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# The molecular structure of $\text{Cr}[(\text{CH}_2)_2\text{PMe}_2]_3$ : dimethylphosphonium-bis-methylide chromium compounds as inner-phosphonium-alkyl-ate- or 2-phospha-allyl-complexes?

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Dedicated to Dr. habil. Erhard Kurras on the occasion of his 75th birthday

## Abstract

The molecular structure of the chromium(III) complex  $\text{Cr}[(\text{CH}_2)_2\text{PMe}_2]_3$  (**1a**) was determined by X-ray crystallography. The bonding mode of the chelating dimethylphosphonium-bis-methylide ligand is discussed either as a part of an inner-phosphonium alkyl-ate-complex or as a 2-phospha-allyl system. In principle it seems possible to extend this consideration also to the bridging dimethylphosphonium-bis-methylide ligands in the chromium(II) complex  $\text{Cr}_2[(\text{CH}_2)_2\text{PMe}_2]_4$ . Regarding the electron delocalization in such ligands the structural parameters of **1a** are compared to the results of recently described quantum chemical calculations.

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**Keywords:** Chromium; Dimethylphosphonium-bis-methylide; Molecular orbital calculations

## 1. Introduction

Phosphorus ylides or ylides in the canonical formulas  $\text{R}_3\text{P}^+ - \text{CR}_2^-$  and  $\text{R}_3\text{P} = \text{CR}_2$  are interesting zwitterionic and neutral ligands which form a special type of alkyl compounds by coordination of the carbanionic function at the metal center. These compounds are stabilized by the inductive effect of the positive phosphonium center as onium-metallates (inner-ate-complexes)  $\text{R}_3\text{P}^+ - \text{CR}_2 - [\text{M}]^-$ . An analogous stabilization by an electrophilic center, e.g. by lithium cations, is found in the typical lithium organyl ate-complexes  $\text{Li}^+ \cdots \text{CR}_3 - [\text{M}]^-$  (2e3c-bond) (Scheme 1). The details of the manifold coordination chemistry of phosphorus ylides have been described in many excellent reviews [1], and also a few examples exist for the application of such complexes in catalysis with the SHOP process as the most important application [2].

For the special case of the trimethyl-methylene-phosphorane  $\text{Me}_3\text{P} = \text{CH}_2$  it was reported [3] that it can

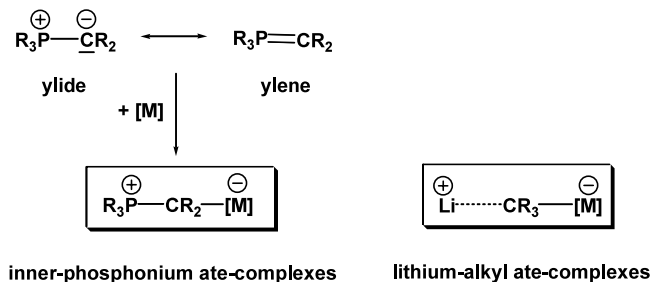
be deprotonated to the dimethylphosphonium-bis-methylide ligand  $[\text{Me}_2\text{P}(\text{CH}_2)_2]^-$  [3a,b,c] which acts as a chelating (A) or as a bridging ligand (B) for many transition metals (Scheme 2) [1].

As the first example for the chelating bonding mode the hexacoordinated chromium(III) complex with six Cr–C–σ bonds  $\text{Cr}[(\text{CH}_2)_2\text{PMe}_2]_3$  (**1a**) was published [4]. Starting from the σ-phenyl-ate-complex  $\text{Ph}_6\text{Cr}(\text{Li} \cdot \text{Et}_2\text{O})_3$  [5] (which forms by elimination of three equivalents of LiPh the σ-phenyl-complex  $\text{Ph}_3\text{Cr}(\text{THF})_3$  [6] and, after dissociation of THF, mixtures of π-(arene)-chromium compounds [6]), the elimination reaction of LiPh in the presence of the phosphonium salt  $[\text{Me}_4\text{P}]\text{Cl}$  gives instead of π-(arene)-complexes, a stabilization of the 'Ph<sub>3</sub>Cr' by the initially formed ylide and the intermediate  $\text{Ph}_3\text{Cr}(\text{CH}_2 - \text{PMe}_3)_3$ . Under stepwise elimination of benzene and metalation of three methyl groups complex **1a** was formed, presenting a system which starts from σ-phenyl and ends unexpectedly at a σ-alkyl complex.

