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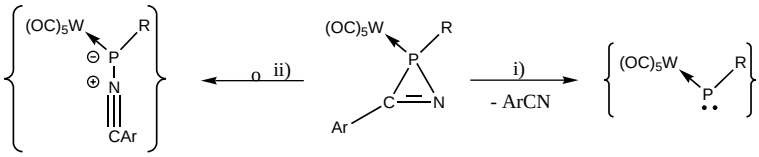
Rearrangement of Molecular Complexes

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1 Introduction

Experimental and computational investigations of rearrangement and decomposition pathways of molecular phosphine transition-metal complexes are of fundamental interest in coordination and organometallic chemistry and in catalysis. One of the central topics of our research group is the chemistry of 2*H*-azaphosphirene complexes **1** and the generation, reaction and/or rearrangement of reactive intermediates **2** (i) (so called phosphinidene complexes) and **3** (nitrilium phosphanylide complexes) (ii) from precursor **1**[1–3]. Recently, we had discovered that electrophilic terminal phosphinidene tungsten complexes **2** with bulky substituents at phosphorus (R = C_5Me_5 or $CH(SiMe_3)_2$) do not dimerize in the absence of trapping reagents[4]. Therefore we became interested in their fate. The computational studies comprise a density functional method-based study of the hypersurfaces of phosphinidene complexes **2** and nitrilium phosphanylide complexes **1** as well as a characterization of bonding situations by the method of the compliance matrix; probing and establishing this rarely used method - especially in the field of transition metal complexes - makes it a goal in itself and will be discussed below.



3 **1** **2**

Scheme 1. Rearrangement and decomposition of 2*H*-azaphosphirene complexes **1**.

2 Computational Methods

All optimizations and frequency calculations were performed using GAUSSIAN 03 RevB.03[5] on the IBM Regatta p690 cluster (JUMP) of the John von Neumann Institute for Computing (NIC) at the Forschungszentrum Jülich. The standard method throughout this work is B3LYP/6-311G(d,p) combined with an effective core potential description of tungsten using the Los Alamos LanL2DZ (for short: B3LYP/6-311**/LanL2DZ)[6]. Stationary points have been characterized by analytical second derivatives (the Hessian) with respect to redundant cartesian coordinates. Transition states (one imaginary frequency)

were identified by a reaction path following (IRC). The Hessian provided by the GAUSSIAN 03 calculation was transformed to non-redundant internal coordinates using Pulays INTC/FCTINT set of algorithms[7]. The inversion of the transformed Hessian to the compliance matrix was accomplished by standard methods.[8]. A typical production job, e.g. $C_{19}H_{24}NO_5PSi_2W$ **1** (Scheme 1) with 242 electrons, uses more than 1000 Gaussian-basis functions and thus needs parallelized computations on fast processors, *which can only be provided by a computing centre like the John von Neumann Institute for Computing (NIC).*

3 Usage and Interpretation of the Compliance Matrix

The physical model behind force constants and thus compliance constants is a spring model: if the molecule at equilibrium geometry is distorted by a vibrational movement the various internal coordinates (modeled by springs) interact according to the molecular force field. In the harmonic approximation to vibrational theory the molecular hypersurface describing a vibrational movement is locally approximated by a quadratic form (H_{ik}) in the displacements of the internal coordinates (bonds, angles, dihedrals and linear combinations thereoff) from their equilibrium values

$$2V = \Delta x^t (H_{ik}) \Delta x, \tag{1}$$

where (H_{ik}) is the matrix of second derivatives (Hessian) at a stationary point, the diagonal elements H_{kk} are the force constants[9]. Equivalently the change in potential energy during a vibration is described by a quadratic form in the forces (force displacements Δf to be precise) instilled in the coordinates upon distortion from equilibrium geometry

