_3) and **5** (X = $P(NH_2)_2$, X′ = $PH_3(+)$). The latter possess an almost linear configurations at the carbon center.[45,49] In fact, for the push−pull Bertrand-type carbenes, the inversion barriers at the central carbon atom appear rather small.[49] The strong linearization of the carbenes with increasing phosphanyl substitution can be attributed to the overall tendency of electropositive ligands to make a carbene linear.[50,51]

Upon transition metal complexation, the carbenes respond differently. The aminocarbenes **6** and **7** preserve their free carbene structures. The CN bonds are only marginally affected, e.g., in **6** lengthened by 0.3 pm and in **7** shortened by 0.3 pm. In addition, the changes in ∠XCX′ angles are fairly small (**6**, +3.1°; **7**, +1.7°). The planarity of the amino groups is maintained. In contrast to the aminocarbenes, the phosphanylcarbenes change their geometry considerably on coordination: (a) the PC bonds substantially lengthen (**2**, +9.0%; **3**, +5.4%), (b) the angles ∠XCX′ considerably shrink (**2**, 6.9°; **3**, 17.2°), and (c) the phosphorus atoms increase pyramidalization. Most strongly pronounced are the effects for the push−pull-substituted carbenes **4** (ΔPC = 7.7%, ΔPCX′ = 19.2°) and **5** (ΔPC = 7.7%, Δ∠XCX′ = 69.9°). The view on different bonding in amino- versus phosphanylcarbenes is further corroborated by the NBO population analysis (not recorded here in detail). Accordingly, bonding in a Fischer-type complex can be schematically sketched as shown in Scheme 4. Forward donation, a (from the σ-orbital at the carbon into the d_{z^2} orbital of the metal fragment), is superimposed by back-donation, b. On the other hand, back-donation competes with the π-overlap of X (amino or phosphino group) with the p-orbital at carbon, c. The back-donation (b) is at a disadvantage for the aminocarbenes, due to the effective strong π-conjugation of the amino groups (c). Consequently, the metal fragment is more loosely bound to the carbon than in the phosphanylcarbenes. This bonding situation is witnessed in the Wiberg bond indices (see Table 1) and the W−C bond distances. The smaller π-conjugation in the phosphanyl- as compared with the aminocarbenes is also documented in smaller singlet−triplet energy separations. Concomitantly, stronger pyramidalization at the phosphorus upon coordination is induced (see vide infra).

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Table 2. Bonding (ΔE_1), Distortion (ΔE_2), and Free (ΔG) Energies (in kcal/mol) for Transition Metal Complexation of Phosphanyl- and Aminocarbenes

structure	ΔE_1[a]	ΔE_2[b]	ΔG[c]
1C	−76.0	0.2	−67.1
2C	−58.8	3.0	−48.4
3C	−51.3	5.1	−40.4
4C	−41.4	31.3	−29.5
5C	−36.8	36.0	−23.6
6C	−58.6	0.4	−48.4
7C	−52.8	5.1	−42.4
8C	−54.9	0.5	−43.7
9C	−52.8	5.1	−41.6

[a] $E(XX'C{-}W(CO)_5) - E(XX'C) - E(W(CO)_5)$, with zero-point vibration energy corrections; negative energy values correspond to an exothermic energy balances. [b] Distortion energy = E(carbene, bent) − E(carbene, equilibrium). [c] Free energies for reaction 1, at 298 K.

A peculiar bonding situation is met in the Arduengo-type carbenes **8** and **9**. For these cases a bent carbene geometry (required for suitable transition metal coordination) is already provided by the imposed ring structure.

As a consequence of the metal complexation, the phosphanylcarbenes have to shrink their ∠XCX′ angles to reach maximum overlap with the transition metal fragment. A detailed energetic analysis of these factors can be considered in two consecutive steps: reaction 1 refers to the energy balance for transition metal complex formation from the carbene in its equilibrium structure with a tungsten fragment ($W(CO)_5$). On the other hand, reaction 2 provides the distortion energy required to bring the carbene into the actual geometry of the transition metal complex.[52]

$$XX'C\ (\text{equilibrium}) + W(CO)_5 \rightarrow XX'C{-}W(CO)_5 + \Delta E_1 \quad (1)$$

