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$[Cp_2M]$ Metallocene Species Promoted Reductive Coupling of $Cl_2C{=}PR$: Synthesis, Structure, and Reactivity of the First 3,4-Dihalo-1,2-dihydro-1,2-diphosphetes[†]

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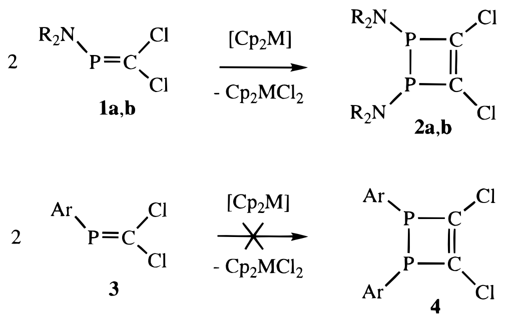
Early metallocene transition complexes $[Cp_2M]$ (M = Zr, Ti) react with C-dihalogenated phosphaalkenes $R_2NP{=}CCl_2$ [R_2N = 2,2,6,6-tetramethyl-*N*-piperidyl (TMP), $(Me_3Si)_2N$] to give 3,4-dihalo-1,2-dihydro-1,2-diphosphetes $(R_2NPCCl)_2$. A single crystal X-ray determination of $[(TMP)PCCl]_2$ reveals an unprecedented stretched phosphorus−phosphorus bond (2.320(4) Å) due to a negative hyperconjugation between the nitrogen lone pairs of the amino groups and the antibonding σ^*_{PP} orbital. Experimental results, ab initio 6-31G(d,p)//MP2 calculations, and photoelectron analysis are consistent with a strong interaction of the π-HOMO of $R_2NP{=}CCl_2$ and the $2a_1$ orbital of the metallocene $[Cp_2M]$ fragment as the first step in the formation of $(R_2NPCCl)_2$.

Since one of our main interests is the use of group 4 elements for the synthesis of original heterocyclic compounds,[1] we started searching for a new type of zirconium-mediated organic reaction by taking into consideration the high halophilicity of group 4 elements.[2] Synthetic equivalents of group 4 metallocenes $[Cp_2M]$ (M = Ti, Zr) have been recently studied and used to carry out reductive unsaturated organic molecule coupling reactions,[3] C−C bond cleavage reactions,[4] and ring expansion, contraction, or opening reactions.[3,4] We have developed a new synthetic approach mediated by $[Cp_2M]$ group 4 metallocenes (M = Ti, Zr) for the preparation of the attractive 1,2-dihydro-1,2-diphosphete derivatives[5] starting from C-halogen-substituted phosphaalkenes. We report in this paper the first synthesis and X-ray crystal structure of a 3,4-dihalogenated 1,2-dihydro-1,2-diphosphete. A reaction pathway for the formation of the 3,4-dihalo-1,2-dihydro-1,2-diphosphete based on photoelectron spectral measurements and theoretical calculations will be proposed.

Scheme 1. Synthesis of 3,4-Dihalo-1,2-dihydro-1,2-diphosphetes 2[a]



[a] **1a**: NR_2 = 2,2,6,6-tetramethyl−*N*−piperidyl. **1b**: NR_2 = $N(SiMe_3)_2$. Ar = 2,4,6-*t*-$Bu_3C_6H_2$.

Treatment of $[Cp_2Ti(CO)_2]$ as the metallocene $[Cp_2M]$ source[6] with either the phosphaalkene **1a** (NR_2 = 2,2,6,6-tetramethyl−*N*−piperidyl) or **1b** [NR_2 = $N(SiMe_3)_2$] in the molar ratio 2:1 in toluene at 35 °C led, respectively, to the isolation of **2a** or **2b** as an air and moisture stable compound with the correct composition (elemental and mass spectral analysis) for the $(R_2NPCCl)_2$ structure (Scheme 1). Formation of $[Cp_2TiCl_2]$ was identified by ^1H NMR and mass spectral analysis. The use of Negishi's system $[Cp_2ZrCl_2/2\ {}^nBu_2]$ (a precursor to the zirconocene complex of *n*-butene)[7] in the reaction with **1a,b** (2 equiv) at −78 °C gave **2a**,**b** in

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(2) Igau, A.; Dufour, N.; Mahieu, A.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 95. Mahieu, A.; Igau, A.; Jaud, J.; Majoral, J. P. *Organometallics* **1995**, *14*, 944−52.