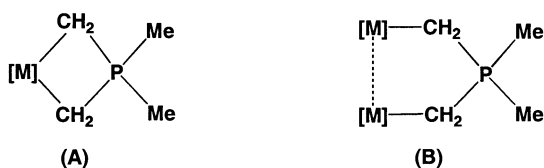
At least four different methods for its preparation were elaborated: the above described reaction of  $\text{Ph}_6\text{Cr}(\text{Li} \cdot \text{Et}_2\text{O})_3$  with the phosphonium salt  $[\text{Me}_4\text{P}]\text{Cl}$ ,

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Scheme 1. Complexation of ylides/ylenes and formal analogy of inner-phosphonium- to lithium-alkyl ate-complexes.



Scheme 2. Chelating and bridging of the dimethylphosphonium-bis-methylide ligand.

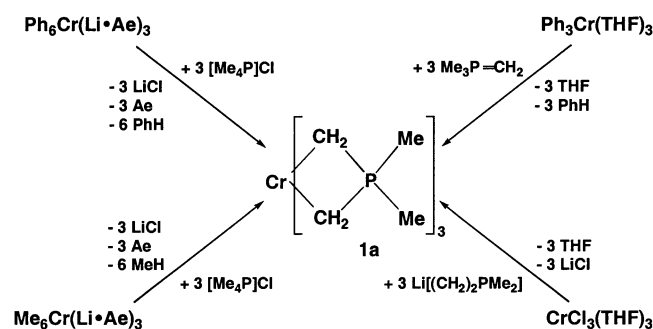
the reaction of  $\text{Ph}_3\text{Cr}(\text{THF})_3$  with  $\text{Me}_3\text{P}=\text{CH}_2$ , the interaction of the methyl compound  $\text{Me}_6\text{Cr}(\text{Li}\cdot\text{Et}_2\text{O})_3$  [7] with  $[\text{Me}_4\text{P}]\text{Cl}$  and the salt elimination of  $\text{CrCl}_3(\text{THF})_3$  and the metallated ylide  $\text{Li}[(\text{CH}_2)_2\text{PMe}_2]$  (Scheme 3).

Detailed contributions on the formation of **1a** via the firstly formed not isolated tris-ylide complex  $\text{Ph}_3\text{Cr}(\text{CH}_2\text{—PMe}_2)_3$  as well as the isolated mono  $\sigma$ -phenyl complex  $\text{PhCr}[(\text{CH}_2)_2\text{PMe}_2][(\text{CH}_2)_2\text{PMe}_2]$  [4c], on reactions [4a,c] and the UV-vis spectra [4b] were made.

Later this chemistry was conducted also for chromium(II) complexes, giving  $\text{Cr}_2[(\text{CH}_2)_2\text{PMe}_2]_4$  (**2a**) [8] by reaction of  $\text{Cr}_2\text{Me}_8(\text{Li}\cdot\text{Et}_2\text{O})_4$  [9] with  $[\text{Me}_4\text{P}]\text{Cl}$  or by salt elimination starting from  $\text{CrCl}_2$  and the metallated ylide  $\text{Li}[(\text{CH}_2)_2\text{PMe}_2]$  (Scheme 4).

Complex **2a** was characterized by its molecular structure [8d,e] and UV spectra [8b,c].