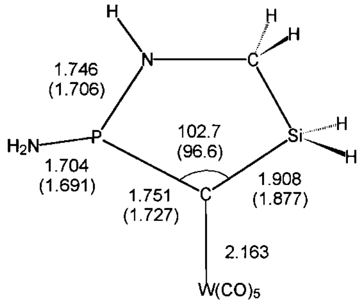
$$XX'C\ (\text{equilibrium}) \rightarrow XX'C\ (\text{distortion}) + \Delta E_2 \quad (2)$$

The energy balances for reactions 1 and 2 are given in Table 2. The resulting energy quantities ΔE_1 (in kilocalories per mole, including corresponding zero-point vibrational energy corrections) are throughout exothermic, while the ΔE_2 values are endothermic. We have also calculated corresponding values for free energy differences ΔG (in kilocalories per mole) between educts and products, determined for room temperature (298 K). Again, the quantities are exothermic. However, in general, the values for ΔG are smaller than the electronic energy differences ΔE_1.

On the basis of our findings, the reluctance of the carbene **4** to form metal complexes is due to the widened valence angles at the central carbon atom. It is even more prononced for the phosphino-phosphonium carbene **5**, which indicates an almost linear equilibrium geometry of the free carbenic species and, respectively, the largest ΔE_2 value. It is noteworthy that, in the latter case, the central valence angle decreases by almost 70° on complexation! In line with these findings are the overall diminished bond energies for transition metal complex formation of **4** and **5**. In comparison, for the Arduengo carbenes **8** and **9**, the corresponding ∠XCX′ angles are already shrunk, and the distortion energies are fairly small (ΔE_2 = 0.5 kcal/mol for **8**, 5.1 kcal/mol for **9**), which results in overall strong bond energies (see Table 2).

The distortion energies required to bend the free phosphinocarbenes can be further bisected into energy contributions of (a) PC bond stretching and (b) ∠XCX′ angle compression. Both bonding parameters depend on each other: on bending the valencies at carbon, the PC bond increases. More details of this aspect will be given elsewhere.[53]

Scheme 5



4/8

Thus, on the basis of our findings, the reluctance of the carbenes to form metal complexes is primarily due to the almost linear equilibrium geometry of the free carbene species. In comparison with, for the Arduengo carbene, **8**, the distortion energy is fairly small. It is better prepared for complexation.

A further additional important structural change upon coordination of the phosphinocarbenes may be noted here. The C−W bond lengths decrease with increasing pyramidalization at phosphorus (see also Table 1). The largest pyramidalization via complexation (and hence the shortest C−W bond) is observed for the Bertrand-type carbene, **5**. In contrast, the complex **4C**, with essential residual planarity at phosphorus, is characterized by a relatively weak C−W bond. Therefore, a linear relationship between the bond energies (Table 1) and C−W bond lengths does not hold.

It is of interest to study bonding in “hybrid structures”, such as **4/8**, which contains the features of the Bertrand-type carbene, **4**, as well as that of the Arduengo-type carbene, **8**. The push−pull substitution is confined here to a five-membered ring system. Hitherto, this type of carbene is experimentally not verified (Scheme 5). The calculations (values for the bonding parameters in angstroms and degrees of the free carbene are in parentheses) indicate a slight increase of the ∠PCSi angle by transition metal complexation. Simultanously, the PC distance is slightly elongated. The energy balances are $\Delta E_1 = -53.7$ kcal/mol, $\Delta E_2 = 11.9$ kcal/mol, and $\Delta G = -49.7$ kcal/mol. Thus, the exceptional stability of this species is a peculiarity of the five-membered ring system. Hence, the bonding energy for complexation is slightly larger for **4/8** compared to that for the Arduengo carbene, **8**.

For comparison, we have included in our considerations the transition metal complex with parent methylene, $H_2C{-}W(CO)_5$, **1C**. Owing to the absence of the concurrent stabilizing interaction, it can be considered as the most stable carbene complex with respect to reaction 1. Our value ΔE_1 = 76.0 kcal/mol agrees well with the recently reported value of 73.3 kcal/mol based on coupled-cluster calculations.[43]

There is a further aspect which has to be discussed here. The phosphanylcarbene complexes are known to form metallaphosphirene derivatives,[21,22] e.g., as sketched in type **IV**. The first step in their preparation is the formation of η^1 complexes, type **III**. Corresponding η^2 complexes have been calculated for the parent phosphanylcarbene, **2**, and its push−pull-substituted congeners, **4** and **5**. The results on the most important bonding parameters are shown in Figure 2. In parentheses are the corresponding Wiberg bond indices. They indicate a weak bond between the phosphorus and tungsten, while the PC and NC

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(52) The concept of preparation energies was first introduced in the following: Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1−10. Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558−1565.