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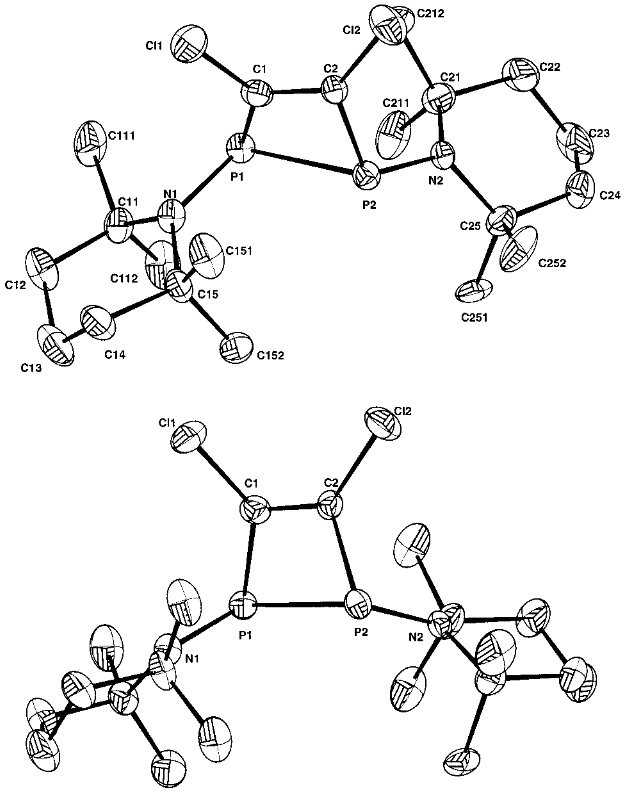

Figure 1. CAMERON diagram (at the 30% level, hydrogen atoms omitted for clarity) of **2a**.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 2a

	Distances		
P1−P2	2.324(4)	P1−C1	1.81(1)
P2−C2	1.80(1)	P1−N1	1.671(9)
P2−N2	1.687(8)	C1−C2	1.33(1)
Cl1−Cl	1.72(1)	Cl2−C2	1.70(1)
	Angles		
P2−P1−C1	72.2(4)	P1−C1−C2	104.1(8)
P1−P2−C2	73.1(4)	P2−C2−C1	103.2(8)
	Torsion Angles		
C1−P1−P2−C2	15.3	N1−P1−P2−N2	134.3
P1−C1−C2−P2	26.4	Cl1−C1−C2−Cl2	10.6

better yield. The NMR signals of the phosphorus atoms (**2a** δ = 19.7, **2b** δ = 29.4),[8] of the sp^2-hybridized framework carbon atoms (**2a** δ = 127.8, **2b** δ 118.6) and of the carbons and protons of the amino groups were clearly indicative of the high symmetry of the dihydrodiphosphetes **2a**,**b**. However as the spectra were not unequivocal with respect to the nature of the heterocycle formed,[9] the cyclic structure of compounds **2** has been fully established by a single-crystal X-ray analysis of **2a** (Figure 1, Table 1). The molecular geometry of **2a** is governed by its C_2 symmetry. The ClC═CCl unit is nearly planar (sum of bond angles around the two sp^2 carbons, 359.3° and 359.6°). The geometry of the C═C double bond is distorted as shown by the value of the Cl−C═C [127.5(9)°] and P−C═C [103.2(8)°] angles. The short C═C bond length [1.34(1) Å] is as expected for these structures (Table 2).[10] The geometry of the NP−PN subunit, which revealed a trans arrangement of the lone pair of the phosphorus atoms, is of much interest. A low pyramidalization of the nitrogen atom ($\sum N = 355°$) with a configuration corresponding to a "gauche" form was observed. The strain at phosphorus as measured by the P−P−C angle is more pronounced than those described in the literature for the other 1,2-dihydro-1,2-diphosphete structures.[10] More surprising is the stretched P−P bond length for **2a** of 2.320(4) Å, which is significantly longer than those already observed up to now in 1,2-dihydro-1,2-diphosphete structures.[10,11] As a consequence of all of these geometrical features, the cyclic system PCCP is a highly distorted nonplanar trapezoid (folding angle 28.8°).

