Synthesis and Characterization of Primary Cyclopentadienylphosphines and Cyclopentadienylarsines

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Primary cyclopentadienylphosphines and cyclopentadienylarsines have been prepared by reduction of the corresponding dichloro derivatives and characterized by NMR and photoelectron spectroscopy and mass spectrometry. Their fluxional behavior has been established by both low-temperature NMR experiments and theoretical (DFT) calculations. The structure and the possible pathways to the circumambulatory rearrangement have been determined by quantum chemical computations. The high rate of the 1,2-rearrangement which favors retention of configuration at the migrating atom is explained by a low barrier due to the aromaticity of the transition states. The NMR and photoelectron spectra were assigned by making use of HF-GIAO and OVGF computations, respectively. The observed splitting of the photoelectron bands, compared to those of cyclopentadiene and EX_3 (E = P, As; X = H, Cl), was attributed to a hyperconjugative interaction between the cyclopentadienyl ring and the carbon−element bond.

Introduction

The cyclopentadienyl group has been attracting increased interest in various areas of chemistry. Although transition metal complexes with cyclopentadienyl ligands are the most studied derivatives, numerous compounds with a cyclopentadienyl substituent connected with a σ bond to a heteroatom of the main group have also been prepared. Extensive theoretical studies have been devoted to the π-facial selectivity in Diels−Alder reactions of dienophiles with such cyclopentadienes.[1,2] These compounds are of particular interest because of the properties due to the association of a cyclopentadienyl ring with a heteroatom on the allylic carbon. The circumambulatory rearrangement easily observed by NMR spectroscopy for numerous derivatives leads to signals at chemical shifts dependent on the temperature and the nature of the substituents.[3] Numerous experimental studies and theoretical calculations have been reported on silicon,[4−6] germanium,[6,7] phosphorus,[8,9] or arsenic derivatives.[10,11]

However, for the simplest compounds bearing one or more hydrogen atoms on the heteroatom (Scheme 1), only the cyclopentadienylsilane **1**[4] and the cyclopentadienylgermane **2**[7] have been synthesized. Since 1973, no other unsubstituted compound has been isolated and only derivatives stabilized by the presence of various substituents on the cycle or/and on the heteroatom have been prepared.[2,8,10−12]

Recently, some of us have reported the first synthesis of a variety of simple α,β- and β,γ-unsaturated compounds using a particular experimental procedure.[13,14]

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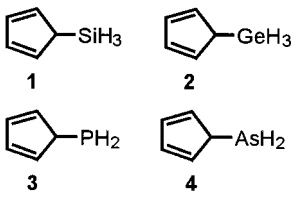
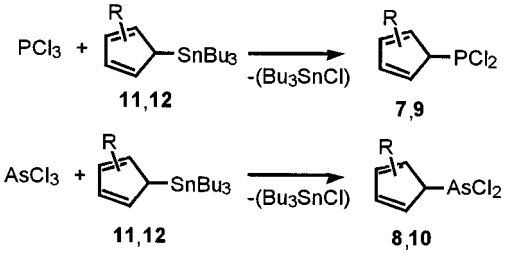
Scheme 1



Scheme 2



We report here the preparation and spectroscopic characterization of the cyclopentadienylphosphine **3** and arsine **4** and the methylcyclopentadienylphosphine **5** and arsine **6**. The correlation between the nature of the heteroatom (P, As), its substituents (H, Cl), and the rate of migration is clearly evidenced. Phosphine **3**, arsine **4**, and the corresponding dichloro derivatives were also investigated by photoelectron spectroscopy. We also analyzed the NMR and photoelectron spectra by making use of HF-GIAO and OVGF computations, respectively.

Results and Discussion

Cyclopentadienyldichlorophosphines and Arsines. The cyclopentadienyldichlorophosphine **7**[15] and arsine **8**[10] and methylcyclopentadienyldichlorophosphine **9** and arsine **10**[11] were easily prepared by the reaction of the corresponding cyclopentadienyltributylstannanes **11** and **12**[16] with PCl_3 and $AsCl_3$, respectively (Scheme 2), and purified by distillation in vacuo. Compounds **7**−**10** were kept at −40 °C under dry nitrogen.

The ^{1}H NMR spectrum of phosphine **7** exhibits at room temperature three signals which can be attributed to the hydrogens on the sp^2 or sp^3 carbons of the cyclopentadienyl ring. Similarly, the three signals observed in the ^{13}C NMR spectrum correspond to these carbon atoms (Figure 1). A faster circumambulatory rearrangement at the NMR time scale for the arsine **8** leads to the observation of only one signal in the ^{1}H and ^{13}C NMR spectra recorded at room temperature. At low temperature (178 K), the signals of the sp^2 and sp^3 carbons and their corresponding hydrogens are easily differentiated (Figure 2). Similarly, on heating at 363 K, only one signal is observed by ^{1}H NMR spectroscopy for phosphine **7**, which exhibits a very low stability at this temperature.

For the methylcyclopentadienyl derivatives **9** and **10**, three isomers, α−γ, can be drawn for each compound (Scheme 3). Five and six signals are observed in the ^{1}H and ^{13}C NMR spectra respectively of phosphine **9**. The ^{1}H and ^{13}C NMR spectra of methylcyclopentadienyldichloroarsine **10** recorded at room temperature show three and four signals, respectively. On the other hand, arsine **10** cooled at 178 K presents NMR spectra similar to the ones of phosphine **9**. The spectra recorded at 178 K for **10** and at room temperature for **9** are consistent with the structure of only one compound, tentatively attributed to isomer γ.

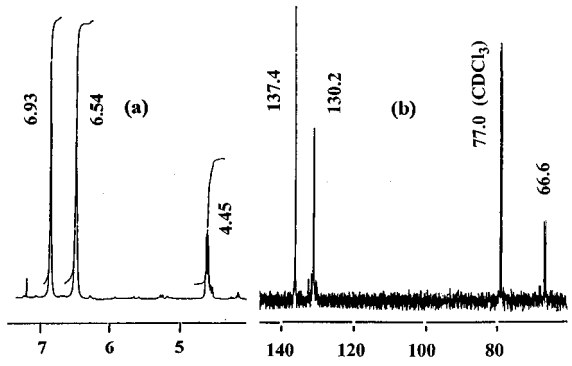


Figure 1. ^{1}H (a) and ^{13}C NMR (b) spectra of **7** at 293 K.

