Main-Group Chemistry

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Stepwise Expansion of a Cp* Ring at Pentelidene Complexes and Stereoselective Formation of Triphosphines**

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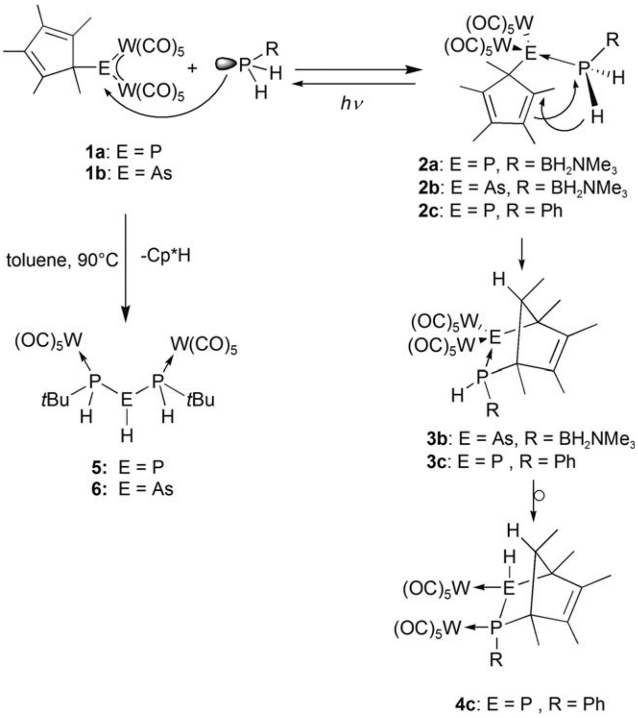
Dedicated to Professor Martin Jansen on the occasion of his 65th birthday

The pentamethylcyclopentadienyl ligand (Cp*) is one of the most frequently used ligands in organometallic transition-metal chemistry. It combines decisive steric and electronic factors to increase the stability of metal complexes.[1] Moreover, the solubility of the complexes is usually increased. Besides the traditional use in the organometallic chemistry of transition metals, it has also been shown in the field of main-group chemistry to be an effective substituent to stabilize unusual structures and moieties.[2] In these cases, the coordination mode of Cp* is very flexible and can range from η^5 to η^1. In line with its impressive stability, only a few examples are known in which Cp* is transformed. The most prominent of these are cycloaddition reactions (usually [2+4]-cycloaddition) induced by early transition metals; such reactions are more common for the parent Cp ligand, C_5H_5.[3] Recently, a C−C coupling of ligating Cp* moieties on a uranium center was reported.[4] Moreover, for P-bound Cp* groups, Jutzi and co-workers observed a formal [2+3]-cycloaddition,[5] and Russell and co-workers[6] showed a Lewis acid induced Diels–Alder-like reaction to form P,C cage compounds. Recently, Streubel and co-workers reported on the formation of cage ligands from such systems.[7] In contrast to these not completely understood reactions of Cp*, we have now found a selective intramolecular hydrophosphination reaction of the σ-bound Cp* moiety of the pentelidene complexes $[Cp^*E\{W(CO)_5\}_2]$ (**1**: E = P (**a**), As (**b**)) by primary phosphines to enlarge the Cp* ring in a stepwise manner to form 2,3-dipentelanorborn-5-ene derivatives. Moreover, at the end of the reaction cascade, complex-stabilized 1,2,3-trihydrotriphosphines and 1,2,3-trihydro-2-arsadiphosphines are formed, the former in a diastereomerically pure form; we report these results herein.

Stirring the dark blue solution of $[Cp^*E\{W(CO)_5\}_2]$ (E = P (**1a**), E = As (**1b**))[8] in toluene with one equivalent of $H_2PBH_2NMe_3$ at −78 °C results in a rapid color change, which indicates the nucleophilic attack of the lone pair of the primary phosphine at the main-group center E of the pentelidene complexes to disturb the 3-center-4-electron π system. The resulting compounds $[Cp^*E\{W(CO)_5\}_2\{H_2PBH_2NMe_3\}]$ (E = P (**2a**), As (**2b**)) can be isolated in good yields (Scheme 1). The crystals of **2a** are stable under inert atmosphere at 8 °C, unlike those of **2b**, which is only stable for a short time at −25 °C. Both complexes undergo decomposition to the starting materials after exposition to daylight.