(53) Schoeller, W. W.; Rozhenko, A. B. *J. Organomet. Chem.*, in press.

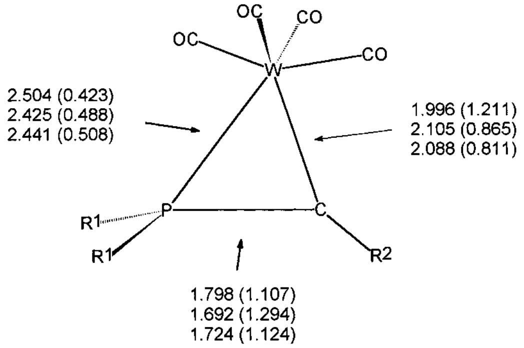

Figure 2. Relevant bonding parameters (bond lengths in angstroms) of η^2 complexes. From top to bottom: R^1/R^2 = H/H, H_2N/SiH_3, $H_2N/PH_3(+)$.

bonds can be assigned to single bonds. The nature of the P(lone pair) → W (σ*) donor−acceptor interaction is substantiated by further inspection of the Laplacian of the electron density[54] (not further recorded here). The reaction 3 provides the energy balance for the formation of the η^2 structures. The reaction is

$$\eta^1\text{-}R^1PCR^2\text{-}W(CO)_5 \rightarrow \eta^2\text{-}R^1PCR^2\text{-}W(CO)_4 + CO + \Delta E_3 \tag{3}$$

overall endothermic, decreasing for the push−pull-substituted carbenes: the quantity ΔE_3 is 30.7 kcal/mol for **2**, 17.1 kcal/mol for **4**, and 15.0 kcal/mol for **5**. Thus, there is an increasing tendency to enhance η^2 complex formation. Nevertheless, the overall process remains endothermic.

(b) Cyclization of the Diphosphanylcarbenes. The diphosphanylcarbene, **3**, possesses a rather small energy separation between singlet and triplet (8.4 kcal/mol at B3LYP/6−31 g** level, plus zero-point energy correction).[45] The energy difference between both electronic states further decreases when the hydrogens (at P) are replaced by more electronegative amino groups. For the bis(diaminophosphino)carbene, $C(P(NH_2)_2)_2$, the singlet and triplet lowest in energy resulted in almost equal energies (0.6 kcal/mol, in favor of a singlet ground state, given the same level of sophistication).[45] The amino groups at the phosphorus atoms tend to increase the inversion barriers at these atoms such as to inhibit favorable π-overlap of the lone pairs (at P) with the empty p-orbital at the central carbon atom. On the other hand, π-overlap is a prerequisite for a stable singlet ground state of the carbene. Hence, the carbene $C(P(NH_2)_2)_2$ can be considered as a species with large open-shell character in its ground state. It raises the question of an alternative stable structural valence isomer, i.e., of **10a** vs **10b** (Scheme 6). In terms of canonical structures, **10b** is closed-shell in nature but is strongly polar. Hence, one would expect that **10b** is higher in energy than **10a**.

To analyze this aspect in more detail, quantum chemical calculations have been employed to address this question. They give for both structures energy minima, i.e., stable structures, in favor of the C_2-symmetrical pseudo-allylic structure **10a** (see Table 3), which is 29 kcal/mol more stable than the cyclic congener **10b**. Furthermore, single-point calculations on the optimized geometries of **10a** and **10b** with an improved basis set (see Table 5) yield a similar energy difference between both canonical structures (26.0 kcal/mol, B3LYP/6-311++g(d,p), see Table 5). We note that **10b** can be considered as a new type of closed-shell structure within low-coordinated phosphorus chemistry. The quantum chemical calculations reveal for **10b** a three-membered ring structure in which all ring bonds are slightly shorter than the corresponding single bonds (C_2 symmetry), CP = 1.752, PP = 2.053, and PN = 1.701 Å, indicating π-delocalization. The NBO population analysis confirms the dipolaric nature of the ring structure and gives the following Wiberg bond orders: CP = 1.345, PP = 0.955, and PN = 0.786, 0.771. Also in agreement are further investigations of the Laplacian of the electron densities.[54]

