The Quest for Isophosphaalkynes (Isophosphocyanides) C≡P−R — Still an Elusive Class of Compounds

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Dedicated to Professor Heinrich Nöth on the occasion of his 75th birthday

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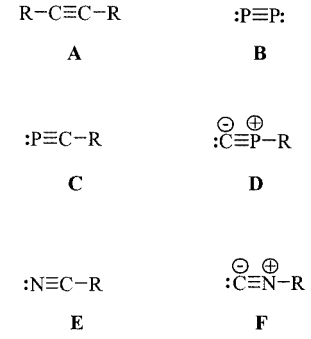
This review gives an account on the quest for isophosphaalkynes, a class of compounds that still resists isolation and/or spectroscopic detection. Synthetic attempts toward this target are reported. On the other hand, a number of coordination compounds featuring isophosphaalkyne ligands have been prepared, the syntheses, structures, and chemistry of which are discussed.

1. Introduction

The concepts of isolobal compounds and the diagonal relationship between carbon and phosphorus in the periodic table of elements have proven exceedingly fruitful for the development of the chemistry of phosphorus in low coordination states.[1] Accordingly, alkynes **A** are closely related to diphosphorus **B**, which exists only in the gas phase, as well as to phosphaalkynes **C** and to isophosphaalkynes **D** (Scheme 1).

The chemistry of phosphaalkynes has been well developed and has been documented comprehensively in a series of review articles and text books.[2] In contrast, our knowledge of their isomers of type **D** is scarce. At a first glance this lack of examples is surprising, especially if one formally extends the relationship of phosphaalkynes and isophosphaalkynes to their nitrogen homologues, the cyanides (nitriles) R−C≡N (**E**) and isocyanides R−N≡C (**F**). Both classes of compound are familiar to the chemist as versatile and useful reagents in organic[3] and coordination chemis-



Scheme 1. Isoelectronic compounds featuring triple bonding

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Lothar Weber was born in 1944 in Langenöls in Schlesien. He studied at the Universität Marburg and received his doctorate there under the direction of Professor Günter Schmid in 1973. Afterwards, he carried out postdoctoral studies with Professor Barry M. Trost at the University of Wisconsin in Madison, USA. On his return to Marburg, he began the experimental work leading to his Habilitation, which was completed in 1982 at the Universität Essen. His work focussed on the coordination chemistry of sulfur ylides. In 1985, he became a C2 Professor and then joined the Fakultät für Chemie der Universität Bielefeld. His research interests include the chemistry of compounds with low-coordinate elements of the fifth main group, the synthesis of homo- and heterocycles with heavy elements, as well as new aspects in boron chemistry.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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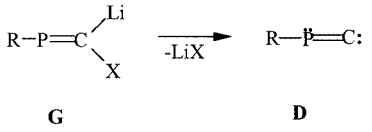
try.[4] At this point, it should be mentioned that the comparison of species of type **C** with alkynes **A**, rather than cyanides **E**, usually is given preference on the grounds of their polarity, their MO sequences and, consequently, their reactivity. In this account, both kinds of relationships are addressed where appropriate.

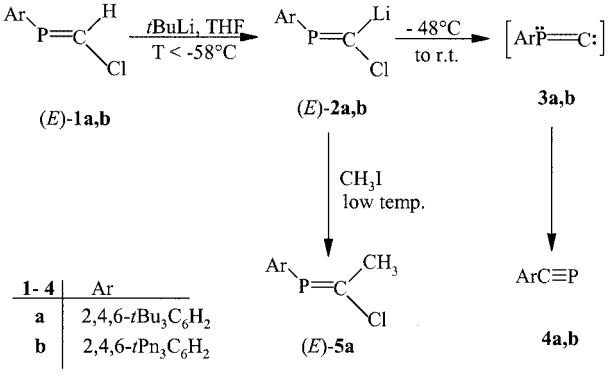
2. Attempted Syntheses of Isophosphaalkynes

The most prominent synthetic principle for preparing isophosphaalkynes is based upon the α-elimination of lithium halides from phosphaalkenylidene carbenoids **G** (Scheme 2).



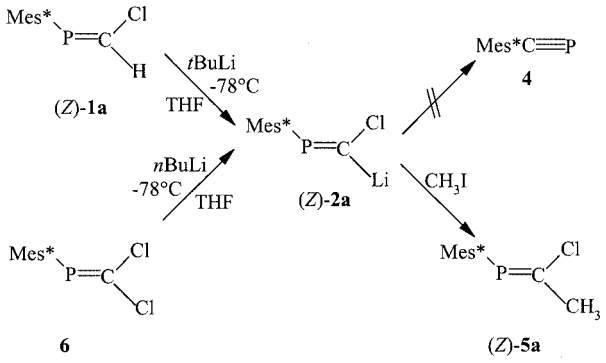
Scheme 2. Synthesis of isophosphaalkynes by α-elimination of lithium halides from phosphavinylidene carbenoids **G**

The reactive precursors may be synthesized by several routes. The outcome of their decomposition, however, strongly depends on the nature of the halide substituent as well as on the stereochemistry about the P=C double bond. The (*E*)-configured 2-chloro-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (**1a**) was lithiated in THF at −58 °C with a slight excess of *tert*-butyllithium to result in the complete conversion of **1a** into the corresponding *cis*-lithium compound **2a** (Scheme 3). Warming of the mixture to −48 °C completed the formation of **4a** within 10 min. No intermediates were detected by ^{31}P NMR spectroscopy. The identity of *cis*-**2a** was further substantiated by quenching the compound with methyl iodide at low temperature to give the (*E*)-configured phosphaalkene **5a**. Similar reactions were observed with the 2,4,6-tri-*tert*-pentylphenyl group as a substituent at the phosphorus atom[5a][5b] or with Mes* P=C(Br)Cl as a precursor.[5c]