Huttner et al. described a number of adducts of Lewis bases such as ethers[9] or amines[10] of bridging phosphinidene complexes $[RP\{ML_n\}_2]$ (R = *t*Bu, Ph; $ML_n = Cr(CO)_5$, $CpMn(CO)_2$) which have not been structurally characterized. In comparison to **2a**,**b**, these compounds are less stable, and the Lewis bases are easily removed in vacuo. Whereas



Scheme 1. Reaction sequence of the pentelidene complexes **1** with primary phosphines.

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pentelidene complexes **2a**,**b** undergo light-dependant formation and degradation (Scheme 1), the phosphinidene adduct **2a** dissociates at room temperature into the starting materials. In contrast, at that temperature the arsenidene complex **2b** reacts further by hydrophosphination of the PH function of the $H_2PBH_2NMe_3$ moiety at a double bond of the σ-bound Cp* ligand to form the novel 3-arsa-2-phosphanorborn-5-ene complex **3b** (Scheme 1). The two double bonds in the Cp* ligand are chemically equivalent, and therefore two enantiomers of **3b** are formed in a racemic mixture. The intramolecular hydrophosphination of **2b** is unusual, as only intermolecular hydrophosphination reactions into unactivated or weakly activated C–C double bonds are known; these reactions are mainly induced by radical initiators or take place under basic conditions.[11]

Furthermore, another primary phosphine was used in this reaction protocol. By monitoring the reaction of H_2PPh with $[Cp^*P\{W(CO)_5\}_2]$ (**1a**) in toluene by ^{31}P NMR spectroscopy between −70 and −35 °C, an adduct **2c** (Scheme 1) is detected showing the expected two doublets at $\delta = -17.7$ and −24.8 ppm ($^1J_{P,P} = 344$ Hz), similar to those of **2a** ($\delta = -59.6$ and −56.7 ppm; $^1J_{P,P} = 276$ Hz). At room temperature the signals of **2c** have disappeared, and two doublets of the new compound **3c** ($\delta = -19.0$ and 54.1 ppm; $^1J_{P,P} = 282$ Hz) can be observed. Compound **3c** was isolated in moderate yields and is similar in structure to **3b**. As the reaction mixture of **3c** shows a series of new signals indicating that other subsequent reactions occur, thermolysis of isolated **3c** in toluene was carried out until the signals of the starting material disappeared (15 min). The ^{31}P NMR spectrum of the reaction mixture shows a large number of signals; however, the strongest can be assigned to **4c**. This main product of the thermolysis was isolated, and the crystal structure analysis indicates that a rearrangement of the $W(CO)_5$ moiety and an H atom in **3c** has occurred. Thus, **4c** is an isomer of **3c**.

tert-Butylphosphine was also used in the reaction procedure with **1a**,**b** (Scheme 1). Since at low and room temperature no reaction occurred, the temperature was increased to about 90 °C, leading to complete conversion within 45 min. Cp*H could be detected in the reaction solutions. From these solutions the novel complexed triphosphine **5** and the arsadiphosphine **6** were isolated in moderate yields. It should be noted that the best yields are obtained if two equivalents of $t\mathrm{BuPH_2}$ are used. Even at low temperatures the parent compound $(H_2P)_2PH$ easily undergoes thermal decomposition to give PH_3 and P_2H_4.[12] Organic substituted 1,2,3-trihydrotriphosphines are unknown; only the 1,3-diaminotriphosphine $H_2N(H)P\text{-}P(H)\text{-}P(H)NH_2$ was synthesized in liquid ammonia in its diastereomerically pure form (as determined by ^{31}P NMR spectroscopy), and it is only stable in this solvent.[13] Only 1,3-dihydrotriphosphines of the type $(RPH)_2PR'$ with bulky substituents ($R = 2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$, $R' = (C_5H_4)CpFe$ ($Cp = C_5H_5$),[14] and $R = R' = t\mathrm{Bu}$[15]) are stable at room temperature, usually forming mixtures of three diastereomers. Significantly, the isolated triphosphine **5** shows only the A_2M spin system of one diastereomer in the ^{31}P NMR spectrum, whereas for the arsadiphosphine **6** an A_2 and an AM spin system of a 1:1 mixture of two diastereomers have been found.[16] Interestingly, suitable single crystals of only one diastereomer of **6** were found.