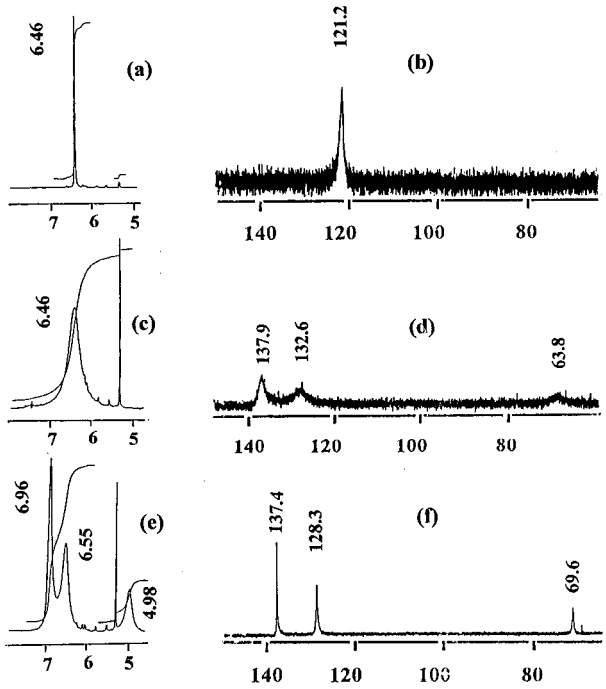
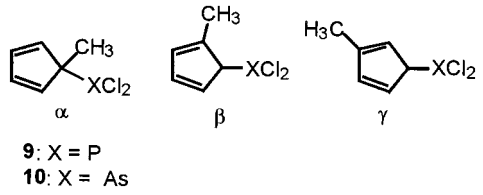


Figure 2. ^{1}H and ^{13}C NMR spectra of **8** 293 K (a, b), 203 K (c, d), and 178 K (e, f).

Scheme 3



Primary Cyclopentadienylphosphines and Arsines. The reduction of cyclopentadienyldichlorophosphine **7** to cyclopentadienylphosphine **3** was performed with lithium aluminum hydride (LAH) in tetraglyme in a 52% yield (Scheme 4). Cyclopentadienylarsine **4** was obtained in pure form in 77% yield starting from arsine

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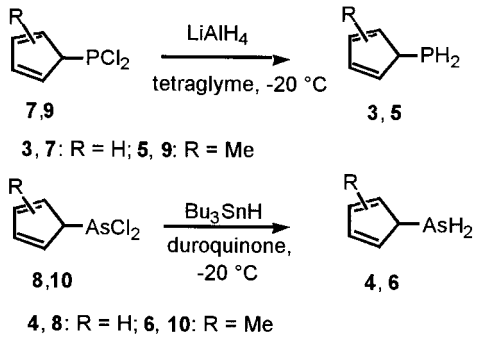
Scheme 4



8 and Bu_3SnH as reducing agent. LAH can also be used, but the yield is only 17%. To limit its decomposition, phosphine **3** and arsine **4** were distilled off in vacuo (10^{-1} mbar) from the cooled reaction mixture (−10 °C) during the course of the addition of **7** or **8** and separated from the less volatile products by a cold trap (−40 °C) before condensation at −75 °C. The condensation/revaporization of arsine **4** led to an important loss of product.

The phosphine **3** was characterized by ^{31}P NMR spectroscopy, and the signal at −135.3 ppm ($^1J_{PH}$ = 190.2 Hz (t)) is characteristic of a primary phosphine. The presence of phosphine **3** and arsine **4** was confirmed by the observation of the corresponding molecular ion by high-resolution mass spectrometry (HRMS). The ^1H and ^{13}C NMR spectra of **3** recorded at room temperature are similar to that of **4**. By comparison with the chloroarsine **8**, the presence of two hydrogen atoms on the arsenic atom of **4** decreases the rate of the circumambulatory rearrangement at the NMR time scale so that the coalescence of the signals was not observed.

The reduction of phosphine **9** led to methylcyclopentadienylphosphine **5**. The signal observed by ^{31}P NMR spectroscopy at −128.7 ppm was tentatively attributed to (3-methyl-2,4-cyclopentadienyl)phosphine, the isomer **5**γ. The two hydrogens on the phosphorus atom being diastereotopic, the signals are those of an AB system. After a few hours at room temperature, another isomer was observed. On the basis of ^{31}P, ^1H, and ^{13}C NMR spectra, the signals were tentatively attributed to (2-methyl-2,4-cyclopentadienyl)phosphine **5**β. An AB system was also observed for the two hydrogens on the phosphorus atom. At the end, a 1:1 ratio of the two isomers **5**β and **5**γ was obtained. The isomer **5**α has never been detected. It should be noted that the synthesis of methylcyclopentadienylsilane[4,6] and germane[7] led to mixtures of isomers β and γ even when the reaction of the cyclopentadienyl anion with the silicium or germanium halide was performed at low temperature (−78 °C). The formation of only one isomer in our approach with phosphine **5** could be attributed to the mild basic conditions and the short time the product remains in the reaction mixture.

The reduction of arsine **10** in the methylcyclopentadienylarsine **6** was only efficient using a very short vacuum line and without condensation/revaporization of the product or selective removing of the high-boiling compounds in a cold trap. The crude product was obtained in a 32% yield and in about 43% purity in the presence of methylcyclopentadienes and traces of tributyl tin derivatives. The low-temperature (−40 °C) ^1H and ^{13}C NMR spectra unambiguously show the presence of the two isomers β and γ in a 1:1 ratio. An AB system was observed for each group of the two hydrogens on the arsenic atom. It is not possible to conclude if both isomers were formed as products in the reduction of **10** or only one isomer is produced and quickly rearranged at low temperature.

Cyclopentadienylphosphines **3** and **5** diluted in $CDCl_3$ can indefinitely be kept at −40 °C but exhibited low stability at room temperature ($\tau_{1/2}$: 5 h) to give insoluble brown materials. In pure form, the half-life of phosphine **3** is about 7 h at −78 °C. At room temperature, cyclopentadienylarsines **4** and **6** diluted in $CDCl_3$ ($\tau_{1/2}$: 30 min) gave the corresponding cyclopentadiene in a nearly quantitative yield and insoluble orange-brown containing arsenic compounds.

