

Nitrogen-bridged bidentate phosphalkene ligands*

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Abstract: Nitrogen-bridged bidentate phosphalkenes reveal several exceptional properties as a new class of P=C-unsaturated diphosphinoamine (PNP) ligands: N–Si bond cleavage of the first *N*-silylimino-bridged bis-phosphalkene (R₂C=P)₂NSiMe₃ (R = *i*PrMe₂Si) with chlorides of Ag^I, Au^I, and Rh^I leads to complexes of the 5c-6π-heteropentadienide imidobisphosphalkene anion; double Cl[−] transfer from PtCl₂ and PdCl₂ to coordinated phosphalkene phosphorus atoms of *P*-diphenylphosphanyl amino phosphalkenes R₂C=PN(R')PPh₂ (R' = Me₃Si or *i*PrMe₂Si; R = *t*Bu, 1-Ada) furnishes unprecedented bis-chelate *P*-chloroylid complexes M[R₂CP(Cl)N(R')PPh₂]₂ (M = Pd, Pt); CO- and Rh^I-induced coupling of two *P*-diphenylphosphanyl amino phosphalkenes under disilylketene elimination provides trigonal-bipyramidal Rh^{III} complexes with novel tetradentate dianionic “PNP–C–PNP” ligands R₂C[P^(−)N(R')PPh₂]₂.

Keywords: ligand properties; molecular rearrangements; organophosphorus chemistry; palladium; platinum; rhodium, X-ray structure.

INTRODUCTION

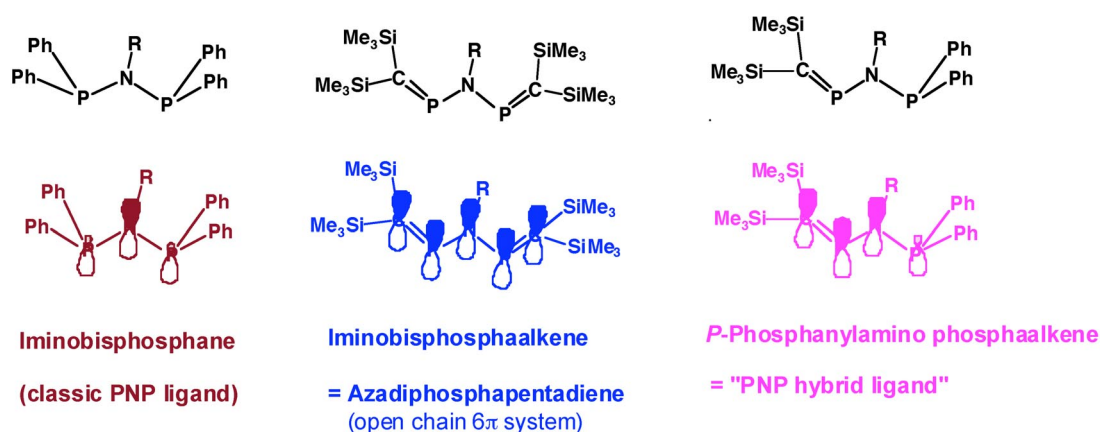
The invention of an innovative ethene oligomerization catalyst a decade ago by D. F. Wass et al. [1] using chromium chlorides, an *ortho*-methoxy-substituted derivative of the classic “PNP (diphosphinoamine) ligands” (Ph₂P)₂NR, and methylaluminum oxide (MAO), led us to search for yet unknown, i.e., patent-free, classes of PNP ligands that might be useful tools in catalysis.

In 2000, unexpected observations in course of some reactions of *P*-phosphanyl phosphalkenes with sulfur, selenium, and tellurium [2] had led us to synthesize the first chalcogeno-bisphosphalkenes (R₂C=P)₂E (R = Me₃Si; E = O, S, Se) [3,4]. When at a regional “Ph.D. student seminar” in 2002, the structure determination of the chelate complex [Mo(CO)₄(R₂C=P)₂Se] was presented, a colleague referred to D. F. Wass’ invention, mentioning that different from our (purely academic) selenium-bridged complex, nitrogen-bridged ligands [(Me₃Si)₂C=P]₂NR' (Scheme 1, center) would be fair candidates for catalytic applications.

Since ligands of the type (R₂C=P)₂NR' (R = Me₃Si) had not yet been reported in literature, our group took the challenge to develop a synthetic pathway. A couple of years later, when it appeared that

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Scheme 1 Classic and P=C-unsaturated PNP ligands.

we might never isolate a stable single-crystalline compound of the type $(R_2C=P)_2NR'$, we added the "mixed" or "hybrid" ligand system $R_2C=PN(R')PR''_2$ to our program. The very unusual properties of the latter came to light after 2008 [5], when we were still in stage of repeated crystal drawing experiments with the first of our "symmetric" ligands of type $(R_2C=P)_2NR'$ with bulkier silyl groups ($R = iPrMe_2Si$) [6].

In this overview, we present: (1) Synthesis and structures of PNP ligands $(R_2C=P)_2NR'$, and reactions of the *N*-silylimino-bridged bis-phosphaalkene $(R_2C=P)_2NSiMe_3$ ($R = iPrMe_2Si$) with chlorides of Ag^I , Au^I , and Rh^I ; (2) Unprecedented bis-chelate *P*-chloroylid complexes $M[R_2CP(Cl)N(R)PPh_2]_2$ ($R = Me_3Si$, $R' = tBu$, 1-Ada) from mono-unsaturated PNP ligands $R_2C=PN(R')PPh_2$ with $PtCl_2$ and $PdCl_2$; (3) CO- and Rh^I -induced coupling of two ligands of the type $R_2C=PN(R')PPh_2$ under disilyl-ketene elimination providing Rh^{III} complexes of novel tetradentate dianionic ligands with the topology $Ph_2PN(R')P^{(-)}-CR_2-P^{(-)}N(R')PPh_2$.