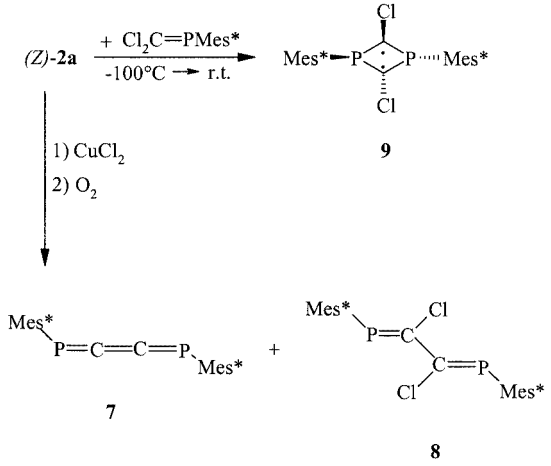
Scheme 3. Generation of phosphaalkynes **4a**,**b** and phosphaalkene (*E*)-**5a** from phosphavinylidene carbenoids (*E*)-**2a**,**b**

In contrast to this reactivity, the (*Z*)-configured phosphaalkylidene carbenoid (*Z*)-**2a**, obtained either by deprotonation of (*Z*)-2-chloro-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene [(*Z*)-**1a**] with *tert*-butyllithium or by a chlorine/lithium exchange of Mes*P=CCl$_2$ (**6**, Scheme 4) with *n*-butyllithium in THF at −78 °C, did not produce **4a** upon warming. Quenching of (*Z*)-**2a** with methyl iodide at any temperature gave (*E*)-**5a**.[5a]



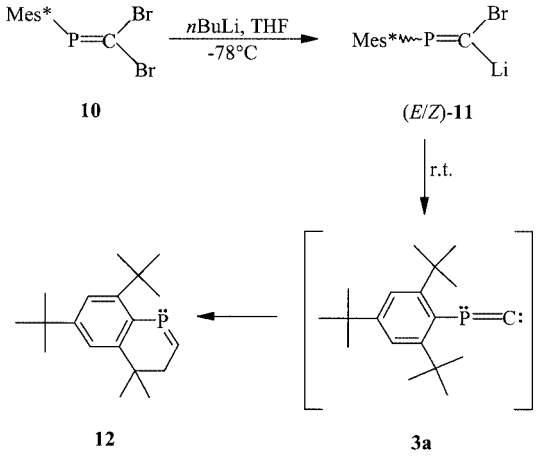
Scheme 4. Preparation and methylation of phosphavinylidene carbenoid (*Z*)-**2a**

It was assumed that solvation about the lithium atom in (*E*)-**2a** destabilizes the molecule, because of steric congestion between the bulky supermesityl group and the solvents coordinated around the lithium atom, which, thus, facilitates the α-elimination and formation of **4a**. Such a severe steric crowding should be absent in (*Z*)-**2a**, which increases its thermostability.[5a] In line with this assumption, single crystals of (*Z*)-Mes*−P=C(Cl){Li(dme)$_2$} were grown from a 1,2-dimethoxyethane solution at −60 °C and were subjected to an X-ray structure determination.[6] Lithium compound (*Z*)-**2a** served as a valuable precursor for the syntheses of interesting organophosphorus species, such as 1,4-diphosphabutatriene **7**, 1,4-diphosphabutadiene **8**,[7] and 1,3-diphosphacyclobutane-2,4-diyl[8] **9** (Scheme 5). From a formal point of view, compound **7** may be envisaged as a dimerization product of isophosphaalkyne **3a**, although synthetic routes are conceivable that circumvent the free vinylidene-like **3a**.



Scheme 5. Synthesis of **7**, **8**, and **9** from phosphavinylidene carbenoid (*Z*)-**2a**

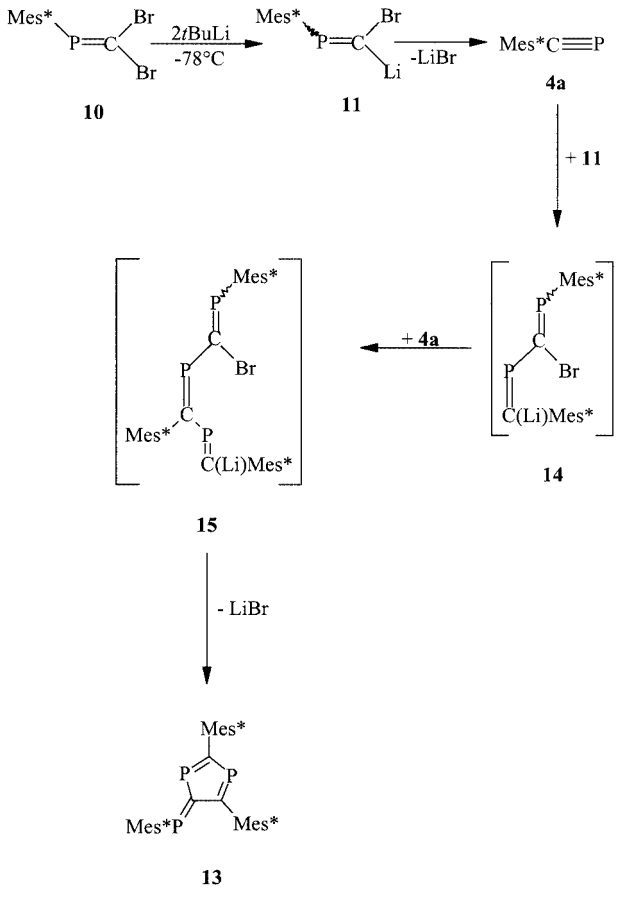
A different reaction pattern has been observed with 2-bromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethenyllithium, which was obtained as an (*E*)/(*Z*) mixture (1:5) by treatment of Mes*−P=CBr_2 with *n*-butyllithium in THF at −78 °C (Scheme 6).