Scheme 6

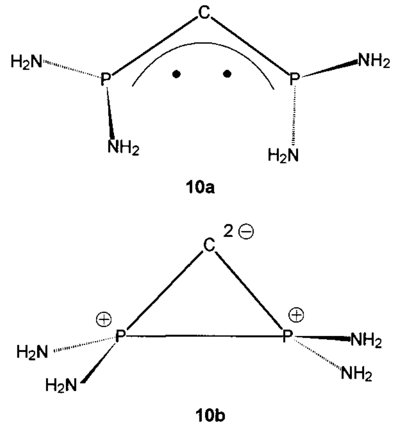

Table 3. Relevant Bonding Parameters (Bond Lengths in Angstroms, Bond Angles in Degrees) and Bonding Energies (in kcal/mol) for Transition Metal Complex Formation of **10a** and **10b**

structure (symmetry)	C−W	C−P	∠PCP	ΔE^a	ΔG^b
10a (C_2)		1.728	134.5	0.0	
10b (C_{2v})		1.753	71.7	−29.0 (−26.0)[c]	
10a(C) (C_1)	2.240	1.810; 1.771	117.0	0.0	−37.6
10b(C) (C_2)	2.251	1.741	74.7	−10.8	−50.4

[a] *E*(ring) − *E*(allyl); B3LYP/ECP-31g* with zero-point vibrational energy corrections. [b] Free energies for corresponding reaction 1, at 298 K. [c] B3LYP/6-311++g(d,p), at level (a) energy optimized structures.

We have probed the effect of transition metal coordination on **10a,b**. Corresponding Molden plots[55] of the equilibrium structures are collected in Figure 3; the relevant bonding parameters together with the bonding energies are also summarized in Table 3. The resulting W−C distances in **10a(C)** and **10b(C)** are similar (2.240 vs 2.251 Å) albeit slightly longer than in the corresponding η^1 structures **4C** or **5C**. In **10a(C)**, C_1 symmetry is adopted (PC = 1.810, 1.771 Å, ∠PCP = 116.4°). Hence, the transition metal coordination decreases again the ∠PCP valence angle. In **10b(C)**, C_2 symmetry is preserved, and the bond lengths of the ring (PC = 1.741, PP = 2.113 Å) are almost unchanged compared to those of the metal-free structure. We note that, since no clear-cut relationship between bond lengths and bond energies can be drawn (see section (a)), the stability of the transition metal complexes cannot be predicted from the W−C bond lengths. A corresponding analysis of the bond energies (Table 3, last column) reveals energy quantities which are comparable in magnitude to the corresponding bond strengths for metal complexation in the Arduengo-type carbenes. The transition metal complexation essentially reduces the energy difference between **10a** and **10b**. It can be attributed to (a) the larger distortion energy for complexation of **10a** (as compared with that for **10b**) and (b) the additional ability of the transition metal fragment to stabilize

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(54) Bader, R. F. W. *Atoms in Molecules*; Clarendon Press: Oxford, 1994.

(55) Schaftenaar, G., Molden 3.4. URL: http:/www.caos.kun.ul/schaft/molden/molden.html, 1999.