The photoelectron spectrum of **2a**, reported in Figure 2a, shows the three first bands at 7.9, 8.5, and 9.5 eV. On going to He II, the relative intensity of the latter decreases. An *ab initio* calculation was carried out for the parent system $(H_2NPCH)_2$ **A** with the 6-31G(d,p)//MP2 level, to obtain information concerning the geometrical parameters and to support the PE spectral interpretation of **2a**. The slightly favored isomer is the one that has the phosphorus lone pairs in the trans position (ΔE = 16.8 kJ/mol). The calculated geometrical parameters for **A**, shown Figure 3, are in good agreement with the experimentally determined values. The cyclic system PCCP is a highly distorted nonplanar trapezoid, and a low pyramidalization of the nitrogen atom ($\sum N = 349°$) with a configuration corresponding to a "gauche" form was observed. This cycle can be viewed as two subunits, trans diphosphene and dichloroethylene, in interaction. One notable characteristic is the interaction between the $\pi_{C=C}$ double bond and the same symmetry phosphorus lone pair combination (n_P^-); this means that a π delocalization of the system takes place.

The stabilization of this system proceeds from the σ skeleton, and more particularly from the stabilizing antiperiplanar interactions between respectively the $\sigma_{CP}/\sigma^*_{CH(Cl)}$, $\sigma_{PP}/\sigma^*_{CH(Cl)}$, and $\sigma_{CP}/\sigma^*_{PH(NH)}$. It may be noted that if we compare these results with quantum chemical calculations on the model compounds $(HPCH)_2$ and $(HPCCl)_2$, substitution by an amino group introduces a supplementary interaction[12] between the nitrogen lone pair and the antibonding σ^*_{PP} orbital (49.68 kJ/mol according to NBO analysis[13,14]). Such negative hyperconjugation induces the P−P bond lengthening in

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[8] $^{31}P\{^1H\}$ NMR spectra of the crude mixture showed only one signal corresponding to compound **2a**. No phosphaalkyne $R_2NC{\equiv}P$ (δ $^{31}P\{^1H\}$ −103.7 ppm) was observed. Markovskii, L. N.; Koidan, G. N.; Marchenko, A. P.; Romanenko, V. D.; PovolotskiiI, M. I.; Pinchuk, A. M. *Zh. Obshch. Khim.* **1989**, *59*, 2133.

[9] Niecke, E.; Fuchs, A.; Baumeister, F.; Nieger, M.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 555−7.

[10] (a) Charrier, C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3−8. (b) Becker, G.; Becker, W.; Uhl, G. *Z. Anorg. Allg. Chem.* **1984**, *519*, 31−41. (c) Charrier, C.; Maigrot, N.; Mathey, F.; Robert, F.; Jeanin, Y. *Organometallics* **1986**, *5*, 623−30. (d) Philips, I. G.; Ball, R. G.; Cavell, R. G. *Inorg. Chem.* **1988**, *27*, 2269−75. (e) Maigrot, N.; Charrier, C.; Ricard, L.; F. Mathey, F. *Polyhedron* **1990**, *9*, 1363−7. (f) Binger, P.; Wettling, T.; Schneider, R.; Zurmühlen, F.; Bergsträsser, U.; Hoffmann, J.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 207. (g) Geissler, B.; Barth, S.; Bergsträsser, U.; Slany, M.; Durkin, J.; Hitchcock, P. B.; Hofmann, M.; Binger, P.; Nixon, J. F.; von R. Schleyer, P.; Regitz, M. *Ibid.* **1995**, *34*, 484−7. (h) Knoch, F.; Kummer, S.; Zenneck, U. *Synthesis* **1996**, 265−8.