The chromium(III) complex  $\text{Cr}[(\text{CH}_2)_2\text{PMe}_2]_3$  (**1a**) could now be confirmed by X-ray crystallography and should allow in principle a formal comparison of the dimethylphosphonium-bis-methylide complex to the corresponding described structures of  $\text{Cr}(\pi\text{-C}_3\text{H}_5)_3$  [10]



Scheme 3. Preparation of **1a**.

and  $\text{CrMe}_6(\text{Li}\cdot\text{Et}_2\text{O})_3$  [7c]. In a series of dinuclear chromium(II) complexes  $\text{Cr}_2[(\text{CH}_2)_2\text{PMe}_2]_4$  (**2a**) [8d,e] is compared to compounds such as  $\text{Cr}_2(\eta^3\text{-C}_3\text{H}_5)_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_5)_2$  [11] and  $\text{Cr}_2\text{Me}_8(\text{Li}\cdot\text{Et}_2\text{O})_4$  [9].

These complexes were investigated by Erhard Kurras 30–40 years ago in a series of outstanding pioneering contributions concerning the general fundamental question of the existence of chromium alkyl compounds. These investigations directly developed from Franz Hein's work on phenyl chromium complexes and were compiled in two excellent essays by Dietmar Seyferth [6e,f] and a monograph [6g].

On the basis of the determination of the structure of **1a** and recently published quantum chemical calculation of the dimethylphosphonium-bismethylide ligand [3c] we report here on discussions to understand this ligand either as a part of polar inner-phosphonium alkyl-ate-complexes or delocalized 2-phospha-allyl systems, regarding both coordination modes as a chelating or a bridging ligand.

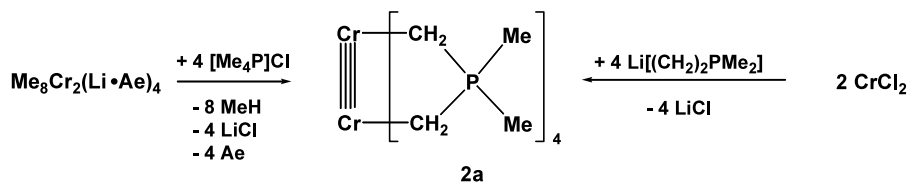
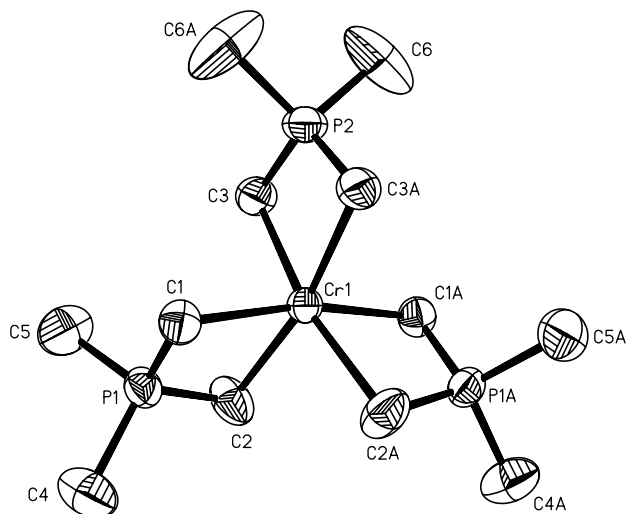
## 2. Results and discussion

### 2.1. Structure of $\text{Cr}[(\text{CH}_2)_2\text{PMe}_2]_3$ (**1a**)

The molecular structure of the chromium(III) complex  $\text{Cr}[(\text{CH}_2)_2\text{PMe}_2]_3$  (**1a**) determined by X-ray crystallography is depicted in Fig. 1 ([12], Table 1).

The coordination geometry at the chromium can be best described as a strongly distorted octahedron with equivalent Cr–C bonds which indicate  $\sigma\text{-Cr-C}(\text{sp}^{2-3})$  bonds (Table 2). This was supported also by UV-vis spectra [4b].