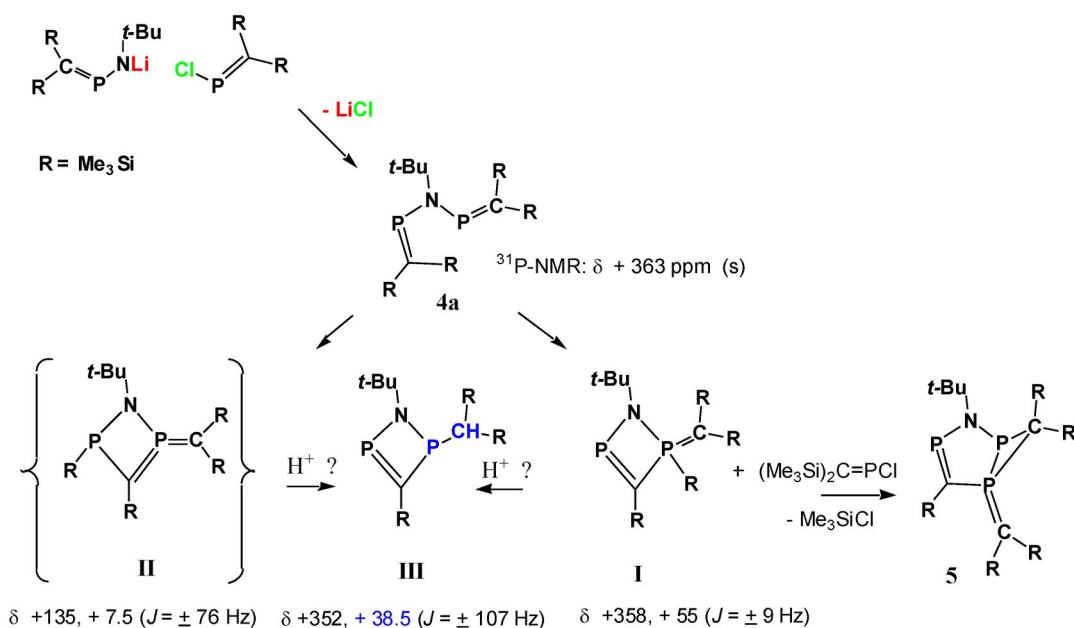
NITROGEN-BRIDGED BIS-PHOSPHAALKENES

Drawbacks and successes in $(R_2C=P)_2NR'$ synthesis

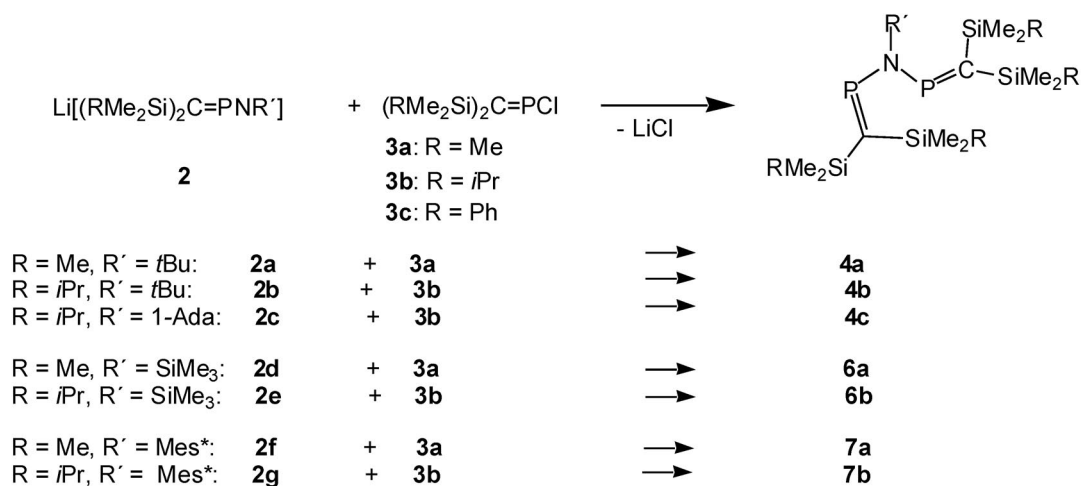
N-Alkylimino-bridged bisphosphaalkenes (*N*-alkyl-2,4-diphospha-3-azapentadienes) $[Ph(Me_3Si)C=P]_2N(nC_3H_7)$, the first *N*-alkyl-2,4-diphospha-3-azapentadiene detected in solution by ^{31}P NMR, is thermally unstable [7]. For related compounds $[(Me_3Si)_2C=P]_2NR$, it was necessary to turn to alkali metal chloride elimination procedures based on the deprotonation of aminophosphaalkenes **1** such as $(Me_3Si)_2C=PN(H)tBu$ [8], followed by coupling of the in situ-prepared lithium derivatives **2** $Li[(Me_3Si)_2C=PNR]$ [9–11] with the *P*-chlorophosphaalkene $(Me_3Si)_2C=PCl$ (**3a**).

Since it turned out that insufficient stability of the product **4a** from $Li[(Me_3Si)_2C=PNtBu]^-$ (**2a**) with **3a** precluded its isolation (Schemes 2 and 3) [6], precursors with bulkier silyl groups at carbon were developed. These reactions are based on the new starting material $(iPrMe_2Si)_2C=PCl$ (**3b**) [6,12]. To improve crystallization properties of thermolabile products, *N*-1-adamantyl derivatives and the new *P*-chlorophosphaalkene $(PhMe_2Si)_2C=PCl$ (**3c**) were also used (Scheme 3) [6].

Metalated aminophosphaalkenes $Li[(RMe_2Si)_2C=PNtBu]$ (**2a**: $R = Me$; **2b**: $R = iPr$) react with the corresponding *P*-chlorophosphaalkenes at low temperatures furnishing solutions of the desired *t*-butylimino-bridged bis-phosphaalkenes **4a**, **4b** (Schemes 2 and 3) which exhibit singlet signals in ^{31}P NMR [6]. Raising the temperatures to 0 °C and above leads to formation of products from rearrangement reactions indicated by the occurrence of one or more "growing" ^{31}P NMR signals that appear as AX-type patterns.



Scheme 2 Formation and rearrangements of the bisphosphaalkene **4a**.



Scheme 3 Formation of symmetric alkyl-, silyl-, and arylimino-bridged bisphosphaalkenes.

In the case of $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]\text{N}t\text{Bu}$ (**4a**), one of the new AX patterns ($\delta^{31\text{P}} = 358.4$ and 55.1 , $J = 9$ Hz; species **I** in Scheme 2) indicates the presence of a phosphalkene-type $^{31\text{P}}$ nucleus coupling with a tri- or tetra-coordinated phosphorus atom. The second AX pattern ($\delta^{31\text{P}} = 135.0$ and 7.7 , $J = 76$ Hz; species **II**) involves two nuclei that are both *not* parts of phosphalkene functions, and a third AX pattern ($\delta^{31\text{P}} = 351.9$ and 38.5 , $J = 107$ Hz; species **III**) has to be assigned to another $^{31\text{P}}(\text{=C})$ nucleus coupling with another tri- or tetra-coordinated phosphorus atom that is part of a $^{31\text{P}}\text{-C-H}$ function ($^2J_{\text{PH}} = 13$ Hz) [6].

Addition of **3a** to a reaction mixture containing decomposing **4a** leads to consumption of **4a** and of rearranged species **I** with formation of a new compound **5** exhibiting an AMX pattern in $^{31\text{P}}$ NMR

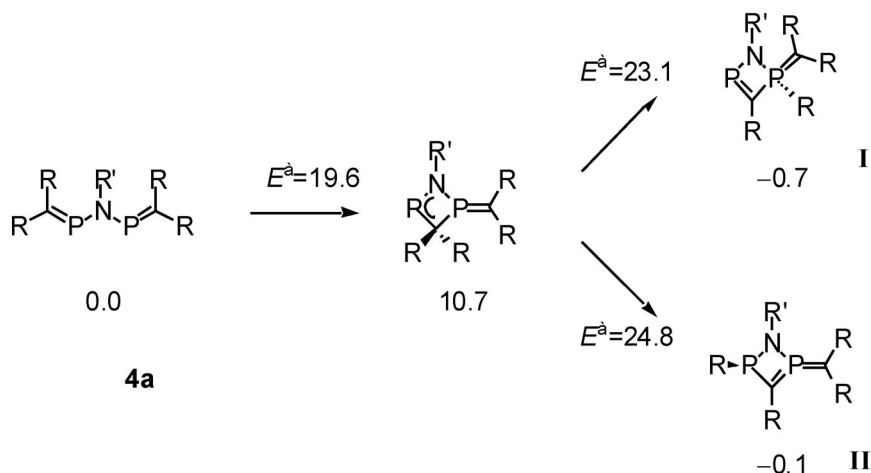


Scheme 4 Formation of bicyclic **5** from **2a** and **3a**.

($\delta^{31}\text{P} = 330.8, -17.1$ and -24.3), involving one $^{31}\text{P}(=\text{C})$ phosphorus atom coupling with two inequivalent “non-P=C” ^{31}P nuclei in a diphosphirane unit. Compound **5** is also formed from the straightforward 1:2 reaction of **2a** with **3a**. Single crystals of **5** were isolated from the latter reaction (Scheme 4) [6].