Scheme 6. Synthesis of 3,4-dihydro-1-phosphanaphthalene **12** from Mes*P=CBr_2

Warming of the reaction mixture to room temperature led to the formation of the 3,4-dihydro-1-phosphanaphthalene derivative **12** in 17% yield. None of the compounds Mes*P≡C (**3a**) or Mes*C≡P (**4a**) was detected in the reaction mixture. It is conceivable that **12** resulted from an intramolecular C−H insertion reaction of transient **3a**. Attempts to trap the isophosphaalkyne with cyclohexene or tetracyanoethylene, however, failed. The contrasting behavior of (*E*/*Z*)-**11** was attributed to the increased tendency of the bromide ion to act as a leaving group, which allows the smooth liberation of **3a** at lower temperatures.[9] Interestingly, the preparation of **12** from precursor **10** via intermediate (*E*/*Z*)-**11** also depends on the nature of the organolithium compound employed. The reaction of dibromophosphaethene **10** with 2 equiv. of *tert*-butyllithium, instead of *n*-butyllithium, in THF at −78 °C afforded (*E*/*Z*)-**11**, and slow warming to ambient temperature yielded 1,3,6-triphosphafulvene **13** (18% yield) in addition to small amounts of Mes*(H)P−C≡C−Mes*, Mes*C≡P (**4a**), and 1-phospha-3,4-dihydronaphthalene **12**.[10] As indicated before, triphosphafulvene **13** was not observed in the corresponding reaction of Br_2C=PMes* with *n*-butyllithium. The mechanism proposed for the formation of **13** involves the liberation of **4a** from (*E*/*Z*)-**11** and the subsequent addition of a second equivalent of **11** to the phosphaalkyne. Addition of the resulting 1,3-diphosphabutadienyllithium **14** to Mes*C≡P should give the 1,3,5-triphosphahexatrienyllithium **15**, which then cyclizes to form the final product (Scheme 7).[10]

Treatment of Mes*P=CI_2 with 2 equiv. of *n*-butyllithium at −120 °C yielded exclusively (*E*)-Mes*P=C(I)Li (**16**), which is stable to ca. −100 °C. At ca. −85 °C, **16** fragmented into Mes*C≡P (**4a**) with a half-life of roughly 4 h. No ^{31}P NMR spectroscopic signals were observed other then those of **16** and **4a**. This result led to the assumption



Scheme 7. Synthesis of triphosphafulvene **13** from Mes*P=CBr_2

that the rearrangement of **3a** into **4a** at this low temperature must be extremely rapid, or that the migration of the supermesityl group from the phosphorus atom to the carbon atom occurs concomitantly with the extrusion of lithium iodide,[11] which circumvents the intermediacy of free **3a**.

3. Theoretical Studies

The failure to synthesize isophosphaalkynes, or at least to obtain reliable proof of their existence as reactive intermediates, has been rationalized on the basis of qualitative considerations as well as detailed quantum chemical considerations. Phosphorus is a high main group element and, thus, it is reluctant to undergo s−p mixing of the valence orbitals.[12a] In other words, phosphorus suffers from "orbital nonhybridization."[12b] This effect has the further consequence that phosphorus, in contrast to its first-row analog nitrogen, prefers structures in which an inert s-orbital contains two nonbonding electrons. While this state is well documented in white phosphorus, its consequence for the formation of linear triple bonds is also apparent. Such an unfavorable sp-hybrid would exist in the isophosphaalkyne, HPC. On the other hand, such a bonding situation is not observed in the phosphaalkyne, HCP. The phosphorus

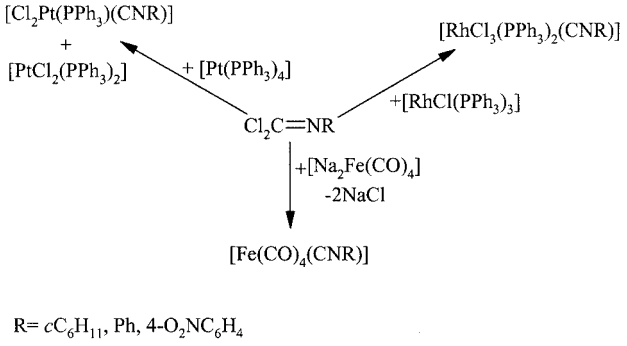
atom here can constitute a nonbonding s-orbital that is not forced to participate in bonding with the neighboring carbon atom.

These qualitative considerations[12a] find support in detailed quantum chemical calculations. According to the ab initio calculations for the HCP/HPC system, the linear HPC and HCP isomers correspond to the energy maximum and energy minimum, respectively, on the energy surface of the singlet ground state, and the relative energy between them is 83.9 kcal/mol at the MP4/6-31g** level.[13a,13b] The existence of a slightly bent HPC structure, however, in which the nonbonding s-orbital at the phosphorus atom is partly freed, is conceivable by other calculations. These calculations predict a local energy minimum that is merely 2.3 kcal/mol below the transition state for the rearrangement to HCP.[13c] In contrast to this prediction, the first-row analog HNC is a stable energy minimum on the electronic hypersurface, since a nitrogen atom can form an sp-hybrid orbital suitable for a linear arrangement of the three atoms in the isocyanide. According to electron-correlated ab initio calculations, the energy difference between the two structures HCN and HNC is ca. 14 kcal/mol.[14]