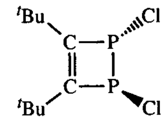
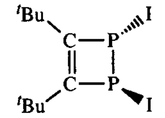
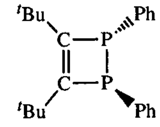
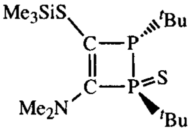
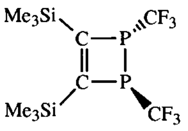
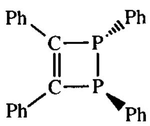
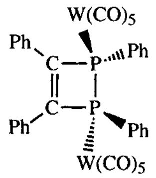
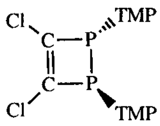
[11] The P−P bond lengths in bis(dialkylamino)diphosphines are 2.250 Å. For examples, see: Bender, H. R. G.; Niecke, E.; Nieger, M.; Westermann, H. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1194−202.

[12] The P−P bond lengths for model compounds $(HPCH)_2$ and $(HPCCl)_2$ are 2.236 and 2.235 Å, respectively.

[13] Foster, J. P.; Weinhold, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 7211−8. Reed, A. E.; Weinstock, R. B.; Weinhold, F. J. *J. Chem. Phys.* **1985**, *83*, 735−46. Reed, A. E.; Weinhold, F. J. *Ibid.* **1985**, *83*, 1736−40.

[14] Reed, A. E.; Curtiss, L. A.; Weinhold, F. J. *J. Chem. Rev.* **1988**, *88*, 899−926.

Table 2. Comparison of Selected Bond Lengths and Angles of 1,2-Dihydro-1,2-diphosphetes[a]

	bond lengths, Å			bond angles, deg		torsion angles, deg		folding angle, deg	work ref
	P—P	P—C endo	C=C	PPC endo	PCC endo	CPPC endo	PCCP endo	P1C1C2/ P1P2C2	
	2.189(2)	1.825(2)	1.363(3)	75.5	102.1	15.1	20.1	27.9	10h
	2.192(4)	1.827(6)	1.334(12)	75.5	102.1	13.0	21.0	23.6	10f
	2.214(4)	1.847	1.357(5)	76.2	102.8	8.0	13.0	14.5	10c
	2.219(1)	1.814	1.360(5)	76.25	103.6	3.0	5.0	5.5	10b
	2.223(1)	1.841(2)	1.356(3)	75.84	102.73	9.7	16.0	18.0	10d
	2.248(1)	1.830	1.358(4)	74.7	102.1	14	24	27.1	10a
	2.281(3)	1.841	1.360	76.0	104.0	1.0	1.0	1.0	10e
	2.320(4)	1.81(1)	1.34(1)	72.7	103.7	15.3	26.4	28.8	b

[a] 1,2-Dihydro-1,2-diphosphete structures with a trans arrangement of the phosphorus suibstituents are compared. [b] This work. TMP = 2,2,6,6-tetramethyl−piperidyl.

2a. Experiment shows a greater lengthening because of the steric factor.

The assignment of ionization potentials is supported by the ionic state descriptions (Koopmans' correlation $E^{v}{}_{i,n} = -\epsilon_j$). The corresponding orbital diagrams are shown in Table 3. The first band (7.9 eV) is attributed to the ejection of an electron of the antibonding combination between the phosphorus lone pairs ($n_P{}^+$) and the nitrogen ones, with a high localization on the piperidyl nitrogen. The second band (8.5 eV) is associated with the ionization of the MO delocalized on the $\pi_{C=C}$ bond and the combination $n_P{}^+$ phosphorus lone pairs. The third band at 9.5 eV arises from the ejection of an electron from the bonding combination of the nitrogen lone pairs and especially with the $n_P{}^+$ combination of the phosphorus lone pairs. This assignment of the experimental IP relies on the He I/He II intensity variation. The relative intensities of the second band