According to an X-ray crystal structure determination, **5** is a bicyclic C_3NP_3 species containing an endocyclic P=C bond [1.679(3) Å] “in conjugation” with an exocyclic ylidic $\text{P}^{(+)}\text{-C}^{(-)}(\text{SiMe}_3)_2$ function [1.688(3) Å] involving one of the two bridgehead phosphorus atoms that form a diphosphirane unit [6]. The motif of a (p-p) π P=C double bond in conjugation with an exocyclic ylidic $\text{P}^{(+)}\text{-C}^{(-)}$ bond from compound **5** is also present in species **I** (Scheme 2).

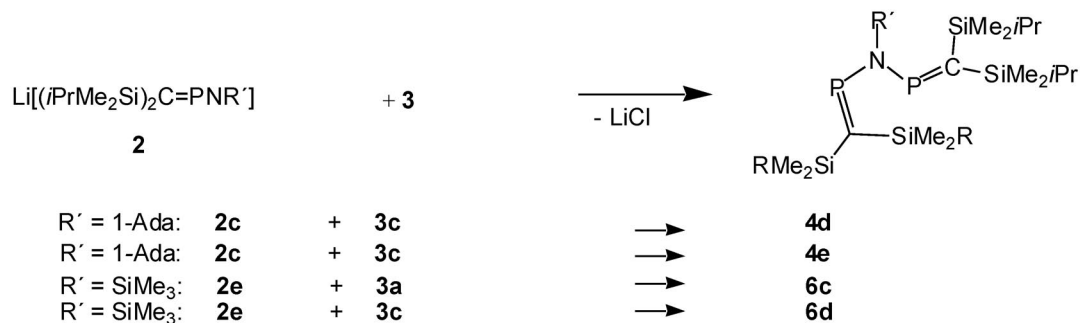
The formation of rearranged products **I** and **II** from **4a** involves trimethylsilyl group migration, and compound **III** can be assigned as a product from protolytic P–Si bond cleavage of **I** and/or **II**, followed by proton migration to the basic ylid carbon atom. Concerning silyl group migration from the decomposition of compound **4a** the energies of transition states and products were calculated (Scheme 5; energies in $\text{kcal}\cdot\text{mol}^{-1}$) [6]. **4a** and the experimentally observed species **I** and **II** are very similar in energy; preceding to silyl group migration a cyclic intermediate with the P–C–P connectivity is formed through bond formation from a nucleophilic carbon atom with an electrophilic phosphorus atom.



Scheme 5 Cyclization pathway of the *t*butyliminobisphosphaalkene **4a** at the MPW1K/6-311+G**/B3LYP/6-31+G* level of theory (R = SiMe₃, R' = *t*Bu) [5,9].

In the case of *t*butylimino-bisphosphaalkene **4b** (with only *i*PrMe₂Si groups at carbon) the rate of silyl migration is significantly smaller than in the case of **4a**, but isolation of pure **4b** was still precluded by decomposition.

Low-temperature single-crystal growing was enabled by switching to the corresponding *N*-1-adamantyliminophosphaalkene anion **2c**, thus furnishing *N*-1-adamantylimino-bisphosphaalkene **4c**, which was structurally characterized as solid tetrahydrofuran (THF) solvate at low temperature. Reacting the (*i*PrMe₂Si)₂C-containing anion **2c** with the chlorophosphaalkenes **3a** and **3c** resulted in the formation of the unsymmetric species **4d** and **4e** (Scheme 6), which were detected in the course of the reactions with the aid of their ³¹P NMR AM patterns, but decomposed on attempted isolation.



Scheme 6 Formation of asymmetric alkyl- and silylimino-bridged bisphosphaalkenes.

Compound **4c** exhibits in solution a ³¹P NMR singlet resonance signal, but in the solid the two P=C moieties of each independent molecule are inequivalent. Different adamantyl group orientations relative to the common “helically distorted” CPNPC skeleton in solid **4c** of the three independent molecules coincide with different contacts to the solvating THF molecules (Fig. 1).

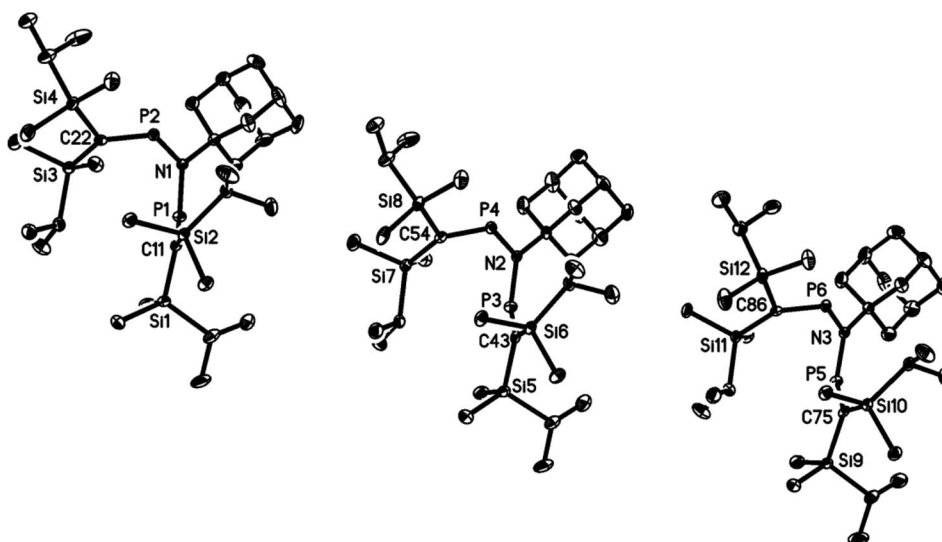
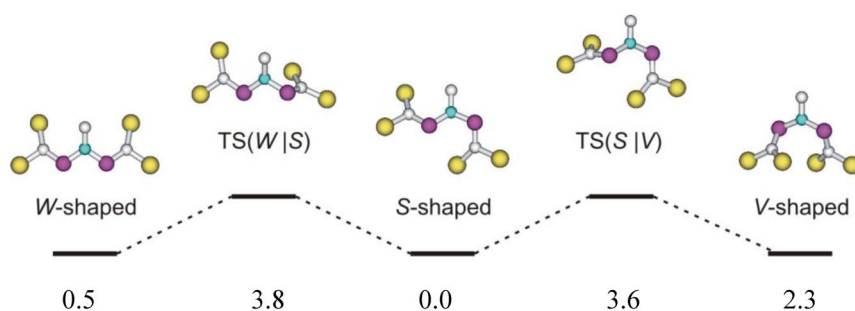


Fig. 1 Arrangement of the three independent molecules of THF-solvated **4c**. Selected bond lengths [Å] and angles [°] of molecule #1: P1–C11 1.6670(3), P2–C22 1.6606(3), P1–N 1.712(2), P2–N 1.737(2), C23–N 1.524(13), P1–N–P2 126.77(13), P1–N–C23 119.36(18), P2–N–C23 113.72(17), C11–P1–N–P2 –40.9(2), C22–P2–N–P1 55.6(2). Hydrogen atoms are omitted for clarity. Atoms are drawn as 50 % thermal ellipsoids.

The conformations of the nonplanar C–P–N(R)–P'C' backbones (in molecule #1: torsion angles C11–P1–N–P2 and C22–P2–N–P1) of the three independent molecules are similar [molecule #1: $-40.9(2)$ and $-55.6(2)^\circ$, molecule #2: $-41.1(2)$ and $-54.2(2)^\circ$, molecule #3: $-48.4(2)$ and $-48.5(2)^\circ$], the P=C moieties being directed out of the NP₂ planes about half way between orthogonal and planar. Within the nonplanar CPNPC moieties, P=C (1.664–1.670 Å) and P–N bonds (1.712–1.737 Å) appear essentially undisturbed by conjugative effects. In this respect, **4c** is comparable to the 2-[6-bis(trimethylsilyl)amino]pyridylimino- and *N*-trimethylsilylimino-bridged bisphosphaalkenes (see below) [12,13].