A further hint at the stability of the isophosphaalkyne has been given by quantum chemical considerations. Electronegative substituents (e.g., fluorine) tend to withdraw p-electrons from a bond. As a consequence, a fluorine atom stabilizes, to a considerable extent, the isophosphaalkyne form, RPC (R = F). For the reasons mentioned above, this stability occurs to a larger extent than that for the corresponding phosphaalkyne form, RCP. Ab initio calculations agree with these considerations.[13b] Although the energy barrier for the rearrangement from FPC to FCP is increased (13−17 kcal/mol), so far FPC has not been characterized experimentally. Principally, it is conceivable that the compound could be observed in an inert matrix at low temperature.[13b]

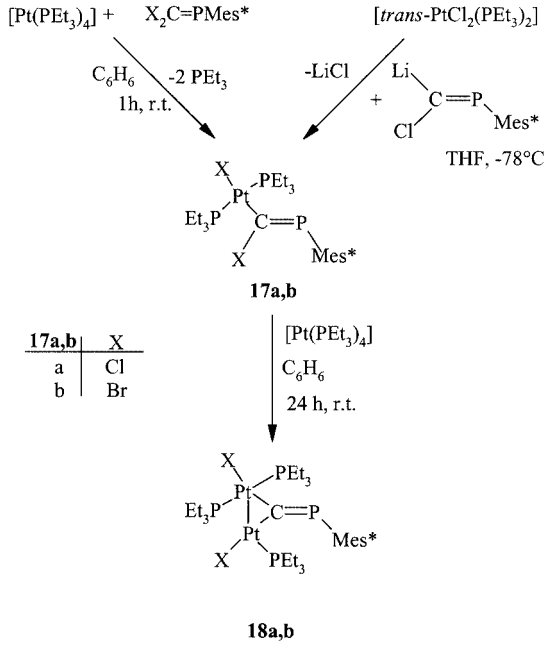
4. Isosphosphaalkyne Complexes

It is obvious that the facile α-elimination of lithium halides from *C*-lithiated *C*-halophosphaalkenes and the marked propensity to rearrangement of the initial products has thwarted the detection and isolation of isophosphaalkynes. Metallation of the dihalophosphaalkenes by transition metal complexes through oxidative addition processes, however, should lead to coordination compounds featuring isophosphaalkyne ligands. A model reaction, in which an isocyanide dichloride was converted into an isocyanide ligand at a transition metal center was reported in the mid-1970s (Scheme 8).[4h]



Scheme 8. Formation of isocyanide complexes from isocyanide dichlorides

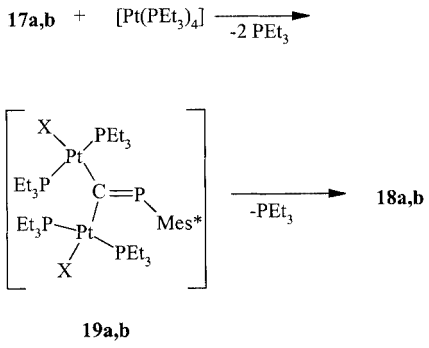
The first examples of stable (arylisophosphaalkyne)metal complexes **18a**,**b** were prepared by reaction of *trans*-[(X)(PEt$_3$)$_2$Pt{C(=PMes*)X}] (**17a**,**b**) with [Pt(PEt$_3$)$_4$] in benzene (or in hexanes) at room temperature (Scheme 9). This oxidative addition-type reaction was complete within 24 h and afforded **18a**,**b** as the only products. The key compounds **17a**,**b** were available either by an oxidative addition of X$_2$C=PMes* (X = Cl, Br) onto [Pt(PEt$_3$)$_4$] in benzene at 25 °C or, in the case of **17a**, by treatment of *trans*-[PtCl$_2$(PEt$_3$)$_2$] with LiC(Cl)=PMes* in THF at −78 °C.[15]



Scheme 9. Synthesis of (μ-isophosphaalkyne)diplatinum complexes **18a**,**b**

The direct synthesis of red, crystalline **18a**,**b** from the dihalophosphaalkenes and 2 equiv. of [Pt(PEt$_3$)$_4$] was also possible, albeit in much lower yield (Scheme 10).[15] A plausible mechanism for the generation of the μ-isophosphaalkyne complexes invokes the intermediacy of the doubly *C*-metalated phosphaalkenes **19a**,**b**, which extrude 1 equiv. of PEt$_3$ under Pt−Pt bond formation.

An X-ray diffraction study reveals **18a** as a dinuclear complex in which a Pt−Pt single bond of 2.6751(5) Å is nonsymmetrically bridged by the isophosphaalkyne ligand (Figure 1). The Pt−C bond lengths between the two inequivalent metal atoms and the bridging ligand are markedly different. The distance Pt(2)−C(1) of 1.86(1) Å is shorter than Pt(1)−C(1) [2.107(9) Å] by 0.22 Å.