Complex **1a** consists of a hexacoordinated chromium which is surrounded by three  $(\text{CH}_2)_2\text{PMe}_2$  chelate ligands in a propeller-shaped arrangement. One of the three formed four membered rings is planar, two of them are nearly planar (mean deviation of the plane defined by C1, P1, C2, Cr1 is 0.0672 Å, dihedral angle of planes defined by C1, Cr1, C2 and C1, P1, C2 12.2°). Accordingly the H atoms of the methylide groups were found to be below and above the chelate ring. The P–C bonds within this ring are clearly shorter than the P–C distances to the methyl groups which are normal single bonds. This is frequently observed in complexes with this ligand and indicates that some of the ylidic character of the P–CH<sub>2</sub> bonds is retained [8d,e]. For  $\text{Me}_3\text{P}=\text{CH}_2$  a value of 1.678(2) Å for the P=C double bond was found in the solid state [3d]. With respect to interatomic distances, an interaction between Cr and P is possible. The angle between the planes defined by C1, P1, C2 and C4, P1, C5 (or C3, P2, C3A/C6, P2, C6A) which is expected to be 90° represent a nearly undistorted tetrahedral conformation at the phosphonium center (Table 2). Further indications for that are the

Scheme 4. Preparation of **2a**.Fig. 1. Molecular structure of **1a**. Hydrogen atoms have been omitted for clarity. The thermal ellipsoids correspond to 30% probability.Table 1  
Crystallographic data for compound **1a**

Crystal color	Red
Habit	Prism
Crystal system	Monoclinic
Space group	<i>C</i> 2/c
Unit cell dimensions	
<i>a</i> (Å)	14.828(3)
<i>b</i> (Å)	9.945(2)
<i>c</i> (Å)	12.521(3)
$\beta$ (°)	96.40(3)
<i>V</i> (Å <sup>3</sup> )	1834.9(7)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.156
Temperature (K)	293(2)
No. of collected reflections	2662
No. of independent reflections	1465
No. of observed reflections	1209
No. of parameters	98
$R_1$ [ $I > 2\sigma(I)$ ]	0.033
$wR_2$ (all data)	0.091

angles at the phosphorus atom (C1–P1–C2 105.2(2), C3–P2–C3A 106.3(2), C4–P1–C5 104.6(2), C6–P2–C6A 104.4(5)°).

The same ligand as in **1a** is found as bridging dimethylphosphonium-bis-methylide in the dinuclear Cr(II) complex  $\text{Cr}_2[(\text{CH}_2)_2\text{PMe}_2]_4$  (**2a**). In contrast to the four-membered rings of the Cr(III) complex **1a** the

Table 2  
Structural data of complex  $\text{Cr}[(\text{CH}_2)_2\text{PMe}_2]_3$  (**1a**)

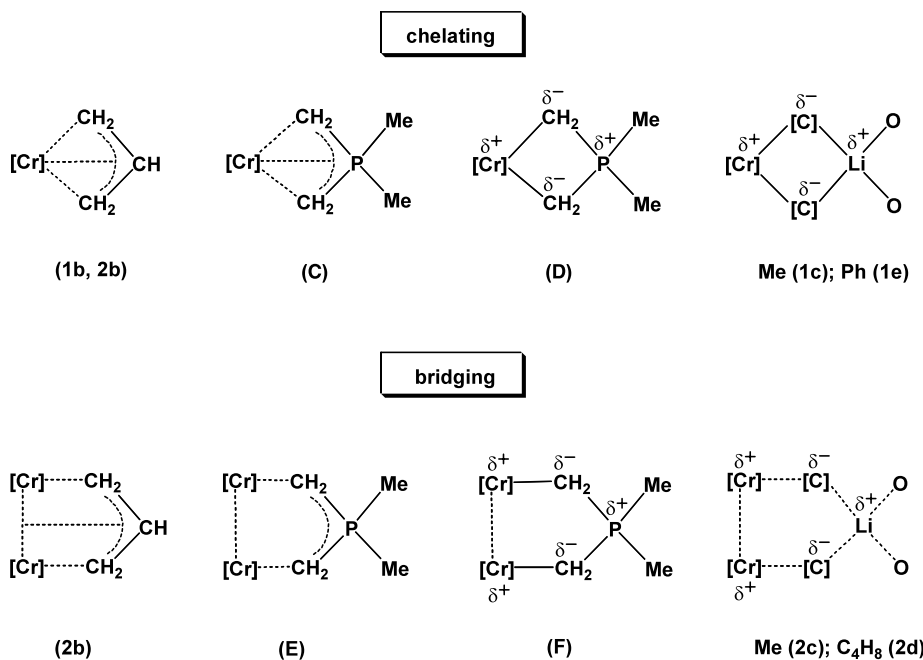
<i>Bond distances</i> (Å)			
Cr–C	Cr1–C1	Cr1–C2	Cr1–C3
	2.206(3)	2.215(3)	2.210(3)
CH <sub>2</sub> –P	C1–P1	C2–P1	C3–P2
	1.739(3)	1.722(4)	1.731(3)
CH <sub>3</sub> –P	C4–P1	C5–P1	C6–P2
	1.803(4)	1.796(4)	1.788(4)
Cr–P	Cr1–P1	Cr1–P2	
	2.768(1)	2.760(1)	
<i>Bond angles</i> (°)			
CH <sub>2</sub> –Cr–CH <sub>2</sub>	C1–Cr1–C2	C3–Cr1–C3A	
	76.9(1)	77.6(2)	
CH <sub>2</sub> –P–CH <sub>2</sub>	C1–P1–C2	C3–P2–C3A	
	105.2(2)	106.3(2)	
CH <sub>3</sub> –P–CH <sub>3</sub>	C4–P1–C5	C6–P2–C6A	
	104.6(2)	104.4(5)	
<i>Dihedral angles</i> (°)			
	C1,Cr1,C2/	C3,Cr1,C3A/	
	C1,P1,C2	C3,P2,C3A	
	12.2	0	
	C1,P1,C2/	C3,P2,C3A/	
	C4,P1,C5	C6,P2,C6A	
	90.0	89.8	