Conformations of 2,4-diphospha-3-azapentadienes were studied by density functional theory (DFT) methods.

At the B3LYP/6-31+G* level three minima of very similar energy have been found on the potential energy surface of the parent [(H₃Si)₂C=P]₂NCH₃ system. They are representing *S*-, *W*-, and *V*-shaped C=P–N–P=C moieties (Scheme 7).



Scheme 7 [(H₃Si)₂C=P]₂NCH₃ rotamers and their connecting transition structures; relative energies (in kcal·mol⁻¹) at the B3LYP/6-31+G* level [6].

All the B3LYP/6-31+G* optimized structures of the [(R₃Si)₂C=P]₂N(SiR₃) molecules (R: H, Me) were nonplanar. For R = H, the minima were located within a 0.9 kcal·mol⁻¹ energy range, including the *S*- and *W*-shaped forms (Scheme 7).

The fact that several conformers exist with similar energies on the rotational potential energy surface is an indication of their low energy interconversion. For R = Me, only the nonsymmetrical *S*-shaped structure could be optimized, in agreement with the X-ray structure (see below). Similar behavior was observed in the case of the di(phosphavinyl)ether analogues [4], indicating the effect of steric encumbrance in determining the final structure. The particular nonplanar distortions of the solid compounds presented in this review will all have steric grounds [6,12,13].

N-Silyl-bridged bisphosphaalkenes

[(Me₃Si)₂C=P]₂NSiMe₃ (**6a**), made from Li[(Me₃Si)₂C=PNSiMe₃] (**2d**) with **3a**, is a thermally unstable oil [12] that cannot be distilled. The reactions of the bulkier deprotonated aminophosphaalkene Li[(*i*PrMe₂Si)₂C=PNSiMe₃] (**2e**) with *P*-chlorophosphaalkenes **3a**, **3b**, and with (PhMe₂Si)₂C=PCl (**3c**) at temperatures below -40°C furnish solutions of more stable *N*-trimethylsilylimino-bridged bisphosphaalkenes **6b–d** (Schemes 3 and 6).

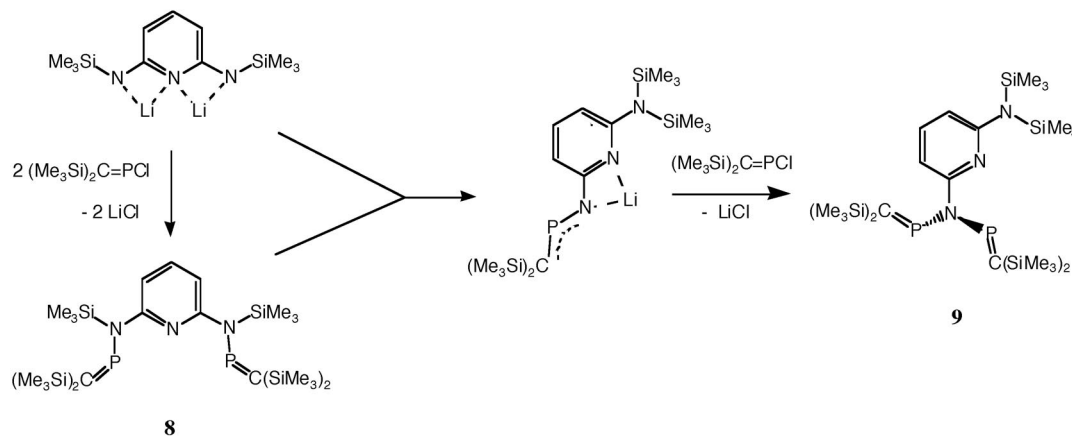
The ³¹P NMR spectra of the “symmetric” compounds **6a** and **6b** exhibit single resonances, whereas the mixed substituted compounds **6c** and **6d** show AM patterns [**6c**: $\delta^{31}\text{P} = 365.4$ and 361.7 ppm, $^2J_{\text{PP}} = 19.6$ Hz; **6d**: $\delta^{31}\text{P} = 370.6$ and 365.6 ppm, $^2J_{\text{PP}} = 19.7$ Hz]. The NMR equivalence of the two ³¹P nuclei of **6a** and **6b** in solution would be consistent with either a symmetric structure or with a less symmetric ground-state conformation (see Scheme 7), which still allows free rotation of the P–N bonds on the NMR time scale at room temperature in solution [12].

The X-ray crystal structure determinations of symmetric **6b** and unsymmetric **6c** at low temperature reveal the presence of helically distorted structures with two inequivalent P=C groups (torsion angles C11–P1–N–P2 and C22–P2–N–P1 -52° and -45°) The P=C and P–N bond distances do not indicate significant conjugation within the C=P–N–P=C moieties [6,12].

N-Aryl-bridged bisphosphaalkenes

A ^{31}P NMR study on *N*-Mes*-bridged bisphosphaalkenes revealed that the reaction mixtures from metalation of $(\text{RMe}_2\text{Si})_2\text{C}=\text{PN}(\text{H})\text{Mes}^*$ (R = Me or R = *i*Pr) with LDA, followed by reactions of the lithium salts with chlorophosphaalkenes (**2f** with **3a** and **2g** with **3b**; Scheme 3), each exhibit in ^{31}P NMR a singlet signal accompanied by an AM pattern of $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{NMes}^*$, **7a**: $\delta = 352$ (s), 329 (d) and 323 (d) ppm, $^2J_{\text{PP}} = 7.4$ Hz and of $[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{NMes}^*$, **7b**: $\delta = 352$ (s), 332 (d) and 326 (d), $^2J_{\text{PP}} = 13.5$ Hz [6] together with another small singlet assignable to $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{O}$ (353 ppm) and $[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{O}$ (354 ppm) [4]. Apparently, the bulky NMes* groups enhance the rotational barrier(s) of rotameric interconversion between symmetric structures **7a-sym** or **7b-sym** and unsymmetric *S*-shaped **7a-asym** or **7b-asym**.

In the context of syntheses of pyridine-bridged bidentate phosphalkene and iminophosphane ligands such as compound **8**, the *N*-pyridylimido-bridged bisphosphaalkene **9** (an isomer of **8**) was detected and structurally characterized [13]. Compound **9** adopts a nonplanar *S*-shaped structure of the heteropentadiene moiety (Schemes 7 and 8). In contrast to **4c**, **4d**, and **6b**, **6c**, the P=C functions of the pyridylimino derivative **9** are directed approximately orthogonal to the CNP_2 plane. According to its AM pattern ($\delta^{31}\text{P} = 340.4$ and 328.9 ppm) in solution ^{31}P NMR at -60°C , **9** also adopts an unsymmetric structure in solution. Equilibration of the two phosphorus nuclei on the ^{31}P NMR timescale takes place at room temperature ($\delta^{31}\text{P} = 336.1$ ppm) [13].