Scheme 10. Proposed mechanism for the formation of **18a**,**b**

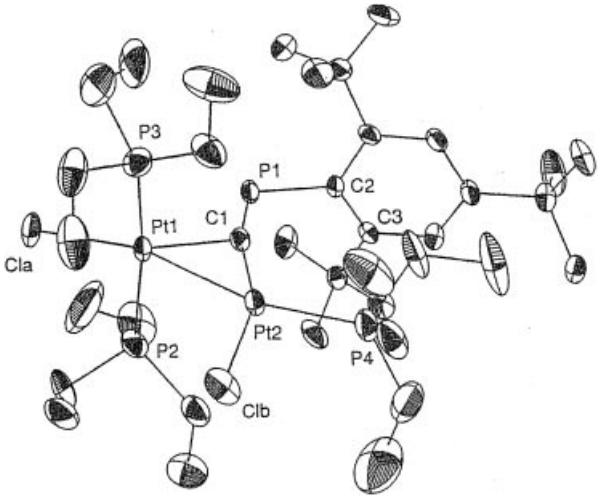
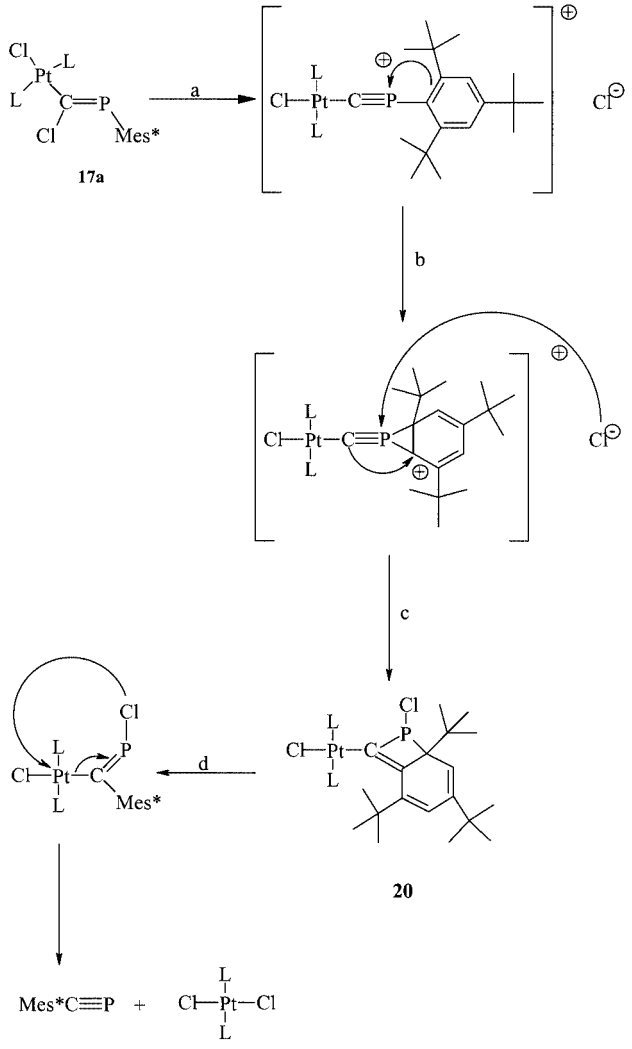


Figure 1. Molecular structure of [(Cl)(PEt_3)Pt(μ-C=PMes*)-Pt(PEt_3)$_2$(Cl)](*Pt*−*Pt*) (**18a**) in the crystal; selected bond lengths [Å] and angles [°]: Pt(1)−Pt(2) 2.6751(5), Pt(1)−C(1) 2.107(9), Pt(2)−C(1) 1.89(1), P(1)−C(1) 1.67(1), P(1)−C(2) 1.89(1); C(1)−P(1)−C(2) 110.7(5), Pt(1)−C(1)−Pt(2) 83.8(4), Pt(1)−C(1)−P(1) 112.0(5), Pt(2)−C(1)−P(1) 164.1(6)

The Pt−C(1)−P(1) angles also differ significantly. The angle Pt(2)−C(1)−P(1) of 164.1(6)° is close to linearity, whereas the angle Pt(1)−C(1)−P(1) of 112.0(5)° is sharply bent. The separation between Pt(1) and P(1) of 3.15 Å excludes any bonding interaction. The bond length C(1)−P(1) of 1.67(10) Å falls in the typical range for a P−C double bond (1.65−1.72 Å), as determined from numerous phosphaalkenes without π-donating substituents at the tricoordinate carbon atom. Therefore, the most reasonable description of the organophosphorus ligand is that of a semibridging group that is strongly coordinated to Pt(2) and interacts more weakly with Pt(1). At this point, it should be mentioned that solutions of the pure key compounds **17a** and **17b** in nonpolar solvents (C_6D_6, hexanes) are stable at ambient temperature under argon for at least one week. In polar solvents, such as CH_2Cl_2, $CHCl_3$, or THF, however, they decompose rapidly to the phosphaalkyne Mes*C≡P (**4a**) and [X_2Pd(PEt_3)$_2$] via the intermediate **20**, the identity of which was authenticated in one case by an X-ray structural analysis (Scheme 11). The propensity for this conversion depends on the metal (Pt < Pd), the halide (Cl < Br) and the phosphane ligand (PEt_3 < PPh_3). At no stage of this transformation is free isophosphaalkyne involved.[15c,15d] In the light of this finding, it is clear that the dechlorination of Cl_2C=PMes* by [Pd(PPh_3)$_4$] to give Mes*C≡P and *trans*-[$PdCl_2$(PPh_3)$_2$] cannot involve free C≡P−Mes* as was claimed in the respective communication.[16]