five-membered rings in **2a** [8d,e] are not planar, the angles between the planes of C<sup>1</sup>, Cr, Cr', C<sup>1</sup> and C<sup>1</sup>, P, C<sup>1</sup> (C<sup>1</sup> involved in the CH<sub>2</sub> group, Cr' symmetry generated atom) being 27.1 and 30.7°, respectively. The angles between the planes C<sup>1</sup>, P, C<sup>1</sup> (C<sup>1</sup> involved in the CH<sub>2</sub> group) and C<sup>2</sup>, P, C<sup>2</sup> (C<sup>2</sup> involved in the Me group) are here 89.5 and 90.3°.

## 2.2. Related 'onium-ate' or '2-hetero-allyl' systems

There are further chromium and dichromium complexes which contain structural elements related to **1a** and **2a** (Scheme 5).

Unfortunately the quality of the in most cases very old structures does not allow a detailed comparison of structural parameters ( $\pi$ -allyl complexes: tris-allyl-chromium  $\text{Cr}(\pi\text{-C}_3\text{H}_5)_3$  (**1b**) [10c] and tetra-allyl-dichromium  $\text{Cr}_2(\eta^3\text{-C}_3\text{H}_5)_2(\mu\text{-}\eta^3\text{-C}_3\text{H}_5)_2$  (**2b**) [11b,c]; ate-complexes: tri-lithium-hexamethyl-chromate(III)  $\text{CrMe}_6(\text{Li}\cdot\text{Et}_2\text{O})_3$  (**1c**) [7c], tetra-lithium-octamethyl-dichromate(II)  $\text{Cr}_2\text{Me}_8(\text{Li}\cdot\text{Et}_2\text{O})_4$  (**2c**) [9c],  $\text{Cr}_2(\text{C}_4\text{H}_8)_4(\text{Li}\cdot\text{ether})_4$  (**2d**) [13]). Additionally, the structural connection to our



Scheme 5. Structural elements of delocalized allyl- and polar ate-complexes.