$$2V = \Delta f^t (C_{ik}) \Delta f, \tag{2}$$

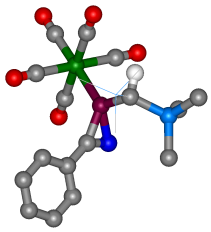
where (C_{ik}) = $(H_{ik})^{-1}$ is the compliance matrix (inverse Hessian) at a stationary point, the diagonal elements C_{kk} of which are the compliance constants (in [Å/mdyn] for bond stretchings and in [rad/mdyn] for angle bendings); the off-diagonal elements are associated with the couplings of the coordinates. While in the spring model force constants H_{kk} describe the stiffness (resistance against distortion) the compliance constants C_{kk} are associated with the compliance of coordinate k[10].

4 Experimental and Theoretical Results

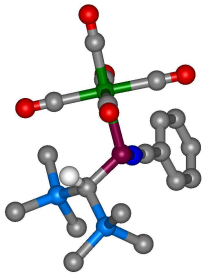
4.1 Formation of a Nitrilium Phosphanylide Complex

From experimental investigations of the thermolysis of 2*H*-azaphosphirene complex **1a**[11] the existence of nitrilium phosphanylide complex **3a** (Scheme 1, path ii), R = $CH(SiMe_3)_2$, Ar = Ph) as a reactive intermediate has been concluded, although, due to its assumed short lifetime, there was no spectroscopic evidence for the intermediacy of **3a**, so far. The DFT-calculations on the hypersurface of **1a** unambiguously showed that nitrilium phosphanylide complex **3a** is an isomer; the formation of which via a still unknown transition state proceeds endergonically by 19 kJ/mol. A comparison of selected experimental (X-ray crystal structure) and calculated bond lengths of **1a** as well as calculated bond lengths of **3a** can be taken from table 1. There is satisfying agreement between experiment and theory concerning the geometry of **1a**. It is noteworthy, that in **3a** the almost linear benzonitrile unit

(angle NCC in **1a**: 135 degree) is attached to a strongly pyramidal phosphorus (sum of bond angles at P: 326 degree); the compliance constant of the P-N contact (0.552 Å/mdyn) provides a likely description of **3a** as a N-P donor adduct of benzonitrile to phosphinidene complex **2b** (see Scheme 2, Figure 2 below).



1a



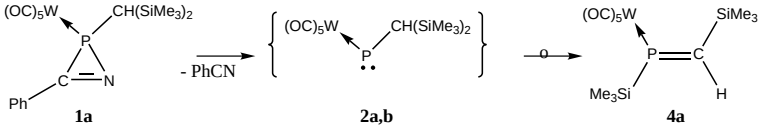
3a

	1a **Exp.** [Å], [°]	**1a** **Calc.** [Å], [°]	**3a** **Calc.** [Å], [°]
W-P	2.470(2)	2.551	2.628
P-C(N)	1.759(5)	1.781	-
P-C(H)	1.808(5)	1.849	1.892
P-N	1.795(4)	1.821	1.752
C-N	1.272(7)	1.271	1.165
Σ ∠ (P)			326

Figure 1. (hydrogens except PCH are omitted) Table 1

4.2 Formation of a *P*-SiMe$_3$-Substituted η^1-*E*-Phosphaalkene Complex[12]

As experimentally shown heating diluted ortho-xylene solutions of 2*H*-azaphosphirene complex **1a** afforded almost quantitatively and stereoselectively the *P*-SiMe$_3$-substituted η^1-*E*-phosphaalkene complex **4a** (Scheme 2). The rearrangement of the thermally generated short-lived phosphinidene complex [(OC)$_5W${PCH(SiMe$_3$)$_2$}] **2** to complex **4** was completely unexpected; we assume that a 1,2-(C-P)-trimethylsilyl shift takes place in this case. Although the chemistry of short-lived electrophilic terminal phosphinidene tungsten complexes[13] has received increased attention during the last years, partially because of the versatility of 2*H*-azaphosphirene complexes,[14] only a single example of a rearrangement yielding a *P*-Cl-substituted η^1-phosphaalkene complex - via a 1,2-chlorine shift - has been reported, so far[15].