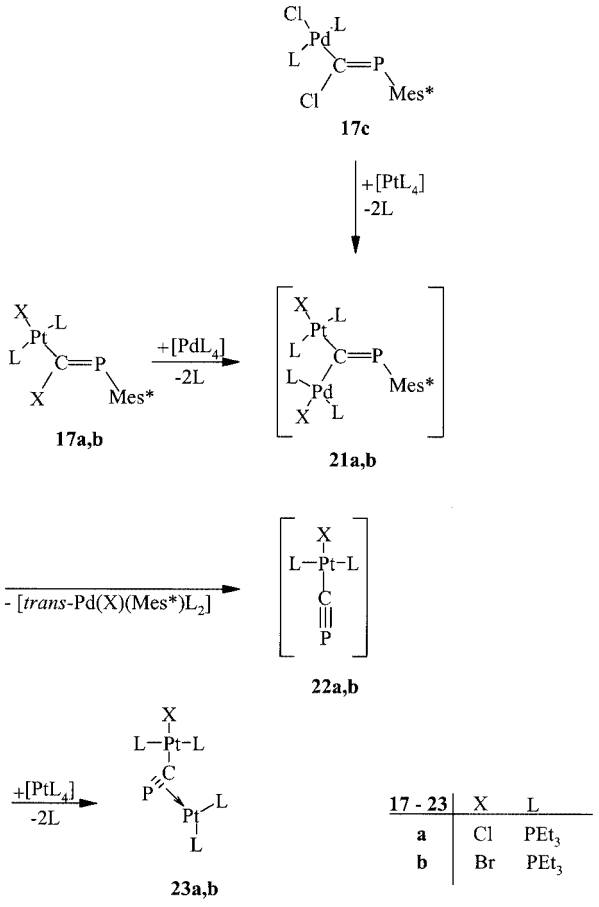


Scheme 11. Proposed mechanism for the decomposition of *C*-platiniophosphaalkene **17a** in polar solvents

One might even speculate that the conversion of Li(Cl)C=PMes* into Mes*C≡P proceeds by a similar mechanism, where lithium plays the role of the platinum center. At this point, it is clear that the synthetic principle realized in Scheme 9 for producing μ-isophosphaalkyne complexes is also limited by the stability of the respective *C*-metallo-*C*-halophosphaalkenes. To be certain of this effect would require a more thorough study concerning the particular role of the metal atom, the halogen atom, the ancillary ligands and the substituents at the phosphorus atom in the process. A first step toward this study was to change the metal complex, which by reaction with precursor metal-

lophosphaalkenes **17a**,**b**, should furnish heterodimetallic analogs of **18a**,**b** as products. When [Pt(PEt_3)$_4$] was replaced by [Pd(PEt_3)$_4$], however, the reaction with **17a**,**b** proceeded in a completely different manner.

After stirring the reaction solution of **17a**,**b** and [Pd(PEt_3)$_4$] for 24 h at ambient temperature, complexes **22a**,**b** and [*trans*-Pd(X)(Mes*)(PEt_3)$_2$] were observed as the only products (Scheme 12). The latter compounds could be separated easily from the mixture by fractional crystallization and were characterized by an X-ray diffraction analysis. Although stable in solution for at least one week, all attempts to isolate **22a**,**b** without decomposition failed and the identification of **22a**,**b** was confined to spectroscopy. The ^{31}P NMR spectroscopic resonance of the unprecedented terminal phosphocyanide ligand was assigned to a triplet at δ = 68.0 ppm (J_{pp} = 9.2 Hz) resulting from coupling to the two equivalent P nuclei of the PEt_3 ligands. Moreover, **22a**,**b** could be trapped by reaction with [Pt(PEt_3)$_4$] to yield the dinuclear complexes **23a**,**b** featuring a bridging phosphocyanide ligand in an η^1:η^2-mode of coordination. Complex **23a** was also accessible by treatment of the *C*-palladiophosphalkene **17c** with 1 mol-equiv. of [Pt(PEt_3)$_4$] under similar reaction conditions.[15b]



Scheme 12. Synthesis of μ-η^1:η^2-phosphocyanide complexes **23a**,**b**

The X-ray analysis of **23a** shows a dinuclear complex containing a bridging C≡P ligand that is η^1-*C*-bonded to Pt(1) and η^2-*C*,*P*-bonded to Pt(2) (Figure 2). The distance between both platinum centers [3.7868(3) Å] eliminates any likelihood of significant bonding occurring between the metal atoms. The atoms Cl, Pt(1), C(1), P(1), Pt(2), P(4), and P(5) are nearly coplanar (to within 0.061 Å), while P(2) and P(3) are located 2.292 and 2.279 Å above and below this plane, respectively. The C(1)−P(1) bond length of 1.666(6) Å compares well to that in [η^2-(*t*BuC≡P)Pt(PPh_3)$_2$] [1.67(2) Å] and is quite typical for η^2-ligated phosphaalkynes. As mentioned above, the preparation of dinuclear complexes with bridging isophosphaalkyne ligands, according to the method devised in Scheme 9, seems to be limited by the nature of the metal atom. Moreover, an additional limitation is given by the few examples of dichlorophosphaalkenes that are available to date and by the demand for bulky substituents that have to be present in these reagents. In a very recent study, the dichlorophosphaalkene $(Me_3Si)_2N-P=CCl_2$ was utilized as an additional candidate for the oxidative addition to two platinum metal centers. The reaction of [Pt(PEt_3)$_4$] with $Cl_2C=PN(SiMe_3)_2$ in THF or hexanes at −50 °C immediately and quantitatively produced the η^1-phosphaalkenyl complex *cis*-[Cl(Et_3P)$_2$Pt{C(Cl)=PN($SiMe_3$)$_2$}] (*cis*-**24**) by oxidative addition of one of the C−Cl bonds. A quantitative *cis*/*trans* isomerization to give *trans*-**24** occurred at 0 °C (Scheme 13).[17]