Calculations

Quantum chemical calculations were performed for the cyclopentadienylphosphines **3** and **7** and arsines **4** and **8** by the Gaussian 98 program package.[17] All structures were optimized at the B3LYP/6-311+G(d,p) level of theory, and stationary points were characterized by second derivative calculations using the same model chemistry. ZPE (zero-point vibrational energy) corrections to the relative energies were computed at the same level. The energy difference of conformers of $CpPH_2$ and $CpAsH_2$ was found to be small and comparable to computational error. Therefore, CCSD(T)/6-311+G(d,p)//B3LYP/6-311+G(d,p) calculations have also been performed for these structures.

Experimental ionization energies (IPs) were compared to those calculated at the ROVGF/6-311+G(d,p) level of theory, on the geometries obtained above. Molecular orbital considerations were made using the Kohn−Sham orbitals and are referred to as molecular orbitals (MOs) in this work. ^1H NMR and ^{13}C NMR chemical shifts were computed at the HF-GIAO/6-311+G(d,p) level on the same geometry and compared to the experimental values. The chemical shifts are given using tetramethylsilane as reference.

For the study of aromaticity of the $CpEX_2$ species, NICS (nucleus independent chemical shift) values were computed using the same method as for the chemical shifts.[18]

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(18) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318. The NICS is the *negative* of the computed chemical shielding at the center of a ring and corresponds to no nuclei: therefore "nucleus independent". Negative NICS values indicate aromaticity, positive values antiaromaticity. Since the σ skeleton of the ring has a strong anisotropic effect on the chemical shielding at the ring center, it is worth computing NICS also at 1 Å above the center where this σ effect is found to be negligible. These values—as well as chemical shifts—are reported in ppm units.

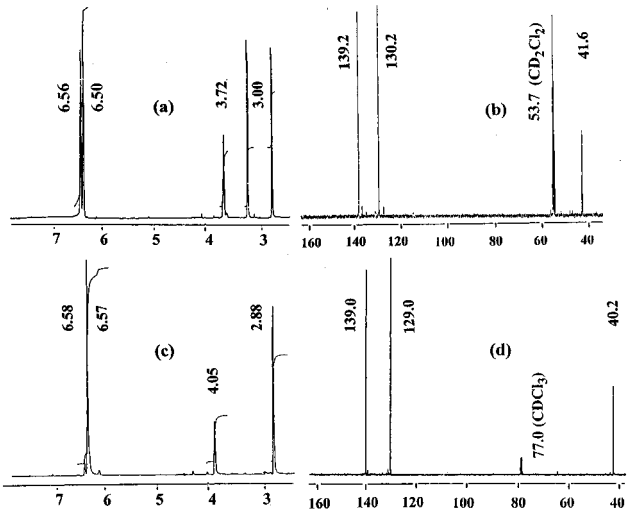

Figure 3. ^{1}H and ^{13}C NMR spectra of 3 (a, b) and 4 (c, d) at 253 K.

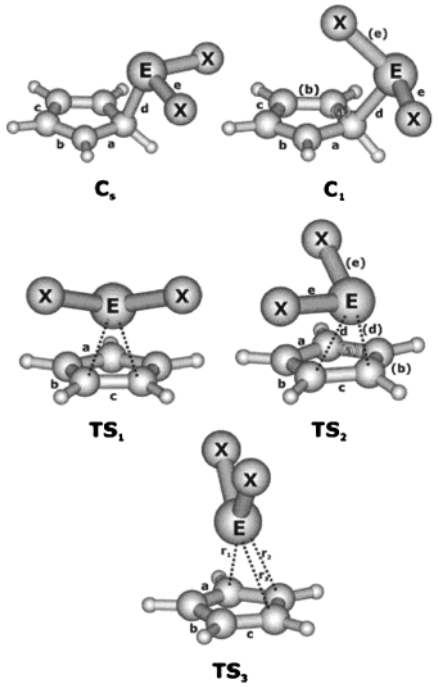

Figure 4. Stable structures and transition states of $CpEX_2$ derivatives as shown by the MOLDEN program.[21]

Table 1. Selected Structural Parameters[a] of the Most Stable Conformer of $CpEX_2$ Derivatives

species	symm	*a*	*b*	*c*	*d*	*e*
CpH	C_{2v}	1.505	1.348	1.468	1.099[b]	
$CpPH_2$	C_1	1.499 (1.504)	1.350	1.465	1.901	1.426
			(1.349)			(1.423)
$CpPCl_2$	C_s	1.501	1.352	1.461	1.880	2.122
$CpAsH_2$	C_s	1.493	1.353	1.460	2.044	1.531
$CpAsCl_2$	C_s	1.489	1.359	1.455	2.028	2.243

[a] Bond lengths in angstroms, according to the notations of Figure 4. [b] Methylene C−H bond length.

Structure of the $CpEX_2$ Species. Cyclopentadienyl phosphines **3** and **7** and arsines **4** and **8** (Figure 4, Table 1) have two stable conformations, a symmetric (C_s) and a nonsymmetric (C_1) one. The cyclopentadienyl group is practically planar. The bond lengths and bond alternations change systematically (decrease from CpH to $CpAsCl_2$) along with the Lewis acidity of the EX_2 group.

Table 2. Selected Geometrical Data[a] of the TS_1 Transitional Structures of $CpEX_2$

species	*a*	*b*	*c*	*d*	*e*
CpH	1.401	1.409	1.489	1.314	
$CpPH_2$	1.402	1.409	1.476	2.221	1.434
$CpPCl_2$	1.404	1.413	1.463	2.182	2.168
$CpAsH_2$	1.404	1.407	1.477	2.346	1.540
$CpAsCl_2$	1.406	1.413	1.463	2.295	2.278

[a] All bond lengths are given in angstroms, according to the denotations of Figure 4.

Table 3. Selected Geometrical Data[a] of TS_2 Transitional Structures of $CpEX_2$

species	*a*	*b*	*c*	*d*	*e*
$CpPH_2$	1.404	1.405	1.479	2.303	1.431
	(1.404)	(1.408)		(2.229)	(1.416)
$CpPCl_2$	1.408	1.396	1.476	2.385	2.162
	(1.404)	(1.407)		(2.233)	(2.073)
$CpAsH_2$	1.406	1.402	1.480	2.432	1.537
	(1.404)	(1.407)		(2.354)	(1.519)
$CpAsCl_2$	1.408	1.396	1.477	2.478	2.278
	(1.404)	(1.408)		(2.327)	(2.200)

[a] All bond lengths are given in angstroms, according to the denotations of Figure 4.