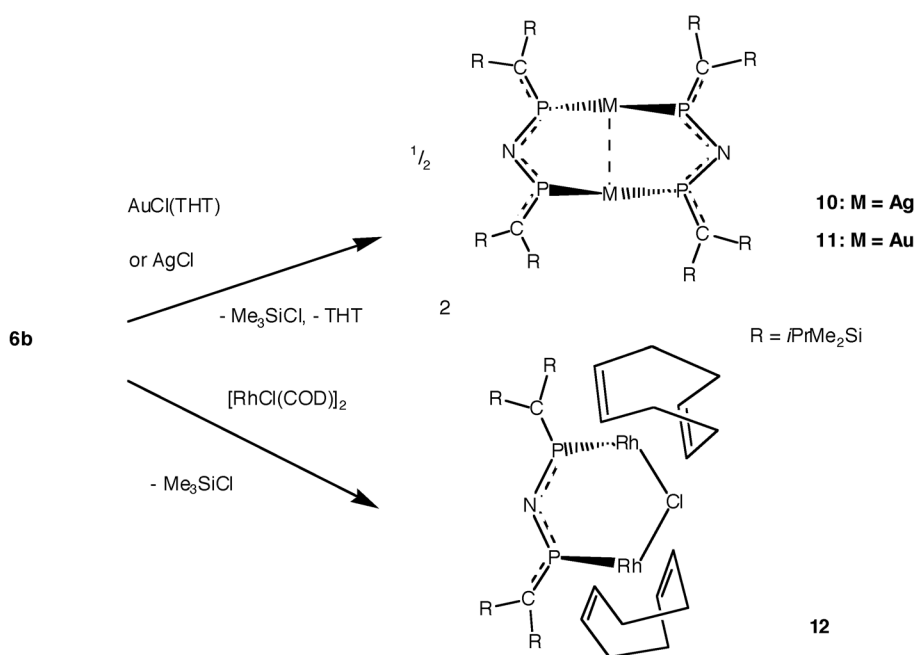


Scheme 8 Formation of the *N*-pyridylimido-bridged bisphosphaalkene **9** [9,13].

The reaction of **9** with nickel tetracarbonyl leads to a product that exhibits according to NMR data η^2 -coordination of both PC functions, one of them with a $\text{Ni}(\text{CO})_2$ acceptor (that appears to be also in contact with the pyridine nitrogen atom), and the other one with a $\text{Ni}(\text{CO})_3$ acceptor [13].

Complexes of the imido-bridged bisphosphaalkene anion

2,4-Diphospha-3-azapentadienyl anions were unknown until recently, when the *N*-silylimino-bridged bisphosphaalkene **6b** became synthetically accessible. Experiments on the reactivity of **6b** with AgCl , with $\text{AuCl}(\text{THT})$, and with $[\text{RhCl}(\text{COD})]_2$ allowed the observation of Si–N bond cleavage under very



Scheme 9 Reactions of **6b** with chlorides of Ag^I, Au^I, and Rh^I leading by N–Si cleavage to metal complexes of the imidobis(phosphaalkene) anion.

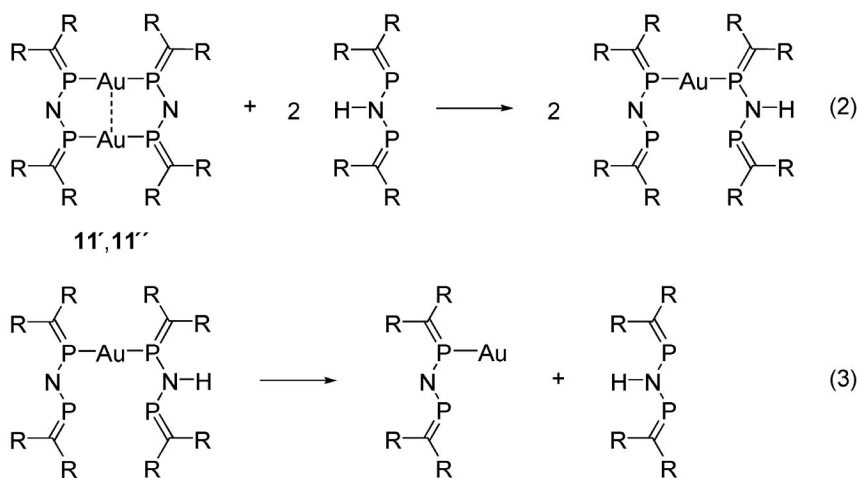
mild conditions by chlorotrimethylsilane elimination furnishing the dinuclear complexes $\{\text{M}[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{N}\}_2$ (**10**: M = Ag; **11**: M = Au) and $\text{Rh}_2\text{Cl}\{[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{N}\}(\text{COD})_2$ (**12**). X-ray crystal structure determinations of **11** and **12** reveal the presence of 2,4-diphospha-3-azapentadienyl anions as *P,P*-coordinated bidentate ligands (Scheme 9) [12].

Yellow **11** [$d(\text{Au-Au}) = 3.02 \text{ \AA}$] is related to the insoluble white bis(diphenylphosphanyl)amide gold complex $[\text{Au}(\text{Ph}_2\text{P})_2\text{N}]_2$ made first by Schmidbaur et al. and Laguna et al. [14,15]. The dinuclear Rh^I complex **12** is related to $[\text{RhCl}(\text{COD})]_2$ [16], containing as bridging ligands one chloride anion and one $[(i\text{PrMe}_2\text{Si})_2\text{C}=\text{P}]_2\text{N}^-$ anion. The selective formation of **12**, which does not react with another equivalent of **6b**, is due to steric protection of complex **12** by the sterically crowded PNP anion [12]. The PN distances in **11** and **12** are about 10 pm shorter than those in the uncharged ligand **6b**. Since the P=C distances are unaffected or even slightly shorter in the complexes, compared with ligand **6b** [12], the large increase of PN bond strength suggests the presence of a highly delocalized heteropentadienide 6π C–P–N–P–C system.

DFT calculations on imido-bridged bisphosphaalkenes

DFT calculations on 2,4-diphospha-3-azapentadienes [12] reveal that, while the $(\text{C}=\text{P})_2\text{NSi}$ moieties in compounds $[(\text{R}_3\text{Si})_2\text{C}=\text{P}]_2\text{N}(\text{SiR}_3)$ are nonplanar even with the small R = H substituent, the $(\text{C}=\text{P})_2\text{NSi}$ moiety in the corresponding imide anion $[(\text{R}_3\text{Si})_2\text{C}=\text{P}]_2\text{N}^-$ is planar in the case of R = H. This planarity, together with the short PN distances, indicates that the stabilization of the anion by delocalization exceeds that of the amine. Indeed, the second-order perturbational analysis of the Fock matrix in the NBO basis provides $37.0 \text{ kcal}\cdot\text{mol}^{-1}$ stabilization energy between the nitrogen lone pair and each $\pi(\text{P}=\text{C})^*$ orbital, exceeding the stabilization energy for $[(\text{H}_3\text{Si})_2\text{C}=\text{P}]_2\text{NH}$ ($19.7 \text{ kcal}\cdot\text{mol}^{-1}$) significantly. $[(\text{Me}_3\text{Si})_2\text{C}=\text{P}]_2\text{N}^-$ has an *S*-shaped and an energetically nearly identical, slightly nonplanar *W*-shaped [still with $33.0 \text{ kcal}\cdot\text{mol}^{-1} n \rightarrow \pi(\text{P}=\text{C})^*$ interaction energy] structure.

The energetic consequences of the aurophilic interaction were estimated using the isodesmic reactions 2 and 3 in Scheme 10. The energy of the reaction 2 is remarkably large (27–30 kcal·mol⁻¹ at different levels of theory), comparable with the Au–P binding energy (30–34 kcal·mol⁻¹) [9,12], which was determined as the reaction energy of eq. 3. It is important to note that this unusually large interaction energy [17] is only partly attributable to the aurophilicity because the extended π -conjugation in the dimeric complex (see the molecular orbital, MO, representing π -delocalization in Fig. 2) also contributes to the overall stabilization of this reaction.



Scheme 10 Isodesmic reactions (**11'**: R = H, **11''**: R = SiH₃, see text).

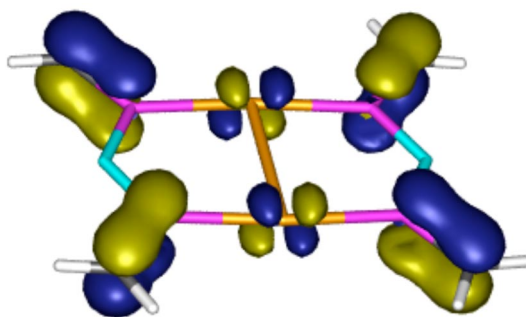


Fig. 2 The highest occupied molecular orbital (HOMO)-3 of the gold complex **11'** [9,12].