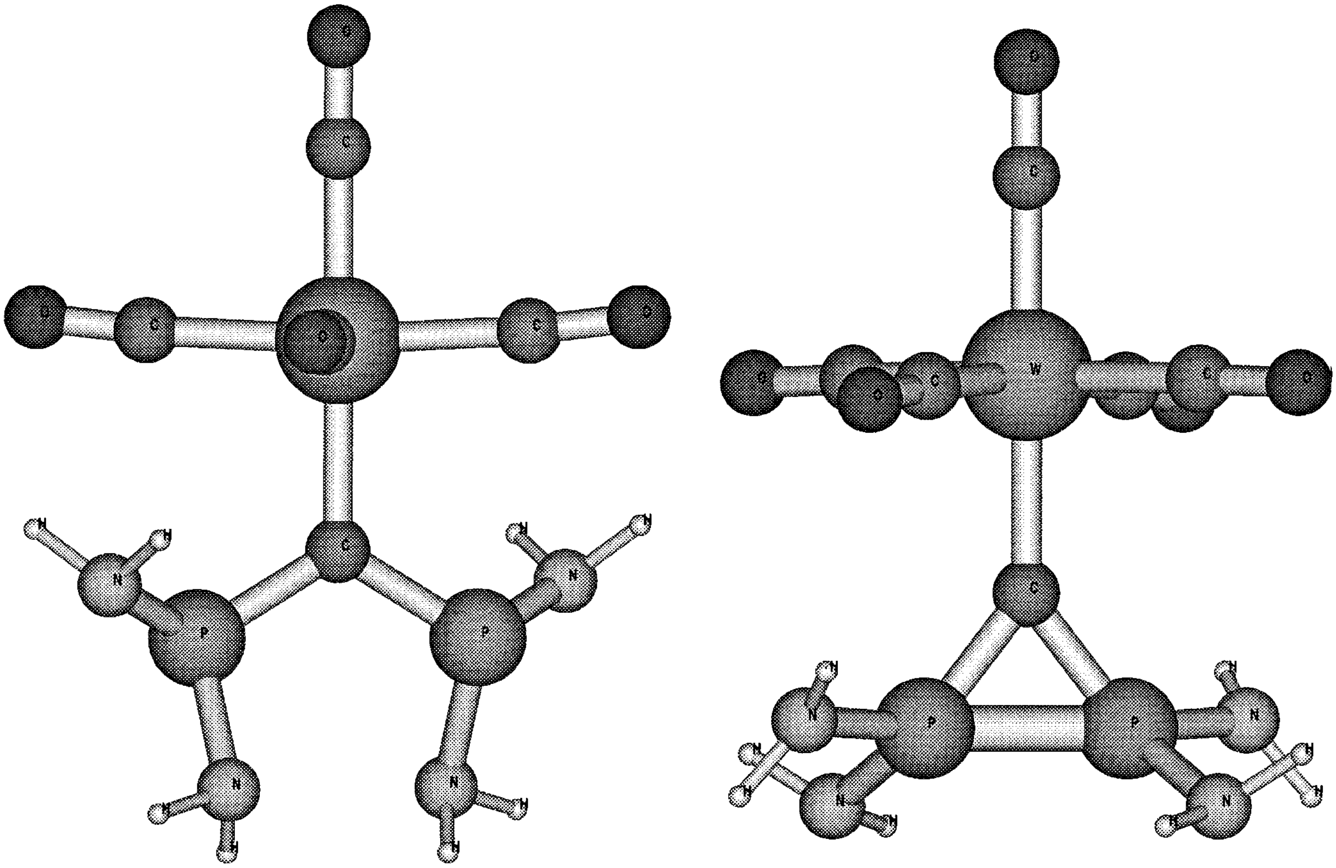

Figure 3. Molden plots of calculated transition metal complexes **10a(C)** (left) and **10b(C)** (right).

the negative charge at carbon in the dipolaric structure. This assertion is witnessed in a population analysis of both structures. In **10b(C)**, −0.395 electrons are withdrawn from the ring moiety toward the W(CO)$_5$ fragment. This value may be compared with −0.219 electrons for **10a(C)**. In other words, the transition metal complexation promotes the formation of a cyclic structure of the diphosphanylcarbene. We also expect that Lewis acids, such as AlCl$_3$ or SbF$_5$, tend to facilitate even more **10b** vs **10a**. Thus, synthesis of the former type of structure which represents a new structural type is an interesting target for verification.

Summary

The results of our investigations can be summarized as follows:

(1) The phosphanylcarbenes in contrast to the aminocarbenes tend to adopt widened valence angles at the central carbon, due to the electropositive character of the phosphanyl group.

(2) As a consequence, conformational changes of the phosphanylcarbenes to a bent carbene structure are required to allow metal complexation. These factors considerably disfavor complexation of an almost linear Bertrand-type carbene.

(3) On the other hand, the Arduengo-type carbenes are confined to a ring geometry. Hence, they are already strongly bent at the divalent carbon. On this basis, the corresponding metal complexes result as quite stable.

(4) Diphosphanylcarbenes can exist in cyclic dipolar structures which are considerably stabilized by transition metal complexation.

(5) The formation of η^2-coordinated metallaphosphirenes is endothermic with regard to loss of one CO ligand at the metal fragment.

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