The alternation is significant even in $CpAsCl_2$, suggesting the absence of cyclic electron delocalization. The P−C and As−C bond lengths are slightly elongated compared to those of $MePH_2$ and $MeAsH_2$ (1.872 and 1.997 Å, respectively, at the same level of theory); the chlorination shortens this bond and reduces the alternation. In both C_s and C_1, the group V heteroatom is situated in the mirror (or quasi-mirror) plane of the molecule perpendicular to the ring. In the C_1 minimum, one of the E−X bonds is roughly tangential to the ring perimeter, and the other bonds are above the ring.

Two transition structures, TS_1 (C_s symmetric) and TS_2 (nonsymmetric), have been found for the 1,2-sigmatropic migration of the EX_2 group (Tables 2 and 3). TS_1 connects two C_s minima, and TS_2 connects two C_1 minima. In the transition structures, the ring is practically planar and the heteroatom E is situated above the reacting C−C bond. The bond lengths in the ring are almost equal; their differences are again smaller in the halogenated derivatives than in the parent phosphine and arsine. Also, the C−E bond shortens on chlorination.

On the basis of semiempirical calculations, Schoeller has suggested[9] two mechanisms for the 1,2-migration of $CpPH_2$ and $CpPCl_2$, one with retention and one with inversion of the phosphorus center, and claimed that $CpPCl_2$ would prefer the reaction path via inversion. TS_1 and TS_2 structures calculated in our work correspond to the first mechanism type. We have found, however, that for the 1,2-shift there is no reaction path corresponding to the inversion, and the "inversion structures" suggested earlier are characterized by two or three imaginary frequencies at the DFT level of theory.

An additional transition state, TS_3, has also been located on the potential surface (Table 4, Figure 4). In TS_3, the EX_2 fragment is situated almost symmetrically above the ring, with the P (As) atom being almost equally close to each C atom of the practically planar ring. The structure of this transition state is similar to that found by Schoeller[9] for the "inversion" type mechanism, but it realizes a new type of rearrangement.

Table 4. Selected Geometrical Data[a] of TS_3 Transitional Structures of $CpEX_2$

species	*a*	*b*	*c*	*d*	*e*	r_1	r_2	r_3
$CpPH_2$	1.400	1.467	1.361	1.457	1.430	2.762	2.778	2.992
$CpPCl_2$	1.408	1.446	1.383	2.172	2.151	2.545	2.533	2.638
$CpAsH_2$	1.401	1.464	1.364	1.571	1.538	1.283	1.834	3.035
$CpAsCl_2$	1.411	1.443	1.388	2.294	2.277	2.595	2.585	2.668

[a] All bond lengths are given in angstroms, according to the denotations of Figure 4.

Table 5. ZPE-Corrected Relative Energies, E_{rel}, and Gibbs Free Energies,[a] G_{rel}, for the Investigated Structures of the $CpEX_2$ Species

		structure				
species		C_s	C_1	TS_1	TS_2	TS_3
$CpPH_2$	E_{rel}	0.3	0.0	20.8	23.6	54.6
	G_{rel}	0.2	0.0	21.2	24.0	48.7
$CpPCl_2$	E_{rel}	0.0	2.4	16.4	24.4	28.7
	G_{rel}	0.0	2.5	16.9	24.7	28.1
$CpAsH_2$	E_{rel}	0.0	0.3	15.2	18.4	40.8
	G_{rel}	0.0	0.4	15.7	18.9	40.2
$CpAsCl_2$	E_{rel}	0.0	3.5	9.4	18.5	18.8
	G_{rel}	0.0	3.5	10.2	18.9	18.4

[a] E_{rel} and G_{rel} are given in kcal/mol; G_{rel} is computed for 298 K and 1 bar in the gaseous phase.

Intrinsic reaction coordinate (IRC) calculations prove that this is a transition state of a 1,3-migration between two C_s structures.

Thermodynamic properties of the $CpEX_2$ species are compiled in Table 5. With the sole exception of $CpPH_2$, the C_s structure is more stable than the C_1. The energy difference for the hydrogenated species, however, falls in the range of computational error. Coupled cluster calculations change this energy difference only a little, from 0.3 to 0.4, and from 0.3 to 0.06 kcal/mol for $CpPH_2$ and $CpAsH_2$, respectively. The rotation of the EX_2 group around the C−E bond is characterized by two transition structures. The barriers for the phosphines were found to be practically the same as for the arsines but dependent on X: ca. 2 and 3 kcal/mol for X = H, while 7 and 10 kcal/mol for X = Cl was obtained, respectively. This is in accordance with a fast rotation of the EX_2 group and the coalescence of the EH_2 proton signals observed in the NMR experiments.

Since the minima have equal stability (and can interconvert via a low barrier) and TS_1 is significantly lower in energy than TS_2, the sigmatropic rearrangement prefers the reaction path via the symmetric TS_1. The order of the barriers ($\Delta G^{\ddagger}$) for the rearrangement is the following: $CpPH_2$ (21.0) > $CpPCl_2$ (16.9) > $CpAsH_2$ (15.7) > $CpAsCl_2$ (10.2 kcal/mol). This agrees with the critical temperature ordering of the coalescence of the ring proton signals in the NMR spectra of these compounds. We should note that this barrier for $CpAsCl_2$ is only 3.3 kcal/mol higher than that of the rotation of the $AsCl_2$ group; that is, the $AsCl_2$ group performs a complex and rapid rotational−migrational motion even at room temperature. The barrier height of the circumambulatory rearrangement is in straight correlation with the Lewis acidity of the substituents.

Due to the high energy content of TS_3, the significance of the 1,3-sigmatropic shift may only be assumed at higher temperatures, and only in the case of $CpAsCl_2$, for which the barrier height is practically equal to that of the nonsymmetric 1,2-shift. Nevertheless the activation energy via TS_1 is still about half.

Spectroscopic Properties of the $CpEX_2$ Species

Magnetic Properties. Chemical shifts have been determined both experimentally and theoretically (Table 6). Also, magnetic properties have been used to evaluate the aromaticity of the minima and the transition states (Table 7).