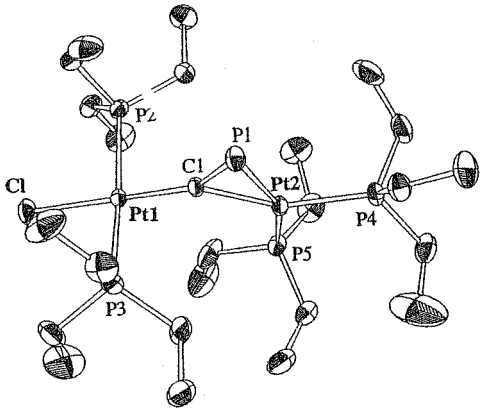
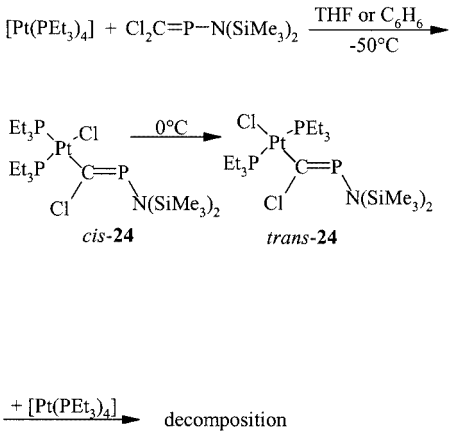


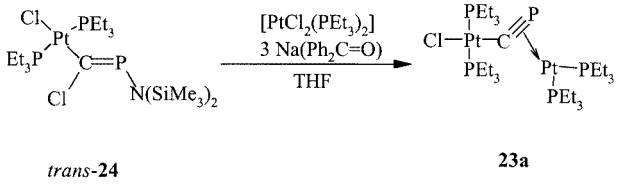
Figure 2. Molecular structure of **23a** in the crystal; selected bond lengths [Å] and angles [°]: Pt(1)−C(1) 1.950(6), Pt(1)−Cl 2.412(2), Pt(1)−P(2) 2.302(2), Pt(1)−P(3) 2.297(2), Pt(2)−C(1) 2.083(5), Pt(2)−P(1) 2.337(2), Pt(2)−P(4) 2.269(2), Pt(2)−P(5) 2.277(2), C(1)−P(1) 1.666(6); Pt(1)−C(1)−P(1) 144.0(3), Pt(1)−C(1)−Pt(2) 139.7(3), C(1)−Pt(2)−P(1) 43.8(2)

Although the molecular structure and the ^{31}P NMR spectrum of *trans*-**24** are very similar to those of *trans*-[Cl(Et_3P)$_2$Pt{C(Cl)=PMes*}] (**18a**), both species differ significantly in their reactivities. In contrast to **18a**, which in THF solution completely decomposed to Mes*C≡P and [Pt(PEt_3)$_2$Cl$_2$] within 24 h, THF solutions of *trans*-**24** are stable for weeks. Treatment of the latter compound with a 2nd equiv. of [Pt(PEt_3)$_4$] did not yield the anticipated μ-isophosphaalkyne complexes, but resulted in decomposition to a mixture of unidentified materials. Complex *trans*-**24** proved, however, to be an excellent precursor reagent for preparing the μ-η^1:η^2-phosphocyanide complex **23a**. Thus,



Scheme 13. Generation of *C*-platiniophosphaalkenes *cis*- and *trans*-**24**

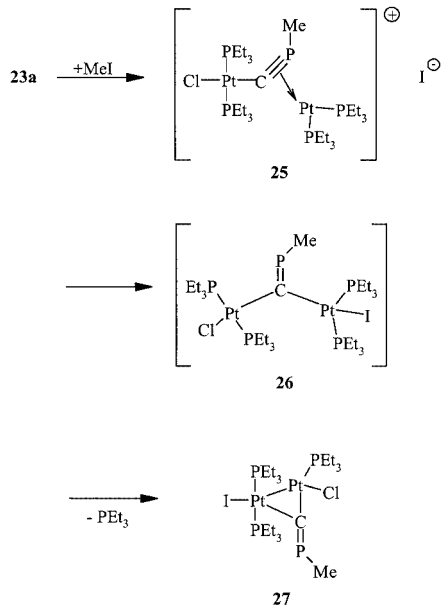
reduction of an equimolar mixture of **24** and $[Pt(PEt_3)_2Cl_2]$ with 3 equiv. of sodium benzophenone ketyl in THF afforded pure crystalline **23a** in 79% yield. This reaction was performed on a scale of several grams without a decrease in yield or purity of the product. It was crucial for the success of this process that the reducing agent be added to the mixture of both metal complexes. This requirement was rationalized by the need to trap the in situ generated dicoordinate complex $[Pt(PEt_3)_2]$ by π-coordination to the P=C double bond of **24** (Scheme 14). To date, this transformation is limited to using PEt_3 as a ligand in the platinum halide complex. Compound **24** remained unaffected in solution in similar reduction experiments with $[PtCl_2(PPh_3)_2]$, $[PtCl_2\{PiPr_3\}_2]$, $[PtCl_2(PCy_3)_2]$, and $[PtCl_2(depe)]$.



Scheme 14. Conversion of *trans*-**24** into **23a**

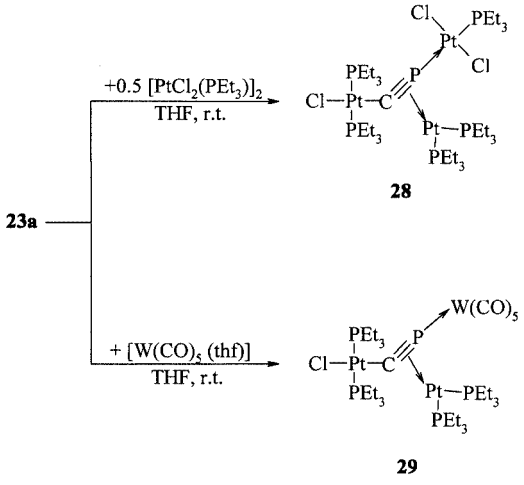
The availability of larger quantities of complex **23a** allowed a thorough investigation of its chemical reactivity to be made. Like classical η^2-phosphaalkyne complexes, the molecule exhibits significant nucleophilicity at the phosphorus atom of the C–P ligand. In keeping with this nucleophilicity, the treatment of **23a** with 3 equiv. of methyl iodide in THF for 12 h at ambient temperature resulted in the formation of the methyl isophosphaalkyne complex $[(Cl)(Et_3P)Pt(\mu\text{-}C{=}PMe)Pt(PEt_3)_2I](Pt{-}Pt)$ (**27**), with $(MePEt_3)I$ as a byproduct (Scheme 15).