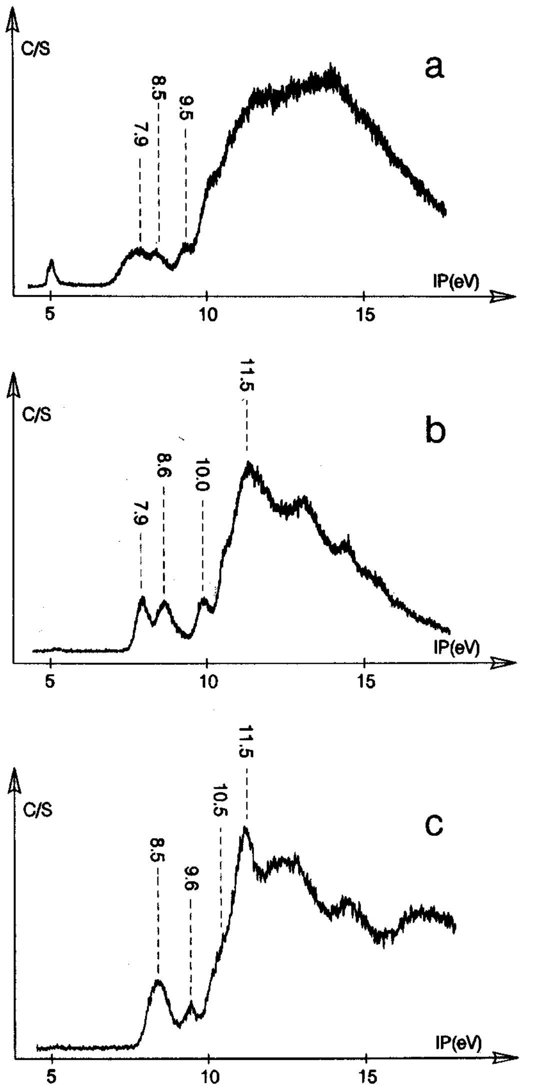


Figure 2. Photoelectron spectra of (a) **2a**, (b) **1a**, and (c) **3**.

and notably of the third band decrease. The next plateau concerns the σ skeleton followed by the chlorine ionization.

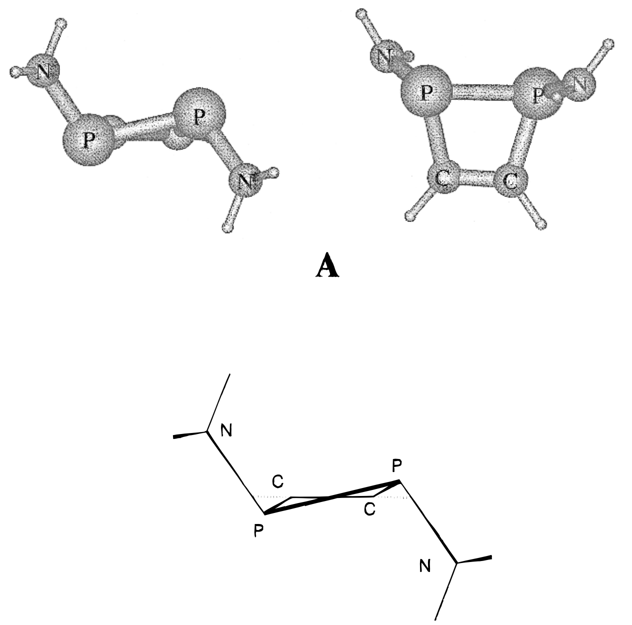


Figure 3. Calculated structure of $(H_2NPCCH)_2$ **A**. Selected bond lengths (Å) and angles (deg): P−P 2.258, C−P 1.819, C−C 1.334, P−N 1.697, C−P−P 74.7, P−C−C 103.7, N−P−P 110.5; torsion angle P−C−C−P 16.8.