The theoretical chemical shifts show tendencies similar to the experimental ones, but the computed ^{1}H NMR and ^{13}C NMR data differ from the observations by about 0.2−0.7 and 0.2−14 ppm, respectively. This is comparable, for most of them, to the change in the experimental shifts on changing the solvent. From both the experimental and the calculated results the same conclusion can be drawn. Comparing the ^{1}H NMR data of the $CpEX_2$ systems to those of the nonaromatic cyclopentadiene, only a small paramagnetic shift can be observed toward the proton chemical shift of benzene (7.3 and 7.5 ppm experimentally and computationally, respectively). For $CpPH_2$, only one EH_2 proton signal (3.00 ppm) was recorded, whereas theory gives two different chemical shifts (3.42 and 2.63 ppm, respectively).[19] This is due to an important difference between the experiments and the computations: while the experiments record an average chemical shift, calculations handle a single conformation where the two protons have different chemical environments. For $CpAsH_2$, which has two equivalent protons on the arsenic atom, both methods give one signal. They can, however, not directly be compared, since the equality is a result of the *time-averaging* (by the rotation of the AsH_2 group) in the experiment, whereas it is a result of the *symmetry* in the computations (2.88 and 4.02 ppm, respectively).

Although the ^{13}C NMR chemical shifts are not as characteristic of aromaticity as ^{1}H NMR shifts are, computed and experimental values are presented for a comparison in Table 6. On the other hand, nucleus-independent chemical shift (NICS) is developed to characterize cyclic electron delocalization. NICS values for the minimum structures and transition states (TS_1) of the $CpEX_2$ derivatives are compiled in Table 7. The small negative $NICS_1$ values (−4 to −5 ppm) obtained for the $CpEX_2$ molecules indicate their nonaromatic character. In contrast, the $NICS_1$ values of about −8 to −10 ppm for the transition structures suggest that the 1,2-sigmatropic shift proceeds via an aromatic structure. The aromaticity of the TS_1 structure of $CpPH_2$ is less aromatic than the other three TS_1 structures, and all of them are as aromatic as the cyclopentadienyl anion (Cp^-, $NICS_0 = -13.9$, $NICS_1 = -10.2$). The more Lewis acidic substituents exhibit higher aromaticity. This indicates a strong correlation of acidity, the rate of the rearrangement, and the aromaticity of the transition state.

Photoelectron Spectroscopy. Ionization energies, as recorded by means of photoelectron spectroscopy and computed at the ROVGF/6-311+G(d,p)//B3LYP/6-311+G-

(19) The ^{1}H NMR spectra of phosphine **3** and arsine **4** have been recorded at various temperature between 158 and 293 K using a 1:1 ratio of CD_2Cl_2 and CCl_3F as solvent. Only one signal has been observed for the two hydrogens on the heteroatom.

Table 6. Experimental[a] and HF-GIAO/6-311+G(d,p) Theoretical[b] Chemical Shifts for the Ring Protons and Carbons of $CpEX_2$ Species

	H_α		H_β		H_γ		C (sp^3)		C_β (sp^2)		C_γ (sp^2)	
species	expt	calc	expt	calc	expt	calc	expt	calc	expt	calc	expt	calc
CpH	3.10	2.93	6.59	6.80	6.71	6.82	41.4	39.7	132.9	143.0	132.2	140.4
$CpPH_2$	3.72	3.08	6.56	6.95	6.50	6.67	41.6	41.9	139.2	153.3	130.2	136.5
$CpPCl_2$	4.62	3.99	6.55	6.81	6.93	7.14	67.2	61.9	130.7	140.2	138.0	146.7
$CpAsH_2$	4.05	3.99	6.57	6.80	6.58	6.92	40.2	40.4	139.0	146.1	129.0	129.3
$CpAsCl_2$[c]	4.98	4.25	6.55	6.89	6.96	7.18	69.6	65.5	128.3	138.7	137.4	145.4

[a] In $CDCl_3$ at 20 °C. [b] At the B3LYP/6-311+G(d,p) geometry (all data are given in ppm; reference is TMS with chemical shieldings $\chi_H = 32.22$ ppm and $\chi_C = 194.56$ ppm, calculated at the same level of theory. [c] Experimental data in this row are obtained at −95 °C; at room temperature the proton signals melt together at 6.46 ppm, the carbon signals at 121.2 ppm.

Table 7. Computed NICS Values for the Minimum Structures and Transition States of the $CpEX_2$ Species (in ppm)

	minimum (C_s) conformer		TS of the migration (C_s or C_1)	
species	$NICS_0$	$NICS_1$[a]	$NICS_0$	$NICS_1$[a]
CpH	−2.1	−5.0	−11.7	−9.6
$CpPH_2$	−3.5	−4.8	−7.0	−8.2
$CpPCl_2$	−3.6	−5.0	−13.5	−9.8
$CpAsH_2$	−4.6	−5.6	−10.7	−9.6
$CpAsCl_2$	−5.0	−5.6	−13.5	−9.8
Cp^-	−13.9	−10.2		

[a] $NICS_1$ is taken on the opposite side of the ring from the EX_2 substituent.

(d,p) level of theory, are summarized in Table 8. The assignment of the ionization bands is based on the calculations that show good agreement with the experimental data (within around 0.3 eV). It can be seen that the two minimum structures (C_s and C_1) have similar stability and an isomer equilibrium close to the 1:1 molar ratio. Also, it can be seen from Table 8 that their ionization energies are very close to each other; therefore a broadening of the photoelectron spectra is expected. The low-energy range of the spectra of the investigated $CpEX_2$ species consists of some well-separated bands that are assigned as follows.

The highest three occupied MOs of all the investigated molecules can be derived from the combination of the π orbitals of cyclopentadiene and the n(E) lone pair orbital of EX_3 units (Figure 5). The HOMO of all the investigated molecules is a π orbital that does not mix with the lone pair of E since it is situated in the nodal plane of this π MO. In accordance, the position of the first PE band is almost unchanged for the EH_2 derivatives and slightly shifted for the ECl_2 derivatives, due to the inductive effect of the halogens. The next two IPs of $CpEX_2$, however, exhibit a strong (1.11−1.63 eV) interaction of n(E) with the π orbital of b_1 symmetry (cyclopentadiene) due to a hyperconjugative interaction of the π system and the σ(E−C) bond. The participation of the n(E) lone pair is rather special, as it does not in general mix with any other orbitals due to its high s character. A similar phenomenon was reported earlier for allylic phosphines and arsines.[14] Although significant interaction was obtained between the cyclopentadienyl and the EX_2 groups, there is no evidence of aromaticity in these compounds.