The X-ray structural analyses[16] of the isostructural molecules **2a** and **2b** (Figure 1) reveal that the coordination of the $H_2PBH_2NMe_3$ ligand at the pentelidene atom changes the formerly trigonal-planar coordination geometry to a distorted tetrahedral environment, which leads to an enlargement of the E–W bonds.[17] The P–B bond (2.000(7) Å) in **2a** is slightly lengthened, unlike the corresponding bond in **2b** (1.970(13) Å), which is in the range of the starting material (1.976(2) Å).[18] The new coordinative P–P and P–As bond lengths (2.237(2) Å and 2.352(3) Å, respectively) are in the area of lengthened single bonds (c.f.: β-P_4: 2.199–2.212 Å;[19] for P–As, see Ref. [20]). They correspond to such dative bond lengths as found in phosphanyl/arsanyl phosphonium cations.[21] The E–P bonds in the heteronorbornene compounds **3b** and **3c** (Figure 2) are shorter than in compounds **2a**,**b** and are in the range of single bonds.

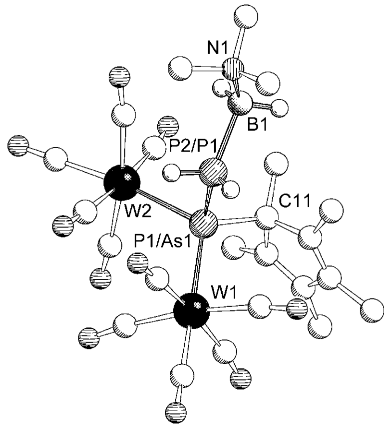


Figure 1. Molecular structures of **2a** (P1,P2) and **2b** (As1,P1). Methyl hydrogen atoms are omitted for clarity.

The molecular structure of **4c** (Figure 3) shows a heteronorbonene cage similar to that of **3b** and **3c**. Complexes with

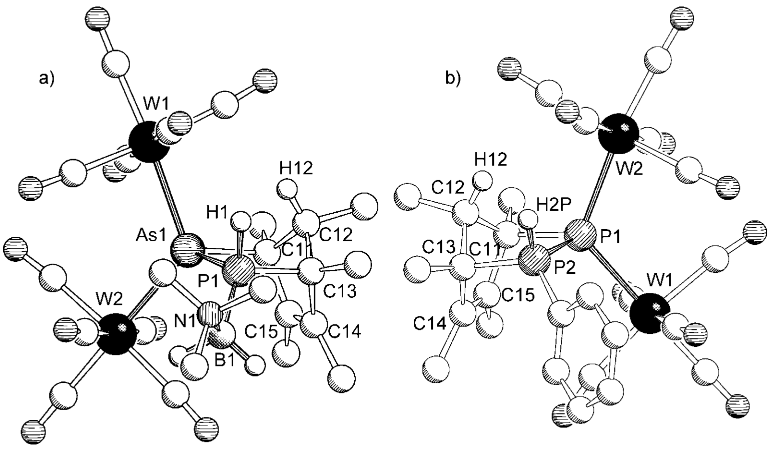


Figure 2. Molecular structure of **3b** (a) and **3c** (b). Methyl and phenyl hydrogen atoms are omitted for clarity.

a diphosphorus norbornene framework were synthesized by Huttner and co-workers[22] and by Niecke and Pietschnig[23] by the reaction of compounds with P–P double bonds with cyclopentadiene, C_5H_6, by [2+4]-cycloaddition but have not been structurally characterized.