Surprisingly no reaction was observed upon addition of $[Cp_2Zr]$ to **3** (Scheme 1). To interpret this lack of reactivity the photoelectron spectra of **1a** and **3** are recorded and are depicted respectively in panels b and c of Figure 2. In the spectrum of **3** the first broad band is observed at 8.5 eV followed by two bands at 9.6 and 11.5 eV with a shoulder at 10.5 eV. The analysis of these bands is carried out considering the effect of substituents. The rotation angle of the mesityl ring (72°)[15] induces a weak interaction with the π system and a more important one with the phosphorus lone pair. It is reasonable to think that the highest occupied molecular orbital is the antisymmetrical combination of the π_{aryl} with the phosphorus lone pair, followed nearly by the orbitals of the phenyl ring (typically 8.5 eV for the mesityl group). Thus the broad band centered at 8.5 eV arises from $(\pi_{aryl} - n_P)$ and π_{aryl} ionizations. Furthermore, with regard, on the one hand, to the destabilizing effect of the chlorine substitution at carbon on the phosphaethene (around 0.5 eV concerning, for example, the ionization of the orbital $\pi_{C=C}$ on passing from ethylene to vinyl dichloride)[16] and, on the other hand, to the inductive effect of the mesityl group, the second band at 9.6 eV could correspond to the ejection of an electron from the $\pi_{P=C}$ (in antibonding interaction with the chlorine lone pair) and the shoulder at 10.5 eV would be associated to the ionization of the orbital $(\pi_{aryl} + n_P)$. The following intense band at 11.5 eV is attributed to ionization of the chlorine lone pair. For compound **1**, taking into account the "gauche" orientation of the piperidyl groups, we expected three first bands at low ionization potentials. The first of them is associated with the antisymmetric combination of the phosphorus−nitrogen lone pairs (7.9 eV). The band corresponding to the π_{PC} ionization should occur at lower potential than in the compound **3** as a result of the inductive effect of the piperidyl substituent. The signal at 8.6 eV is consistent with the latter observation. Finally, the band at 10.0 eV is related to the ionization of the $(n_N + n_P)$ orbital. The comparable steric hindrance between compounds **1** and **3** implies that the reaction is ruled by molecular orbital interactions. If we suppose that a π complex forms at the first step (π_{PC} MO interacting with the $2a_1$ orbital of the metallocene $[Cp_2Zr]$ fragment[17] to form **I**), this interaction will take place better with compound **1** [IP(π_{PC}) = 8.6 eV] than **3** [IP(π_{PC}) = 9.6 eV]. Then it is reasonable to postulate that the reaction proceeds by way of an oxidative addition of the metal fragment across a C−Cl bond[18,19] to give a (phosphaalkenyl)zirconia species **II**,[20] which

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[15] Van der Knaap, Th. A.; Klebach, Th. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* **1984**, *40*, 765−76.

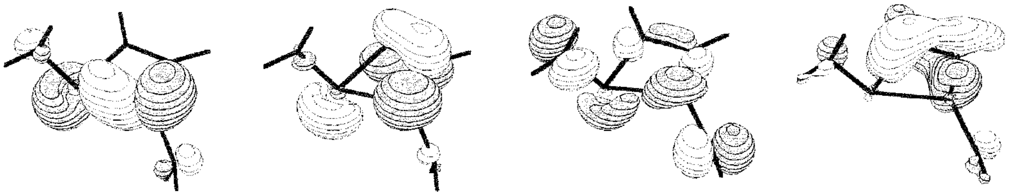
[16] Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazuki, T.; Iwata, S. *Handbook of He I photoelectron spectra of fundamental organic molecules*; Japan Scientific Societies Press, Halsted Press: New York, 1981.

[17] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−42.

[18] Jun, H.; Angelici, R. J. *Organometallics* **1993**, *12*, 4265−6 and references therein.

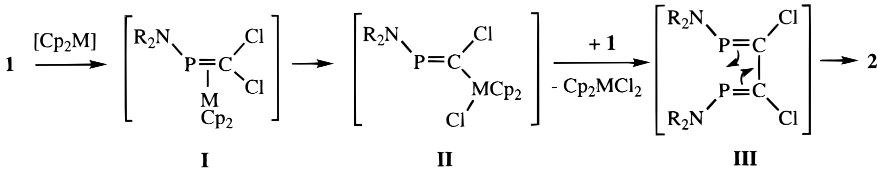
[19] Le Floch, P.; Kolb, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2065−6.