Conclusion

Unsubstituted cyclopentadienylphosphine and arsine have been synthesized and analyzed by spectroscopic methods. The comparison of these compounds with the corresponding acyclic allylic compounds[14] clearly shows the high instability of the cyclopentadienyl derivatives. In addition, these cyclic diallyls are computationally found to perform complex intramolecular motions: the circumambulatory rearrangement is coupled with a fast rotation of the substituent around the carbon−heteroatom bond. The fluxional behavior of these compounds has also been established by NMR experiments. The $CpEX_2$ species (E = P, As; X = H, Cl) have two minima of similar stability, a symmetric (C_s) and a nonsymmetric (C_1) one, separated by a low rotational barrier. The rearrangement was found to be a 1,2-migration that proceeds through an aromatic, low-energy transition state, TS_1. The aromaticity of the transition structures has been found to correlate with both the barrier to the migration and the Lewis acidity of the EX_2 group. Thus the effect of the substituents on the static (structural and electronic) and dynamic (fluxional) properties on the cyclopentadienyl derivatives is evidenced. In addition to the 1,2-sigmatropic shift, a 1,3-shift is also expected for $CpAsCl_2$, though only at elevated temperatures.

The hyperconjugative interaction of the σ(C−E) bond and the π system as well as the unusual n(E)−π interaction—observed earlier also for allylated EX_3 derivatives[14]—have been tested and established by the significant splitting of the n(E)−π bands in the photoelectron spectra. There is no sign of aromaticity of the $CpEX_2$ species.

Experimental Section

Caution: Low-boiling phosphines and arsines are highly toxic molecules. All reactions and handling should be carried out in a well-ventilated hood.

General Remarks. ^1H (400 MHz), ^{31}P (121 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker spectrometer ARX400. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^1H and ^{13}C spectra and external H_3PO_4 for ^{31}P NMR spectra. High-resolution mass spectrometry experiments (HRMS) were performed on a Varian MAT 311 instrument. To record the mass spectra, the phosphines **3** and **4** and arsine **5** were directly introduced from a cooled cell into the ionization chamber of the spectrometer. All the new compounds are too reactive to be characterized by combustion analysis. The yields of the unstabilized derivatives were determined by ^1H NMR spectroscopy with an internal reference.

All manipulations were performed under an atmosphere of dry nitrogen. Tributyl tin chloride, PCl_3, the cyclopentadiene dimer, and the methylcyclopentadiene dimer were purchased from Aldrich and used as received. The cyclopentadienyltributylstannane **11** and (methyl-2,4-cyclopentadien-1-yl)tributylstannane **12** were prepared from the dienes as described.[16]

Table 8. Experimental (He I) and Computed ROVGF/6-311+G(d,p)//B3LYP/6-311+G(d,p) Ionization Energies (in eV) and Their Assignments for the $CpEX_2$ Species

	band 1			band 2			band 3		
		C_s	C_1		C_s	C_1		C_s	C_1
species	expt	OVGF	OVGF	expt	OVGF	OVGF	expt	OVGF	OVGF
CpH[a]	8.58	8.47		10.76	10.77			12.43	
	π			$\pi+\sigma_{CH}$				σ	
$CpPH_2$	8.64	8.54	8.43	9.61	9.43	9.43	10.73	10.57	10.69
	π		π	$n_P+\sigma_{PC}$			$\pi+\sigma_{PC}$		
$CpPCl_2$	9.07	9.08	8.88	9.60	9.58	9.48	11.23	10.98	11.05
	π		π	$n_P+\sigma_{PC}+n_{Cl}$			$\pi+\sigma_{PC}+n_{Cl}$		
$CpAsH_2$	8.61	8.46	8.34	9.58	9.34	9.28	10.69	10.33	10.56
	π		π	$n_{As}+\sigma_{AsC}$			$\pi+\sigma_{AsC}$		
$CpAsCl_2$	9.07	9.05	8.83	9.72	9.50	9.72	11.02	10.71	10.92
	π		π	$n_{As}+\sigma_{AsC}+n_{Cl}$			$\pi+\sigma_{AsC}+n_{Cl}$		

[a] Data correspond to the C_{2v} structure.

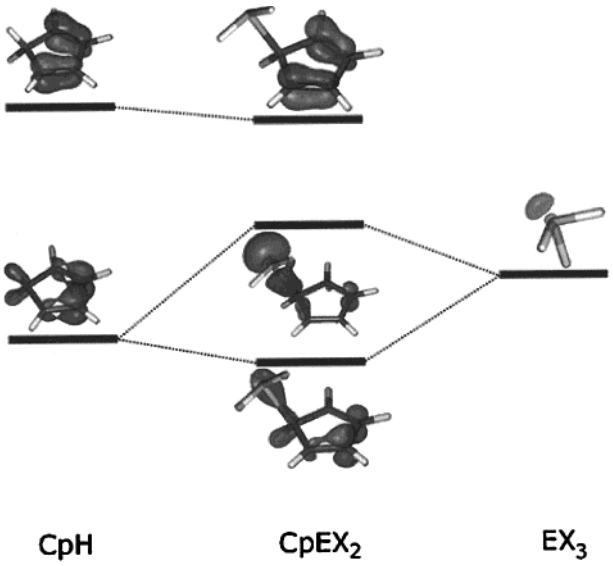

Figure 5. MO correlation diagram of $CpEX_2$ derivatives as shown by the MOLDEN program.[21]

Synthesis of Cyclopentadienyldichlorophosphines 7[15] and 9 and Arsines 8[10]and 10.[11] General Procedure. In a two-necked flask equipped with a nitrogen inlet and a stirring bar were introduced PCl_3 or $AsCl_3$ (10 mmol). The flask was immersed in a bath cooled at −30 °C, and the cyclopentadienyltributylstannane **11** or **12** (10 mmol) was slowly introduced. At the end of the addition, the bath was removed and the solution was stirred for 10 min at room temperature. Phosphines **7** and **9**, purified by distillation on a vacuum line, were selectively condensed in a trap cooled at −40 °C under 10^{-1} mbar. Arsines **8** and **10** were quickly distilled under vacuo (10^{-1} mbar). Compounds **7**−**10** were kept at low temperature (< −40 °C).