In comparison to **3c**, the P–W bond lengths of its isomer **4c**, with *trans*-oriented [$W(CO)_5$] groups, decrease from 2.5948(9) to 2.534(2) Å and from 2.6072(9) to 2.5306(19) Å, whereas the P–P bond length in **4c** increases to 2.239(2) Å (**3c**: 2.1969(12) Å). The reason might be the steric repulsion of the bulky $W(CO)_5$ groups. However, looking at the ^{31}P NMR spectroscopy data, it is possible to postulate a decrease in s character of the P–P bond in **4c** relative to **3c** and its increase in the corresponding P–W bonds ($^1J_{P,P}$ (**3c**: 282 Hz) decreases to 107 Hz in isomer **4c**; $J_{P,W}$ at the phosphinidene P signal at $\delta = -19.0$ of **3c** (151 and 175 Hz) increases to 212 and 230 Hz at both signals of **4c** at $\delta = 0.6$ and 30.4 ppm). This line of thought could also explain the different tendencies in the P–P and the P–W bond lengths.

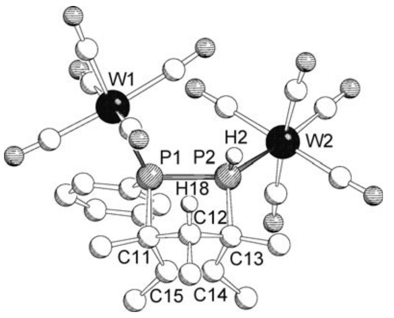


Figure 3. Molecular structure of **4c**. Methyl and phenyl hydrogen atoms are omitted for clarity.

Compounds **5** and **6** are isomorphous and crystallize in the acentric space group $Pna2_1$ (Figure 4). Since the position of the H atom at the central P or As atom could not be determined with confidence (the H atom and the lone pair have similar electron densities), the absolute configuration of the diastereomer could not be assigned. The E–P bonds in **5** and **6** are in the range of single bonds. Owing to the steric influence of the bulky $W(CO)_5$ and *t*Bu groups, the P-P-P bond angle in **5** (103.25(7)°) is slightly decreased in comparison to the calculated one in the parent P_3H_5 (104.50°);[12] the P-As-P angle in **6** (100.23(10)°) is even smaller. The W–P bond lengths in **5** and **6** are comparable with those in $W(CO)_5PH_3$.[24]

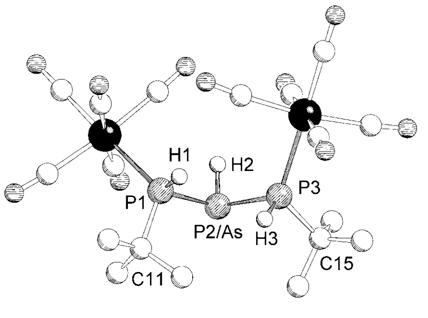
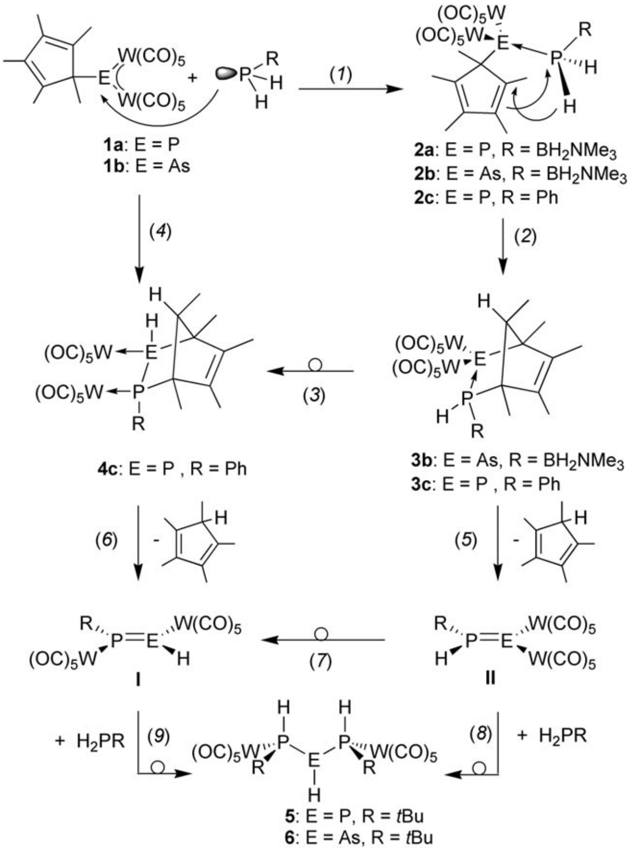


Figure 4. Molecular structures of **5** (P2) and **6** (As). Methyl hydrogen atoms are omitted for clarity.