Table 3. Orbital Diagram and Ionization Potentials (IP) of System A Calculated with the 6-31G(d,p) Basis Set, Koopmans' Approximation



	$n_P^+ - n_N$	$\pi_{C=C} - n_P^-$	$n_P^+ + n_N$	$\pi_{C=C} + n_P^-$
IP Koopmans (eV)	- 8.41	- 9.15	- 10.27	- 10.86

Scheme 2. Proposed Reaction Mechanism for the Synthesis of 2



reacts further with a second equivalent of **1** to give after elimination of [Cp_2MCl_2] (M = Ti, Zr) the 1,4-diphosphabutadiene **III**, which rearranges via cyclization to the more thermodynamically stable diphosphete **2** (Scheme 2).[21]

Investigations on the reactivity of **2** are in progress. The [Cp_2M] (M = Ti, Zr) mediated coupling reaction of C−X (X = Cl, Br, I) unsaturated derivatives for the synthesis of functionalized heterocycles will be extended to other dihalo-heteroalkene derivatives.

Experimental Section

All manipulations were carried out under an argon atmosphere, either on a high-vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, diethyl ether), lithium aluminum hydride (pentane), or CaH_2 (CH_2Cl_2). C_6D_6, CD_2Cl_2, and $CDCl_3$ were treated respectively with $LiAlH_4$ and CaH_2, distilled, and stored under argon. Cp_2ZrCl_2 and Cp_2TiCl_2 were purchased from Aldrich and used without further purification. [Cp_2ZrBu_2],[22] [$Cp_2Ti(CO)_2$],[23] 2,4,6-*t*-$Bu_3C_6H_2P{=}CCl_2$,[24] (TMP) $P{=}CCl_2$,[25] and $(Me_3Si)_2NP{=}CCl_2$[24] were prepared according to literature procedure.

Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker AMX 400, WM-250, and AC-80 Fourier transform spectrometers. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants (*J*) are given in hertz. The ^{13}C NMR assignments were confirmed by proton-decoupled and/or selective heteronuclear-decoupled spectra. Chemical analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. Mass spectra were obtained on a Nermag R10-10H. Melting points were determined in evacuated capillaries and were corrected and calibrated.

Preparation of ($R_2NPCCl)_2$ (2) from [$Cp_2Ti(CO)_2$]. A dry sealable Schlenk tube with a stirring bar was charged with [$Cp_2Ti(CO)_2$] (0.234 g, 1.0 mmol) in a glovebox. The flask was removed from the glovebox and attached to a Schlenk line. A solution of phosphaalkenes **2a,b** (2.0 mmol) in 10 mL of toulene was added *via* syringe. The flask was sealed and heated in an oil bath at 35 °C for 24 h. After the reaction mixture was allowed to cool to room temperature, the volatiles were removed *in vacuo*. The crude product was extracted with pentane (3 × 15 mL). Column chromatography over silica 60 with toluene as eluant resulted in the product **2** in 25% isolated yield.

Preparation of ($R_2NPCCl)_2$ (2) from [Cp_2ZrBu_2]. To a solution of dichlorozirconocene [Cp_2ZrCl_2] (0.584 g, 2.0 mmol) in THF (5 mL) at −78 °C, was added BuLi in hexane (2.5 mL, 1.6 M). The mixture was stirred for 2 h at −78 °C, and then **1a**,**b** (4.0 mmol) in THF (5 mL) was added via cannula. The reaction mixture was warmed slowly to room temperature and stirred for a further 3 h. After removal of the solvent, **2a**,**b** was extracted from the resulting residue with 50 mL of pentane and isolated after flash chromatography in 35% yield.

[(TMP)PCCl]$_2$ (2a): $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 19.7 ppm; ^1H NMR ($CDCl_3$) δ 1.56 (m, 12H, CH_2), 1.31 (s, 24H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 127.8 (pseudo-t, $|^1J_{CP}| = |^2J_{CP}| = 6.4$ Hz, PC=), 41.6 (s, CN), 31.0 (s, CH_3), 29.6 (s, CH_2), 17.1 (s, CH_2). Anal. Calcd for $C_{20}H_{36}Cl_2N_2P_2$: C, 55.10; H, 8.32. Found: C, 54.89; H, 8.56. MS (DCI/CH_4): *m/z* 437 $[M + 1]^+$.