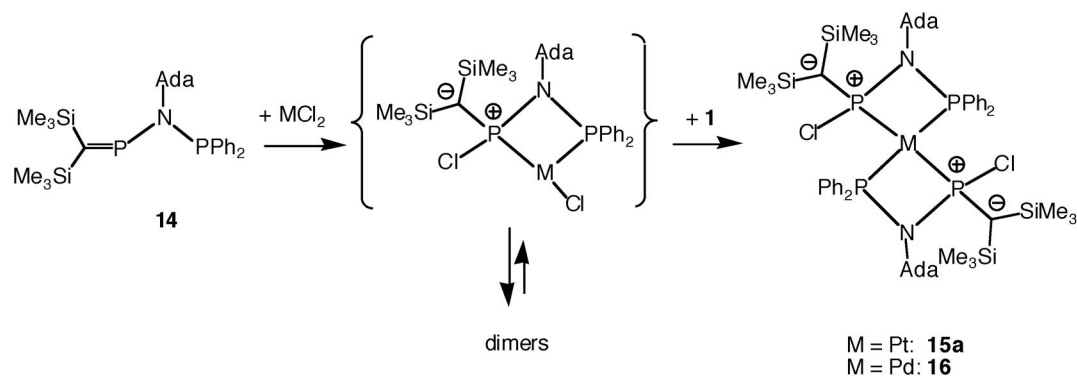
***P*-(PHOSPHANYLAMINO)PHOSPHAALKENES**

Synthesis of *P*-(phosphanylamino)phosphaalkenes (Me₃Si)₂C=P–N(R)–PR'₂

Synthetic experiments on *P*-(phosphanylamino)phosphaalkene ligands (Scheme 1, right) showed that (Me₃Si)₂C=PCl (**3a**) reacts with in situ-prepared lithium iminophosphanides Li[Ph₂PNR] [18,19], to give the *P*-(phosphanylamino)phosphaalkenes (Me₃Si)₂C=PN(R')PPh₂ (**13**: R' = *t*Bu; **14**: R' = 1-Ada) [5] whereas the reaction of the 1-aza-2-phosphaallyl anion [(Me₃Si)₂C=PN*t*Bu]⁻ [8–10] with R₂PCl leads preferentially by P–P bond formation to the undesired phosphanylphosphorane isomers (Me₃Si)₂C=P(=N*t*Bu)PR₂ [9,11]. The molecular structure of solid **14** was determined by X-ray crystallography [5].

Platinum and palladium bis-*P*-chloroylid PNP chelate complexes

After adding a solution of the ligand **14** in an aprotic solvent to an equimolar amount of the PtCl₂ cyclooctadiene (COD) complex suspended in dichloromethane, ³¹P NMR spectra of the orange solution indicate the complete consumption of **14** [AX pattern, δ = +373.5, +37.7 ppm, ²J_{PP} = ±12.1 Hz] and the formation, depending on the reaction conditions, of up to three new species exhibiting AX patterns that all appear in the chemical shift range of +60 to +15 ppm, showing couplings ²J_{PP} and ¹J_{PtP}. Sets of further weak ³¹P NMR signals are assigned to an A₂M₂ pattern [δ = +71, +42; ²J_{PP} = ±21 Hz], and tentatively to higher-order multiplets, partially hidden by platinum satellites of the stronger signals. An X-ray structure determination revealed that the compound with the A₂M₂-like pattern is a very unusual 1:2 chelate complex **15** of PtCl₂ with ligand **14** [5]. When 2 equiv of ligand **14** was used to favor the formation of the 1:2 complex, ligand **14** and the coordinated species giving rise to AX patterns were consumed within several days according to ³¹P NMR, that showed, inter alia, overlapping signals of multiplets including the A₂M₂ pattern of **15** as a major product (Scheme 11).



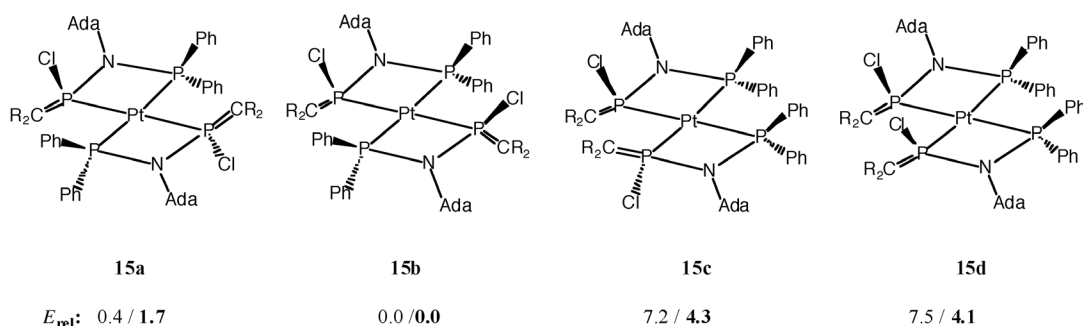
Scheme 11 Reactions of **14** with Pt and Pd dichlorides.

The X-ray crystallographic structure determination confirmed that the solid **15a** is a complex of the composition [PtCl₂(**14**)₂] (as a 1:1 pentane solvate) with tetra-coordinated platinum surrounded by two *trans*-oriented *P,P'*-chelating ligands in a square-planar fashion, but is uniquely different from usual cationic platinum bis-chelates of the type {[PtL₄]²⁺(X⁻)₂}; there are covalent bonds between the phosphorus atoms of the hypothetical cationic moiety [Pt(**14**)₂]²⁺ and the two chlorine atoms. The related 1:1 reaction of ligand **14** with PdCl₂(COD) provided a few crystals of the solid pentane-solvated palladium complex **16**, which is isotypic to **15a** (Scheme 11) [5].

The addition of two chloride ions to the phosphoalkene phosphorus atoms of the hypothetical cationic moiety *trans*-[M(**14**)₂]²⁺ (M = Pd, Pt) leads formally to two four-coordinated stereogenic phosphorus atoms P(C)(N)(Cl)(M) in the resulting molecular complexes. Complexes **15a** and **16** consist of centrosymmetric molecules with *trans*-orientation of the two types of phosphorus atoms around palladium and platinum; the chlorine atoms are *anti*-oriented, one above and below the square plane (*R,S*). The alternative (*R*)- or (*S*)-configurations at phosphorus, together with the intrinsic possibility of *cis*- or *trans*-*P,P'*-chelate ligand orientations around square planar platinum or palladium, mean that up to four stereoisomers **15a–d** (or **16a–d**) are possible (Scheme 12).

Variation of the reaction conditions and of the solvent mixtures for crystallization allowed the isolation of a few single crystals of two further isomers **15b** and **15c** (Scheme 12) of the platinum complex. Solids **15b** and **15c** exist as racemic mixtures of (*R,R*) and (*S,S*) enantiomers.