1a **2a,b** **4a**

Scheme 2. Rearrangement of transient phosphinidene complexes **2a,b** into **4a,b**.

DFT calculations in order to study the rearrangement of pentacarbonyl-tungsten phosphinidene complexes **2a** (*anti*-periplanar) and **2b** (*syn*-periplanar) to the corresponding phosphaalkene complexes **4a** and **4b** revealed that the formation of the C-P double bonds proceeds via transition state complexes **TSa** and **TSb** (Figure 2; hydrogens except P=CH are omitted).

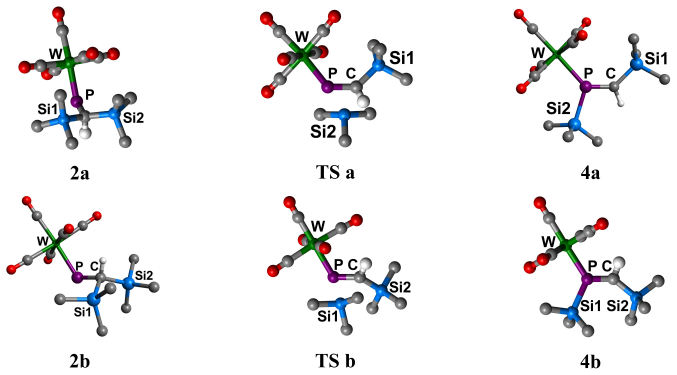


Figure 2. Phosphinidene complexes **2a,b**, transition states **TSa,b** and phosphaalkene complexes **4a,b**.

In consequence, this rearrangement represents an interesting and unique example of an intramolecular 1,2-silyl shift in phosphinidene complex chemistry. Relative energies of the 1,2-silyl migration of **2a,b** to corresponding **4a,b** can be taken from figure 3. *Anti*-periplanar phosphinidene complex **2a** rearranges via transition state **TSa** to the *E*-

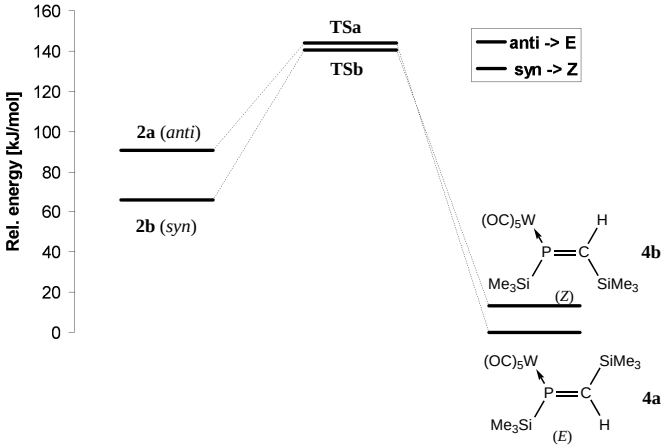


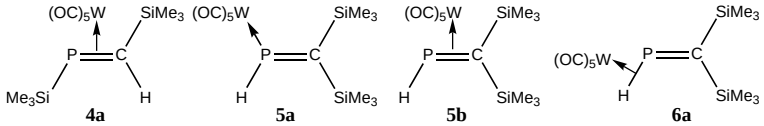
Figure 3. Energy profile of the 1,2-(C to P)-silyl migrations in **2a** and **2b**.