(3-Methyl-2,4-cyclopentadien-1-yl)dichlorophosphine, 9. Yield: 68%; bp 35 °C (0.1 mmHg). ^{1}H NMR ($CDCl_3$): δ 2.10 (d, 3H, $^3J_{HH}$ = 4.6 Hz, CH_3); 4.33 (d, 1H, $^3J_{HH}$ = 6.9 Hz, CHP); 6.11 (s, 1H, HC=C); 6.45 (s, 1H, HC=C); 6.75 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 15.3 (q, $^4J_{PC}$ = 1.6 Hz, CH_3); 66.2 (d, $^1J_{PC}$ = 57.4 Hz, CHP); 124.7 (d, $^3J_{PC}$ = 12.1 Hz, *C*H=C); 130.9 (d, $^2J_{PC}$ = 13.7 Hz, *C*H=C); 141.6 (d, $^3J_{PC}$ = 6.4 Hz, *C*H=C); 149.5 (s, $^2J_{PC}$ = 7.2 Hz, C-Me). ^{31}P NMR ($CDCl_3$): δ 150.0. HRMS: calcd for $C_6H_7Cl_2P$ 179.9662; found 179.967.

(2,4-Cyclopentadien-1-yl)arsonous Dichloride, 8.[10] Yield: 67%; bp 45 °C (0.1 mmHg). $\tau_{1/2}$ (20 °C, neat under N_2): 30 min. NMR spectra recorded at room temperature: ^{1}H NMR (CD_2Cl_2) δ 6.46 (s, 5H); ^{13}C NMR (CD_2Cl_2) δ 121.2. NMR spectra recorded at −95 °C: ^{1}H NMR (CD_2Cl_2) δ 4.98 (s, 1H); 6.55 (s, 2H); 6.96 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ 69.6 (d, CH−As), 128.3 (d, *C*H=C), 137.4 (d, *C*H=C).

(3-Methyl-2,4-cyclopentadien-1-yl)arsonous Dichloride, 10.[11] Yield: 43%; bp 65 °C (0.1 mmHg). $\tau_{1/2}$ (20 °C, neat under N_2): 30 min. NMR spectra recorded at room temperature: ^{1}H NMR (CD_2Cl_2) δ 2.06 (s, 3H); 5.73 (s, 2H); 6.32 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ 15.7, 105.6, 128.0, 147.8. NMR spectra recorded at −95 °C: ^{1}H NMR (CD_2Cl_2) δ 2.10 (s, 3H, CH_3); 4.84 (br s, 1H); 6.21 (br s, 1H); 6.54 (br s, 1H); 6.87 (br s, 1H); ^{13}C NMR (CD_2Cl_2) δ 15.3 (q, CH_3), 68.6 (d, CH-As), 122.6 (d, *C*H=C), 128.6 (d, *C*H=C), 140.4 (d, *C*H=C), 149.4 (s, *C*Me).

Cyclopentadienylphosphines (3, 5) and Arsine (4). General Procedure.[20] In a 25 mL two-necked flask was introduced the reducing agent (**7**, **9**: LAH (200 mg, 5 mmol) and tetraglyme (10 mL); **8**: tributylstannane (4.3 g, 15 mmol)) and few milligrams of duroquinone. The flask was fitted on a vacuum line equipped with a stopcock, a cold trap, and a coldfinger. The flask was cooled (−20 °C) and degassed; the dichlorophosphine **7** or **9** or the dichloroarsine **8** (1 mmol) diluted in tetraglyme (3 mL) was then slowly introduced with a microsyringe or a flexible needle. To limit oligomerization, phosphine **3** or **5** or arsine **4** was distilled off in vacuo from the reaction mixture during the course of the addition of **7**, **9**, or **8**, respectively. High-boiling impurities were selectively condensed in a cold trap (−40 °C), and phosphine **3** or **5** or arsine **4** was condensed in a cold trap (−75 °C) to remove low-boiling impurities (PH_3 or AsH_3, respectively, cyclopentadiene or methylcyclopentadiene, respectively). At the end of the reaction, the phosphine **3** or **5** or arsine **4** was revaporized and condensed with a cosolvent on a coldfinger (−196 °C) (the gaseous flow can also be directly analyzed by PES or HRMS spectrometry). After disconnection from the vacuum line, the apparatus was filled with dry nitrogen and the coldfinger was allowed to warm to room temperature. Thus, compounds **3**−**5** were collected in a Schlenk flask or in a NMR tube and were kept at low temperature (−50 °C).

Cyclopentadienylphosphine, 3. Yield: 52%; bp ≈ − 70 °C (0.1 mmHg). $\tau_{1/2}$ (2% in $CDCl_3$ at 20 °C): 5 h. ^{1}H NMR ($CDCl_3$, −20 °C): δ 3.00 (dd, 2H, $^1J_{PH}$ = 190.2 Hz, $^3J_{HH}$ = 7.0 Hz, PH_2); 3.72 (tm, 1H, $^3J_{HH}$ = 7.0 Hz, CH−P); 6.50 (m, 2H, CH=C), 6.56 (m, 2H, CH=C). ^{13}C NMR ($CDCl_3$, −20 °C): δ 41.6 (d, $^1J_{PC}$ = 12.5 Hz, CH-P); 130.2 (d, $^3J_{PC}$ = 3.6 Hz, *C*H=C); 139.2 (d, $^2J_{PC}$ = 4.8 Hz, *C*H=C). ^{31}P NMR ($CDCl_3$, −20 °C): δ −135.3 (t, $^1J_{PH}$ = 190.2 Hz). HRMS: calcd for C_5H_7P 98.0286, found 98.0291. *m/z* (%): 98 (95), 97 (100), 96 (36), 83 (17), 70 (14), 65 (25).

(3-Methyl-2,4-cyclopentadienyl)phosphine, 5*γ*. Yield: 23%; bp ≈ − 60 °C (0.1 mmHg). $\tau_{1/2}$ (2% in $CDCl_3$ at 20 °C): 5 h. ^{1}H NMR ($CDCl_3$, −20 °C): δ 2.04 (m, 3H); 3.00 (ddd, part A of an AB system, 1H, $^1J_{PH}$ = 190.2 Hz, $^2J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.1 Hz, PH); 3.02 (ddd, part B of an AB system, 1H, $^1J_{PH}$ = 190.2 Hz, $^2J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.1 Hz, PH); 3.68 (t broad,

(20) For similar experiments, see ref 14.