Bond distances and angles of **15b** and **15c** show no significant differences to those of **15a**. In all three isomers, each bidentate ligand **14** unit has acquired one chlorine atom bonded to a (formerly)

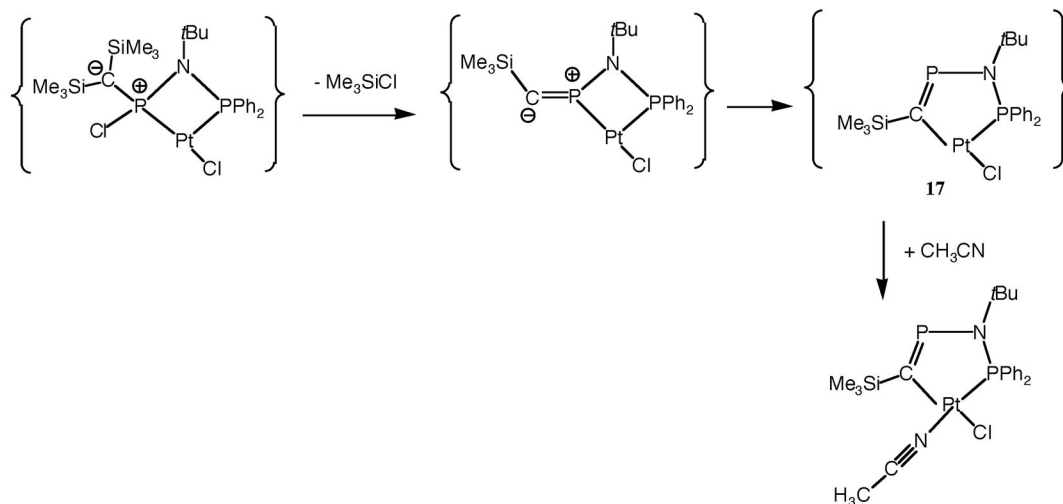


Scheme 12 Relative energies of model complexes related to isomers **15a–d** ($R = \text{Me}_3\text{Si}$) for ligand $(\text{H}_3\text{Si})_2\text{C}=\text{PN}(\text{Me})\text{PMe}'_2$, and for $[(\text{H}_3\text{Si})_2\text{C}=\text{PN}(\text{Me})\text{PPh}'_2]$ in boldface; in $\text{kcal}\cdot\text{mol}^{-1}$ [5,9].

phosphaalkene phosphorus atom. This phosphorus atom acts as a σ -donor towards platinum and as a σ -acceptor towards the chlorine atom, i.e., the phosphaalkene phosphorus atom has *inserted* in a carbene-like fashion into the Pt–Cl bond. In order to understand the remarkable electrophilicity of the *P*-(phosphanyl-amino)phosphaalkene ligands, model calculations based on DFT have been performed [5,9]. On the basis of these results, the known strong electron acceptor behavior of the $\pi^*(\text{C}=\text{P})$ unit [5] is remarkably increased by the silyl groups (the LUMO energy drops). The effect is corroborated by considering phenyl groups at the $\sigma^3, \lambda^3\text{-P}$ atom instead of methyl groups. Further enhancement of the electrophilicity is achieved for the entire ligand by the metal complexation [5].

Side products from chlorotrimethylsilane elimination

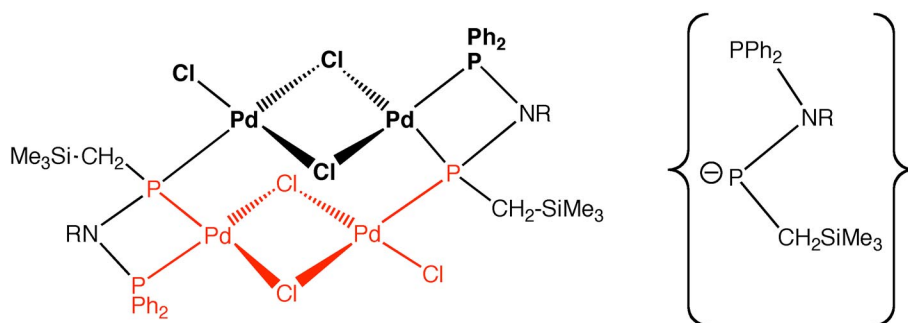
The coordination of ligand **13** to platinum dichloride in dichloromethane solution competes with a reaction that involves elimination of chlorotrimethylsilane, furnishing as a yellow solid the cyclic *C*-metallophosphaalkene **17**, which exists according to NMR as an isomeric mixture of Cl-bridged dimers. Crystallization of this material from acetonitrile led to a monomeric acetonitrile complex **18** (Scheme 13) that was studied by X-ray crystallography. Complex **18** is expected to be formed from a



Scheme 13 Proposed chlorosilane elimination pathway leading from ligand **13** and PtCl_2 to complex **18**.

P-chloroylide complex that may undergo β -elimination of Me_3SiCl , leading to a kind of silyl(phosphanyl)carbene intermediate. From this species, $\text{P} \rightarrow \text{C}$ migration of platinum can lead to the unusual *C*-metalated cyclic phosphalkene that crystallizes as acetonitrile complex **18** [20].

In the course of the attempts to isolate the palladium complex **16** and related species based on ligands **13** and **14**, we also isolated a unique tetranuclear hexachloropalladium complex **19** consisting of two planar Pd_2Cl_3 moieties connected by two of the bidentate anionic hydrogenated phosphane/phosphido ligands $[\text{Ph}_2\text{P}-\text{N}(\text{tBu})\text{P}^{(-)}\text{CH}_2\text{SiMe}_3]^-$ [20]. Each phosphido function bridges two Pd atoms from the two different planar Pd_2Cl_3 moieties, and the PPh_2 groups play their usual role as terminal ligands. The anion (Scheme 14, right) is related to the *C*-coordinated anionic ligand in the platinum complex **17** by addition of two hydrogen atoms to the “carbene” carbon atom (of the “carbene” intermediate, see Scheme 13).

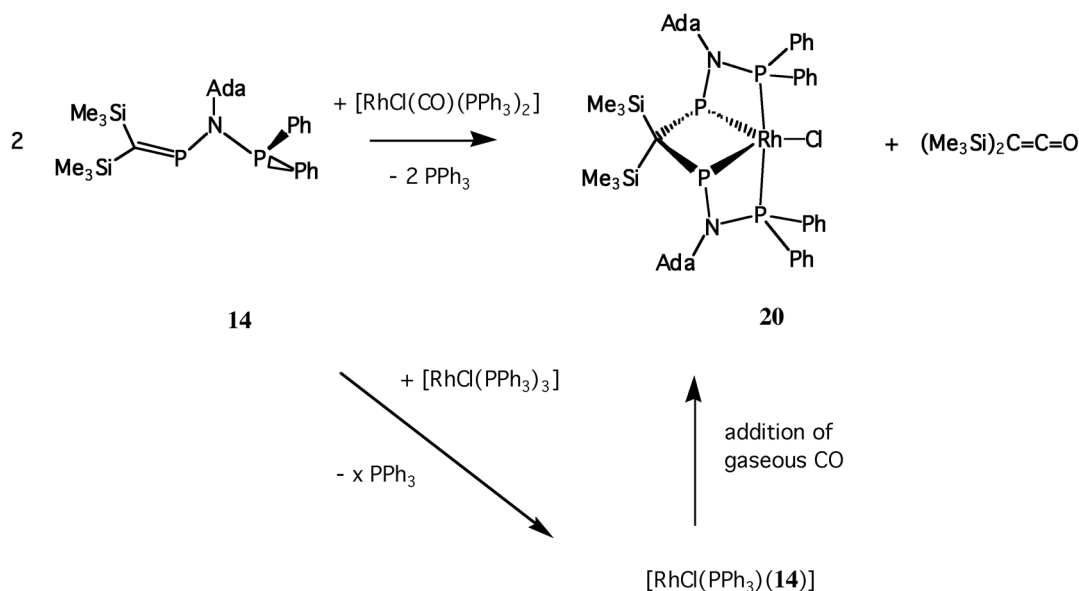


Scheme 14 Left: topology of complex **19**; right: an anionic ligand in **19**; R = *t*Bu [20].