To shed light on the reaction pathway, density functional calculations were carried out (Scheme 2).[16] It is interesting to note that overall reaction energetics (process *(4)*) depend only on the nature of the center E of the pentelidene complexes (for E = P it is about 35 kJ mol^{-1} more exothermic than for E = As) but not on the substituents (both BH_2NMe_3 and Ph show similar exothermicity). However, the reaction profiles are quite different. Process *(1)* of the adduct formation is strongly enhanced by the BH_2NMe_3 group as compared to the Ph substituent (by more than 50 kJ mol^{-1}) but is disfavored by the *t*Bu group by about 50 kJ mol^{-1}. In accordance with this finding, strongly bound adducts **2a** and **2b** have been isolated, while theoretically unstable adduct **2c** has not been isolated. In contrast, processes *(2)* and *(3)* are more exothermic in the case of the Ph group (by 15 and 35 kJ mol^{-1}, respectively). This result suggests enhanced subsequent reactivity of Ph-substituted compounds, as has been found experimentally. The major difference in the reaction pathways between compounds **3c** and **3b** lies in the isomerization reaction *(3)*. Isomerization of **3c** to **4c** in the gas phase is strongly exothermic (by 72 kJ mol^{-1}), while conversion of **3b** into **4b** is endothermic by 7 kJ mol^{-1}. These data are in good agreement with experimental observation of the



Scheme 2. Stepwise reaction of the pentelidene complexes **1** with primary phosphines.

favored isomerization of **3c** but not of **3b**. Subsequent formation of complex-stabilized triphosphines and arsadiphosphines is very thermodynamically favorable. However, the key difference between P and As is seen in the isomerization reaction *(7)*. For all studied substituents,[16] process *(7)* is exothermic for E = P but endothermic for E = As. Thus, the geminal isomer **II** is expected to isomerize to the *trans*-isomer **I** for E = P but not for E = As. Subsequent hydrophosphination reactions should yield one diastereomer in the case of **I** but two diastereomers of **II** after subsequent rearrangement reactions,[16a] in agreement with experimental results.

The results have shown that primary phosphines are able to react with electrophilic pentelidenes to give stable adducts which under mild conditions induce a novel intramolecular hydrophosphination reaction of a σ-bound Cp* substituent. Its stepwise expansion—monitored by NMR spectroscopy and confirmed by structural characterization of isolated compounds—proceeds by rearrangement of a phosphine pentelidene precursor under formation of pentelaphosphanorbornene molecules. With $t\mathrm{BuPH_2}$ the reaction sequence goes to a final stage through Cp*H elimination under formation of complex-stabilized 1,2,3-trihydrotriphosphine in a diastereomerically pure form (E = P) and an arsadiphosphine (E = As). DFT calculations are in very good agreement with the experimentally observed reaction sequence. In addition, the found formation process of triphosphines is completely different from those of former reports on hydrogenation of halogen-containing triphosphines, methanolysis of silylated triphosphines, and the catalytic dehydrocoupling of phosphines.[25] This reaction pattern of the pentelidene complexes **1** is in strong contrast to the Cp* migration process of **1** usually found to form the triply bonded intermediates $[\mathrm{Cp^*(CO)_2W{\equiv}E{\rightarrow}W(CO)_5}]$,[26] which can be trapped by alkynes,[27] phosphaalkynes,[28] and compounds with metal–metal multiple bonds[29] to form transition-metal cages containing Group 15 elements. Moreover, under photolytic conditions, a radical Cp* displacement is found.[30]

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