systems is loose (phosphonium centers replaced by lithium cations) and the coordination of the lithium differs in the ate-complexes, e.g. tri-lithium-hexaphenylchromate(III)  $\text{Ph}_6\text{Cr}(\text{Li}\cdot\text{Et}_2\text{O})_3$  (**1d**) [5b] and di-lithium-tetraphenylchromate(II)  $\text{Ph}_4\text{Cr}(\text{Li})_2(\text{THF})_4$  (**1e**) [14b]. However, the fundamental difference to **1a** is that the allyl ligands in **1b** and **2b** are side on coordinated and form folded four-membered rings which is typical for C3- $\pi$ -allyl systems. The only statement which could be made for the ate complex  $\text{Ph}_4\text{Cr}(\text{Li})_2(\text{THF})_4$  (**1e**) containing a tetracoordinated lithium is that the four-membered rings  $\text{C}^1, \text{Cr}, \text{C}^1, \text{Li}$  are folded too ( $\text{C}^1, \text{Cr}, \text{C}^1/\text{C}^1, \text{Li}, \text{C}^1$ , 52.8°;  $\text{C}^1$  involved in a Ph-ring).

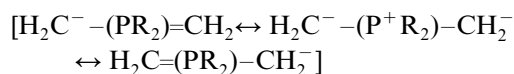
For other metals, besides chromium, also dimethylphosphonium-bis-methylide complexes exist, but data for a complete series of such structures of isoleptic compounds are limited, e.g. for  $\text{M}_2\text{Me}_8(\text{Li}\cdot\text{Et}_2\text{O})_4$  ( $\text{M} = \text{Mo}$ , [16,17] Ni, [18] Pd; [18]),  $\text{M}_2(\text{C}_3\text{H}_5)_4$  ( $\text{M} = \text{Mo}$  [16]) and  $\text{M}_2[(\text{CH}_2)_2\text{PMe}_2]_4$  ( $\text{M} = \text{Mo}$ , [15] Ni, [19] Pd [20]) only some examples are present. Additionally, extended isomerization in some of these complexes was described, e.g. for  $\text{Mo}_2(\text{C}_3\text{H}_5)_4$  [16b] and  $\text{Ni}_2[(\text{CH}_2)_2\text{PMe}_2]_4$  [18], in which the ligands form more complex structures, unsuited for a detailed comparison. In the case of nickel an interconversion between  $\text{Ni}_2[\mu\text{-}\eta^2\text{-(CH}_2)_2\text{PMe}_2]_4$  and  $\text{Ni}_2[\eta^2\text{-(CH}_2)_2\text{PMe}_2]_2[\mu\text{-}\eta^2\text{-(CH}_2)_2\text{PMe}_2]_2$  was found.

For the latter Ni(II)-compound and the Co(III)-complex  $(\text{Me}_2\text{P})_2\text{CoMe}_2[\eta^2\text{-(CH}_2)_2\text{PMe}_2]$ , the chelating dimethylphosphonium-bis-methylide ligand was firstly discussed as a 2-phospha-allyl system (Scheme 6) on the basis of a structural comparison [21]. The result is not absolutely clear. On the one hand it has been stated that for the chelating  $(\text{CH}_2)_2\text{PMe}_2$  ligands an optimal over-

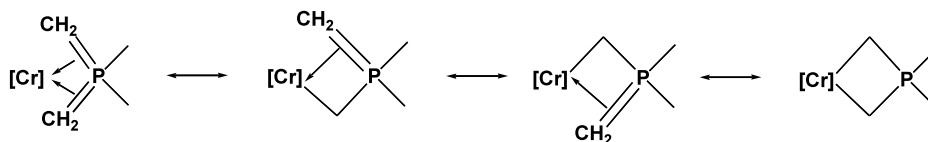
lap of the relevant orbitals ( $p(x,y)$  for C,  $d(x^2-y^2)$  for P) is achieved for a 2-phospha-allyl only in a planar system, unlike C3- $\pi$ -allyl systems. The dihedral angles between the planes  $\text{C}^1, \text{M}, \text{C}^1$  and  $\text{C}^1, \text{M}, \text{C}^1$  were calculated for  $\text{M} = \text{Ni}$  40.8 and for  $\text{Co}$  0° ( $\text{C}^1$  involved in a  $\text{CH}_2$  group). [21] On the other hand the well-known array of  $\pi$ -allyl groups was described for the nickel(II) and a more regular  $\sigma$ -onium bonding type for the cobalt(III) complex [1b].