CO- and Rh^{I} chloride-induced *P*-(phosphanyl-amino)phosphaalkene ligand coupling by expulsion of bis(trimethylsilyl)ketene

In an attempt to extend the concept of *P*-chloroylid chelate complex formation from divalent palladium and platinum to a related metal, that can offer only one chlorine atom for M-*P* chlorotropy, Rh^{I} chloride complexes were chosen as substrates for reactions of *P*-(phosphanyl-amino)phosphaalkene ligands **13** and **14**. Since, fortuitously, the complex $\text{RhCl}(\text{CO})\text{PPh}_3$ was already available in our lab before the beginning of the experiments, it was chosen as first substrate for a reaction with ligand **14**. This experiment led to the unexpected observation of a trigonal-bipyramidal Rh^{III} chloro complex **20** of the novel tetradentate dianionic ligand $\text{R}_2\text{C}[\text{P}^{(-)}\text{N}(\text{R}')\text{PPh}_2]_2$ (Scheme 15) [20a,b]. Adding ligand **14** to $\text{RhCl}(\text{PPh}_3)_3$ leads, according to ^{31}P NMR spectra, under liberation of PPh_3 to $[\text{RhCl}(\text{PPh}_3)(\mathbf{14})]$. The latter complex is completely consumed after bubbling gaseous CO through this reaction mixture, providing the unusual Rh^{III} complex **20** under formation of the ketene $(\text{Me}_3\text{Si})_2\text{C}=\text{C}=\text{O}$ that was identified by the ^{13}C NMR resonance of its carbonyl group.

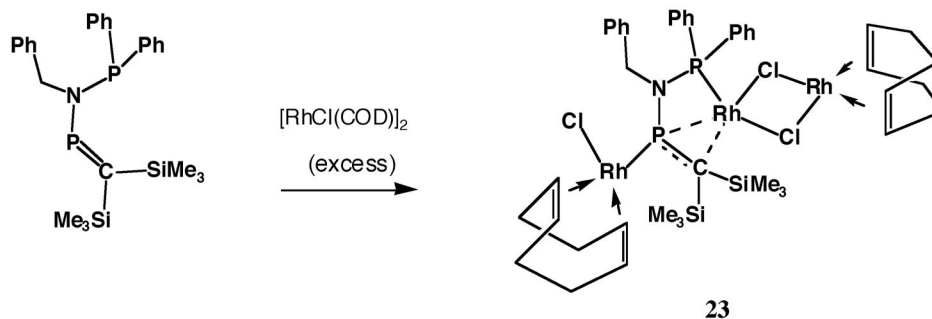
Monitoring the related reaction of the *t*BuN-bridged ligand **13** with $\text{RhCl}(\text{CO})\text{PPh}_3$ by ^{31}P NMR allowed us to detect a transient species through its highly complex ABCDX pattern that is within several hours “consumed” in favor of the multiplet of final product **21** [20]. The four magnetically different ^{31}P nuclei in the transient complex, which is a precursor to **21**, allow us to speculate about a structure that is basically related to the above-mentioned molecular platinum bis-chloroylid chelate (2:1) complexes. There is, however, in the rhodium case only one chlorine atom available to migrate to one of the two PNP ligands, generating a *P*-chloroylid unit. The nucleophilic carbon atom of this chloroylid unit can attack the electrophilic phosphorus atom of the $\text{P}=\text{C}$ moiety from the other coordinated PNP ligand, leading to the $\text{N}-\text{P}-\text{C}(\text{SiMe}_3)_2-\text{P}[\text{C}(\text{SiMe}_3)_2]-\text{N}$ connectivity. Transfer of the new ylidic (terminal) $\text{C}(\text{SiMe}_3)_2$ group to CO will lead to the final products **21** and $(\text{Me}_3\text{Si})_2\text{C}=\text{C}=\text{O}$. This mechanistic hypothesis will offer a rewarding challenge for calculations. The use of a ligand with bulkier silyl



Scheme 15 CO-induced ligand coupling with expulsion of a disilylketene molecule.

groups, $(i\text{PrMe}_2\text{Si})_2\text{C=PN(Ph)PPh}_2$, in an NMR scale experiment showed that the reaction with $\text{RhCl(CO)}_2\text{PPh}_3$ proceeds much slower than in the case of ligands **13** and **14**, but a “coupled” complex related to **20** and **21** can clearly be identified as reaction product.

The presence of CO is essential for the Rh^{I} -induced coupling reaction of two *P*-diphenylphosphanyl amino phosphalkenes under disilylketene elimination (Scheme 15), but additional experiments show that the presence of P=C -unsaturated PNP hybrid ligands like **13** or **14** in excess, or in mixture with PPh_3 as competing phosphane ligand, is also necessary for the unusual coupling reaction. Reactions of **13** or **14** with $[\text{RhCl(CO)}_2]_2$ in the presence of only 1 equiv of the ligand per rhodium furnish “normal” 1:1 complexes like $[\text{RhCl(CO)}(\text{13})]$ (= **22**) that was isolated in pure state [20]. NMR spectra allow us to suggest that in **22** and related complexes the P=C units of the PNP ligands are η^2 -coordinated to the rhodium atom. With excess of $[\text{RhCl(COD)}]_2$, the PNP ligand $(\text{Me}_3\text{Si})_2\text{C=PN(CH}_2\text{Ph)PPh}_2$ can bind up to three rhodium atoms with three different ligand spheres in the solid complex **23** (Scheme 16) [21].



Scheme 16 η^2 - and η^1 -coordination modes of $(\text{Me}_3\text{Si})_2\text{C=PN(CH}_2\text{Ph)PPh}_2$ in complex **23** with three RhCl units.

CONCLUSION

Nitrogen-bridged bidentate phosphalkene ligands $[(RMe_2Si)_2C=P]_2NR'$ ($R = Me, iPr, Ph$) and $(RMe_2Si)_2C=P-N(R')-PPh_2$ are now accessible by salt elimination methods from the corresponding *P*-chlorophosphaalkenes $(RMe_2Si)_2C=PCl$ with lithium imidophosphaalkenes or lithium imidophosphanes. Alkyliminobisphosphaalkenes without *bulky C-*i*PrMe₂Si* substituents undergo intramolecular rearrangements leading to mixtures of four-membered heterocycles. The stable *N*-trimethylsilylimino derivative $[(iPrMe_2Si)_2C=P]_2NSiMe_3$ **6b** reacts with AgCl and with Au^I and Rh^I chloro complexes, furnishing under N–Si bond cleavage binuclear complexes of the 6π -delocalized imidobisphosphaalkene anion $[(iPrMe_2Si)_2C=P]_2N^-$.

A striking property of *P*-(phosphanyl amino)phosphaalkene ligands $(RMe_2Si)_2C=P-N(R')-PPh_2$ is the chlorotropic formation of molecular Pd^{II} and Pt^{II} *P-metallochloroylid* complexes. Three stereoisomers of the 2:1 complex **15** were characterized by X-ray crystallography. Chlorosilane elimination from an intermediate *P*-platina-*P*-chloroylid 1:1 complex can explain the formation of the unusual *C*-platina phosphalkene complexes **17/18** and of the tetranuclear palladium complex **19**, suggesting a considerable synthetic potential of the chloroylid complexes derived from *P*-(phosphanyl amino)phosphaalkene ligands.

CO- and Rh^I-induced coupling of *P*-diphenylphosphanylaminophosphaalkenes $R_2C=P-N(R')-PPh_2$ ($R = Me_3Si, R' = tBu, 1-Ada$) occurs with the unique expulsion of $(Me_3Si)_2C=C=O$, furnishing trigonal-bipyramidal Rh^{III} complexes **20** and **21** that contain novel tetradentate dianionic “PNP–C–PNP” ligands $R_2C[P^{(-)}N(R')PPh_2]_2$.

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