[($Me_3Si)_2NPCCl]_2$ (2b): $^{31}P\{^1H\}$ NMR (C_6D_6) δ 29.4 ppm; ^1H NMR (C_6D_6) δ 0.26 (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 118.6 (pseudo-t, $|^1J_{CP}| = |^2J_{CP}| = 5.4$ Hz, PC=), 1.4 (s, $SiMe_3$). Anal. Calcd for $C_{14}H_{36}Cl_2N_2P_2Si_4$: C, 35.33; H, 7.62. Found: C, 35.02; H, 7.85. MS (EI): *m/z* 476 [M^+].

Photoelectron Spectral Measurements. The photoelectron spectra were recorded on a Helectros 0078 spectrometer using 21.21 eV He I radiation photon sources and connected to a microcomputer system supplemented by a digital analogic converter. Helium and nitrogen ionizations, respectively at 4.98 and 15.59 eV, were used as references.

Computational Details. *Ab initio* calculations were performed with the Gaussian-92 quantum chemistry package.[26] The geometry and frequency are optimized at 6-31G(d,p)[27] and

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(20) For the reactivity of (phosphaalkenyl)metal species see, for example: Van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174−80 and references therein.

(21) 1,2-Dihydro-1,2-diphosphetes have been calculated to be the thermodynamically favored structures for $P_2C_2R_4$ derivatives in general. Barach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040−7 and ref 9.

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subsequently calculated with regard to the electron correlation at the MP2 level.

X-ray Data Collection, Structure Determination, and Refinement for [(TMP)PCCl]$_2$ (2a). **2a** was recrystallized from benzene to produce colorless crystals. A selected crystal (crystal dimension 0.40 × 0.35 × 0.50 mm) was mounted on an Enraf-Nonius CAD4 automatic diffractometer. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinement of the setting angles of 25 well-centered reflections. Three standard reflections were monitored periodically; they showed no change during data collection carried out at room temperature. Selected crystallographic data, data collection parameters, and refinement parameters are given in Table 4. Corrections were made for Lorentz polarization effects, and absorption corrections DIFABS[28] were applied on the data. Computations were performed by using the program CRYSTAL[29] adapted on a PC. Atomic factors for neutral atoms C, Cl, N, H were taken from ref 30. The structure was solved by direct methods using the program SHELXS86.[31] The hydrogen atoms attached to the C atoms were located on a difference Fourier map, but their coordinates were introduced in the process of refinement as fixed contributors (C−H = 0.98 Å) and recalculated after each cycle. They were assigned isotropic thermal parameters 20% higher than those of the carbon to which they were attached. All non-hydrogen atoms were anisotropically refined; full matrix least-squares refinements were carried out by minimizing the function $\sum w(||F_o| - |F_c||)^2$, where F_o and F_c are the observed and calculated structure factors. The model reached convergence with the formula $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ having values listed in Table 4.[32]

Table 4. Crystal Data, Data Collection, and Refinement Parameters for 2a

mol formula	$C_{20}H_{36}Cl_2N_2P_2$
mol wt	437.37
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	14.649(2)
b, Å	14.668(4)
c, Å	11.091(2)
Z	4
V, Å^3	2383(1)
ρ_{calcd}, g cm^{-3}	1.22
μ(Mo Kα), cm^{-1}	4.12
T, K	293
F(000), electrons	936
scan type	$\pi/2\theta$
scan range θ, deg	$0.9 + 0.35 \tan \theta$
no. of reflns collected	3706 ($\pm h,k,l$)
no. of rflns merged	3291 (0.043)
no. of reflns used ($I > 3\sigma(I)$)	1434
no. of variables	237
R, R_w[a]	0.038, 0.045

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Supporting Information Available: CAMERON diagrams and tables of crystal data, atomic coordinates and thermal parameters, interatomic distances, and bond angles (9 pages). Ordering information is given on any current masthead page.

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