Later, for  $\text{Ni}[\eta^2\text{-(CH}_2)_2\text{P(CH}_2)_n]_2$  ( $n = 4, 5$ ) with other substituents at the phosphonium center, a more pronounced pseudo-allylic interaction was discussed [20].

Recently conducted quantum chemical calculations regarding the electron delocalization in the chelating phosphonium-bis-methylide ligand with tetracoordinated phosphorus



were published for  $\text{R} = \text{H}$  [22a] and  $\text{Me}$  [3c]. The NPA charges on the  $\text{R}_2\text{P}$  group relative to the remainder of the molecule were calculated as a measure of the amount of delocalization in the hypothetical diylide anion  $[\text{R}_2\text{P}(\text{CH}_2)_2]^-$ . For  $\text{R} = \text{H}$  the  $\text{H}_2\text{P}-\text{CH}_2$  difference of +0.92/−0.96 ( $\Delta = 1.88$ ) [22a] that was computed at the HF/6-31+G(d) level is reduced in the DFT calculations to +0.75/−0.87 ( $\Delta = 1.62$ ) [3c]. Replacement of H on phosphorus to Me leads to the slightly larger  $\text{Me}_2\text{P}-\text{CH}_2$  difference +0.79/−0.90 ( $\Delta = 1.69$ ) [3c]. Additionally, for this case the distance  $\text{P}=\text{C}$  (1.714 Å), the angle  $\text{Me}-\text{P}-\text{Me}$  (115.5°) and the angle between the planes  $\text{Me}_2\text{P}/\text{PC}_2$  (77.8°) were calculated. The latter represents

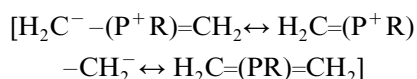


Scheme 6. Bonding modes of chelating phosphonium-bis-methylides.

a typical distortion of the P bonding geometry, as this angle should be 90° in an ideal tetrahedral environment. The extent of this distortion was related to the ylene character of the P–C bond. In conclusion from these calculations it was shown ‘that in the diylide anions a great extent of the negative charge is on the ylidic substituents. However, a typical distortion of the P bonding from the tetrahedral geometry, due to C<sup>−</sup> → π\* (PR<sub>2</sub>) negative hyperconjugation, shows that the ylene character in the P–C(ylide) bonds is not negligible’ [22a].

In contrast to these descriptions the corresponding data of **1a** represent an intact tetrahedral conformation at the phosphonium center, in good agreement to the bonding description as a more polar inner-phosphonium alkyl-ate complex. On the other hand the P–CH<sub>2</sub> bonds are clearly shorter than the P–CH<sub>3</sub> distances.

Additionally, the bonding situation for the dimethylene-phosphorane



with tricoordinated phosphorus was calculated also and described as a π-system with the ‘p’-type lone pair of a planar tricoordinate phosphorus in a 4-electron-3-center π-bonding without d-orbital participation. Its structure was best considered as a strong polar heteroallylic anion [22b,c,d].

To learn more about all of these systems and the competition between allyl- and potential 2-hetero-allyl systems we are investigating reactions of ‘Ph<sub>3</sub>Cr’ not only with Me<sub>3</sub>P=CH<sub>2</sub>, but also with other substituted phosphorus ylides such as Me<sub>3</sub>P=CH–CH=CH<sub>2</sub>, Ph<sub>3</sub>P=CH–C(NMe<sub>2</sub>)=CH<sub>2</sub> and Ph<sub>3</sub>P=CH–C(R′)=O; R′ = Me, Ph.

### 3. Conclusion

On the basis of the molecular structure of complex **1a** with chelating dimethylphosphonium-bismethylide ligands one cannot decide about the electron delocalization in the ligand (Scheme 5, C vs. D). On the one hand the results of quantum chemical calculations favour more the description as a part of a polar inner-phosphonium-ate-complex but on the other one cannot exclude the description of the ligand as a 2-phosphoallyl system. The same seems to be true in the bridging

coordination mode (Scheme 5, E vs. F) of the ligand in **2a**.

### 4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 207035 for compound **1a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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