(21) Schaftenaar, G. *MOLDEN 3.7*; Caos/Camm Center: Nijmegen, 2001.

1H, $^3J_{HH}$ = 7.1 Hz, CH−P); 6.04 (s, 1H, CH=C); 6.40−6.44 (m, 2H, CH=C). ^{13}C NMR ($CDCl_3$, −20 °C): δ 15.2 (q, CH_3), 39.9 (d, $^1J_{PC}$ = 11.2 Hz, CHP), 132.7 ($^2J_{PC}$ = 4.8 Hz); 133.9 (d, $^3J_{PC}$ = 3.2 Hz, *C*H=C), 139.6 (d, $^2J_{PC}$ = 4.8 Hz, *C*H=C); 141.0 (s, $^3J_{PC}$ = 4.0 Hz, CMe). ^{31}P NMR ($CDCl_3$, −20 °C): δ −128.7 (t, $^1J_{PH}$ = 190.2 Hz). HRMS: calcd for C_6H_9P 112.0442, found 112.044. After few hours at room temperature, a mixture of two isomers was observed. Second isomer: **(2-Methyl-2,4-cyclopentadienyl)phosphine, 5*β***. ^{1}H NMR ($CDCl_3$, −20 °C): δ 2.07 (m, 3H); 2.85 (ddd, part A of an AB system, 1H, $^1J_{PH}$ = 190.2 Hz, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 7.4 Hz); 2.97 (ddd, part B of an AB system, 1H, $^1J_{PH}$ = 192.0 Hz, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 7.4 Hz); 3.37 (t, 1H, $^3J_{HH}$ = 7.4 Hz); 6.14 (s, 1H); 6.33 (s, 1H); 6.42 (m, 1H). ^{13}C NMR ($CDCl_3$, −20 °C): δ 14.6 (q, $^3J_{PC}$ = 2.0 Hz, CH_3); 39.9 (d, $^1J_{PC}$ = 11.2 Hz, CHP); 126.3 (d, $^3J_{PC}$ = 1.6 Hz, *C*H=C); 130.5 (d, $^2J_{PC}$ = 16.7 Hz, *C*H=C); 136.5 (d, $^3J_{PC}$ = 4.8 Hz, *C*H=C); 149.2 (s, $^2J_{PC}$ = 3.2 Hz, CMe). ^{31}P NMR ($CDCl_3$, −20 °C): δ −127.3 (t, $^1J_{PH}$ = 190.2 Hz).

Cyclopentadienylarsine, 4. Yield: 77%; bp ≈ − 60 °C (0.1 mmHg). $\tau_{1/2}$ (2% in $CDCl_3$ at 20 °C): 1 h. ^{1}H NMR (CD_2Cl_2, −20 °C): δ 2.88 (d, 2H, $^3J_{HH}$ = 5.9 Hz, AsH_2); 4.05 (t, 1H, $^3J_{HH}$ = 5.9 Hz, CHAs); 6.57 (br s, 2H, CH=C); 6.58 (br s, 2H, CH=C). ^{13}C NMR (CD_2Cl_2, −20 °C): δ 40.2 (d, HC-As), 129.0 (d, *C*H=C), 139.0 (d, *C*H=C). HRMS: calcd for C_5H_7As 141.9764, found 141.977. *m*/*z* (%): 142 (41), 140 (28), 67 (81), 66 (100), 65 (40), 39 (57).

(Methyl-2,4-cyclopentadienyl)arsine 6*β* and 6*γ*. In a 25 mL two-necked flask was introduced the tributylstannane (4.3 g, 15 mmol) and few milligrams of duroquinone. The flask was fitted on a vacuum line equipped with a stopcock and a coldfinger. The flask was cooled (0 °C) and degassed; the dichloroarsine **10** (1 mmol) was then slowly introduced with a microsyringe. Arsine **6** was distilled off in vacuo from the reaction mixture during the course of the addition of **10** and condensed on the coldfinger. At the end of the reaction a cosolvent ($CDCl_3$) was added. After disconnection from the vacuum line, the apparatus was filled with dry nitrogen and the coldfinger was allowed to warm to room temperature. Thus, compound **6** was collected in an NMR tube and was kept at low temperature (−60 °C) before analysis. Yield: 32% (crude). $\tau_{1/2}$ (2% in $CDCl_3$ at 20 °C): 30 min. **6*γ***. ^{1}H NMR ($CDCl_3$, −40 °C): δ 2.08 (s, 3H, CH_3); 2.81 (dd, part A of an AB system, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 5.6 Hz, As−H); 2.86 (dd, part B of an AB system, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 5.6 Hz, As−H); 3.68 (t br, 1H, $^3J_{HH}$ = 5.6 Hz, CH-As); 6.10 (s, 1H, CH=C); 6.44 (m, 1H, CH=C); 6.49 (m, 1H, CH=C). ^{13}C NMR ($CDCl_3$, −40 °C): δ 15.3 (q, CH_3); 39.6 (d, CH−As); 132.3 0 (d, *C*H=C); 132.5 (d, *C*H=C); 139.4 (d, *C*H=C); 145.3 (s, CMe). **6*β***. ^{1}H NMR ($CDCl_3$, −40 °C): δ 2.08 (s, 3H, CH_3); 2.72 (dd, part A of an AB system, 1H, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 6.1 Hz, AsH); 2.80 (dd, part B of an AB system, 1H, $^2J_{HH}$ = 13.0, $^3J_{HH}$ = 6.1 Hz, AsH); 3.37 (t, 1H, $^3J_{HH}$ = 6.1 Hz, CH-As); 6.18 (s, 1H, CH=C); 6.39 (s, 1H, CH=C); 6.44 (m, 1H, CH=C). ^{13}C NMR ($CDCl_3$, −40 °C): δ 15.1 (q, CH_3); 43.3 (d, CH-As), 125.1 (d, *C*H=C), 129.4 (d, *C*H=C), 136.0 (d, *C*H=C), 148.5 (s, CMe).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of phosphine **9** at room temperature and arsine **10** at room temperature, 203 K, and 178 K. ^{1}H and ^{13}C NMR spectra at 253 K of phosphine **3** and arsine **4**. Photoelectron spectra of $CpEX_2$ derivatives **8**, **4**, **7**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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