phosphaalkene complex **4a**. C_1 symmetric phosphinidenes **2a,b** exhibit a long and a short C-Si bond; the former is the one involved in forming the three-membered ring of the transition state which contains a five-coordinated silicon center. From an estimated singlet-triplet gap of about 40 kJ/mol under thermal reaction conditions phosphinidene complex **2a** can choose from two concurrent pathways: either undergo a fast reaction from the triplet excited state or - in the absence of suitable reaction partners - rearrange to *E*-phosphaalkene complex **4a**; the reverse 1,2-silyl shift is hindered by a substantial barrier of about 144 kJ/mol. These findings agree well with experimental results where reaction conditions

could be optimized to synthesize pentacarbonyltungsten phosphaalkene complex **4a** from the 2*H*-azaphosphirene complex **1a**. Apart from a smaller barrier (54 kJ/mol **2a** to **4a** vs. 74 kJ/mol for **2b** to **4b**) the major difference between **TSa** and **TSb** can be seen by comparison of the P-Si and C-Si bond lengths involved in the transition state. While **TSa** is early (according to the C-Si bond lengths) in **TSb** the position of the silicon center is almost in between the originating carbon and the phosphorus.

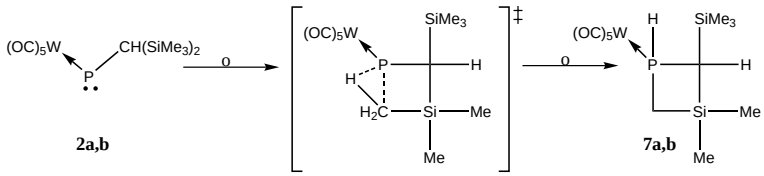
4.3 Further Local Minima on the Hypersurface of $[(OC)_5W\{PCH(SiMe_3)_2\}]$

So far at least six further local minima and a transition state have been located; four of them are shown in scheme 3 and figure 4.



Scheme 3.

Due to the $CH(SiMe_3)_2$ substituent at phosphorus phosphinidene complexes **2a,b** can also undergo a 1,2-*H*-shift to yield phosphaalkene complexes **5a,b** and, by a still unknown transition state, highly unusual complex **6a**. The nature of the related transition-state complex **6b** (figure 4) remains to be clarified since reaction path following calculations were not conclusive yet. There is no automated way to find isomers of a given sum formular. From the literature[16] the ability of phosphinidene complexes to undergo intramolecular C-H insertions is known. Thus we could locate corresponding isomers **7a,b** (Scheme 4, Figure 4; only selected hydrogens are shown for clarity), which are thermodynamically more stable than phosphinidene complexes **2a,b** by 100 kJ/mol and even more stable than the phosphaalkene complexes **4** by 30 kJ/mol (**7b**) and by 20 kJ/mol (**7a**) respectively.



Scheme 4. Intramolecular C-H insertion reaction of phosphinidene complexes **2a,b** to yield **7a,b**.

5 Use of Compliance Constants for the Description of Bonding Situations

A compliance constant is the displacement of a bond due to the application of a unit force on that bond including reorganization. That means, a higher numerical value is connected

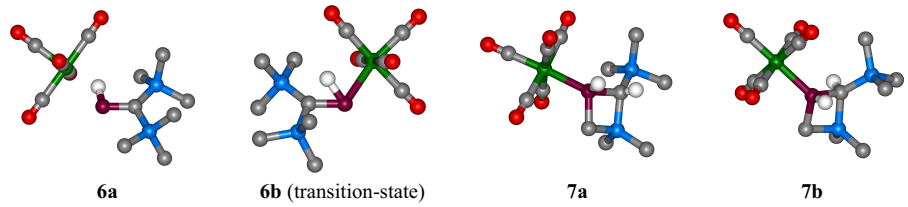


Figure 4.

with a weaker bond. Introduced to vibrational theory by Decius[17] and others[18] experimental compliance fields obtained by Jones and Swanson from vibrational data clarified the bonding forces in metal cyanides and carbonyls[19], while Williams used compliance matrices for the description of chemical reactivity[20]. Calculations of full compliance fields have been used to investigate Ga-Ga[21] and Si-C[22] multiple bonds, the metal-metal bond character in homoleptic transition metal carbonyls[23], hydrogen bonds in Watson-Crick base pairs[24] and polyphosphorus compounds[25]. Recently, Andreoni and coworkers used compliance constants plus Car-Parinello molecular dynamic simulations in order to analyze a proposed Si-Si triple bond[26]. We could show recently the usefulness of compliance constants in the description of agostic interactions[27]. In order to use compliance constants (diagonal elements of the compliance matrix) to assess the strength of a particular bond type (e.g. a tungsten-phosphorus bond) a set of reference compounds has to be calculated (Figure 5). From the statistic three different strengths of bonding interactions can be inferred: tungsten-phosphorus triple bonds range from 0.2-0.3 Å/mdyn while phosphinidene complexes of the type $[(OC)_5WR]$ seem to have a $W(CO)_5$ unit doubly bonded to phosphorus; ordinary W-P single bonds have compliance constants greater than 0.7 Å/mdyn.

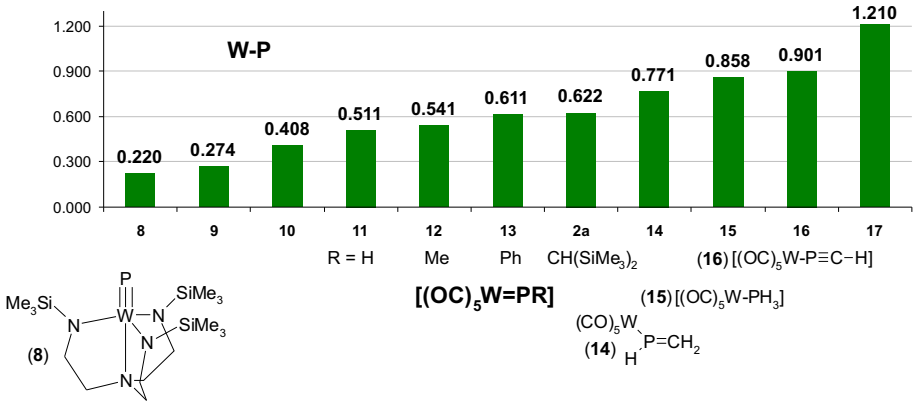


Figure 5. Compliance constants of P-C bonded compounds[28].

By a similar procedure phosphorus-carbon triple (0.1 Å/mdyn), double (0.15-0.2 Å/mdyn) and single bonds (0.3-0.4 Å/mdyn) can be identified (Figure 6). For example the P-C compliance constant of phosphaalkene complex $[(OC)_5W\{HP{=}C(SiMe_3)_2\}]$ (Scheme 3) falls

well within the range of a double bond (0.192 Å/mdyn).

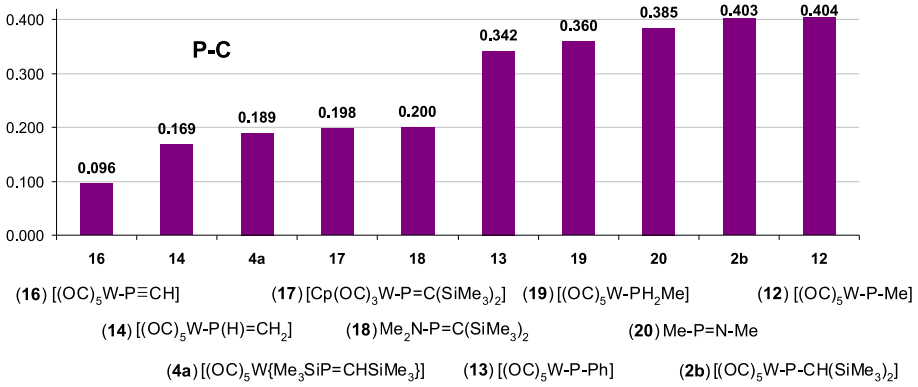


Figure 6. Compliance constants of P-C bonded compounds[29].

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