Most likely this reaction was initiated by the methylation of the phosphorus atom of the C≡P bond to afford the cationic η^1-*C*:η^2-*C*,*P*-isophosphaalkyne complex **25**. Attack of the iodide ion at the zero-valent platinum center gave complex **26**, which may be regarded formally as a *C*,*C*-dimetallophosphaalkene. Extrusion of PEt_3 and Pt–Pt bond formation eventually afforded product **27**. Evidence for this



Scheme 15. Synthesis of μ-isophosphaalkyne complex **27** from **23a** and methyl iodide

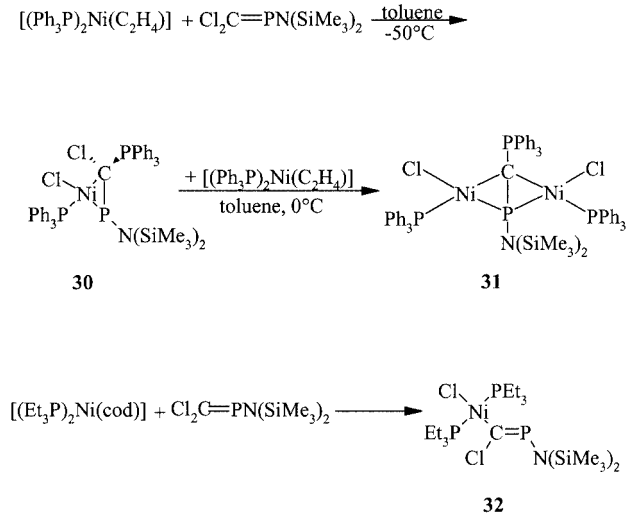
proposal was taken from the clean methylation of **23a** with methyl triflate to give salt $\mathbf{25}^+OTf^-$. The latter salt was converted into **27** by treatment with a tenfold amount of NaI. Moreover, comparison of the NMR spectroscopic data of the triflate of $\mathbf{25}^+$ with the related platinum and tungsten adducts **28** and **29** adds further support for **25** being the initial product of the methylation reaction (Scheme 16).



Scheme 16. Phosphocyanide as an η^1:η^1:η^2-ligand in trinuclear complexes **28** and **29**

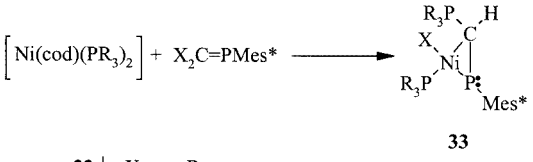
For a successful alkylation, the synthetic sequence depicted in Scheme 15 could represent a more general access to (μ-isophosphaalkyne)diplatinum complexes. More importantly, this approach would no longer be dependent on sterically demanding groups. To evaluate this concept, alkylation of **23a** was performed with benzyl bromide, isopropyl iodide, alkyl bromide, and 2,4,6-tri-*tert*-butylbenzyl bromide under the same conditions as for the methylation. Ac-

cording to ^{31}P NMR spectroscopic observations, however, only the reactions with benzyl bromide and isopropyl iodide yielded μ-isophosphaalkyne complexes analogous to **27**. Unfortunately, the benzyl derivative could not be isolated in a pure state, and the isopropyl derivative decomposed during the course of the alkylation.[17] In a recent paper, the dichlorophosphaalkenes $Cl_2C{=}PN(SiMe_3)_2$ and $Cl_2C{=}$PMes* were treated with zero-valent nickel complexes,[18] which produced interesting and novel organophosphorus compounds instead of the anticipated isophosphaalkyne complexes. The reaction of 0.5 equiv. of $Cl_2C{=}PN(SiMe_3)_2$ with $[(Ph_3P)_2Ni(C_2H_4)]$ in toluene in the range between −78 °C and room temperature produced $[Ni_2Cl_2(PPh_3)_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(PPh_3){=}PN(SiMe_3)_2\}]$ (**31**) in 74% yield. Low-temperature (−30 °C) ^{31}P NMR spectroscopic monitoring showed complex **30** as the only observable intermediate in this reaction. A stoichiometric reaction of $[(Ph_3P)_2Ni(C_2H_4)]$ with $Cl_2C{=}PN(SiMe_3)_2$ at −30 °C yielded **30** quantitatively. This compound could not be isolated because of decomposition, but the addition of a 2nd equiv. of $[(Ph_3P)_2Ni(C_2H_4)]$ to the reaction mixture led to oxidative addition of the remaining C−Cl bond in **30** to $[(Ph_3P)_2Ni(C_2H_4)]$ to give **31** (Scheme 17). The latter complex can be viewed as a triphenylphosphane-stabilized $\eta^2{:}\eta^2$-isophosphaalkyne complex. Attempts to remove the phosphane from **31** with 9-borabicyclo[3,3,1]nonane resulted in complete decomposition.



Scheme 17. Reaction of zero-valent nickel complexes with $(Me_3Si)_2NP{=}CCl_2$

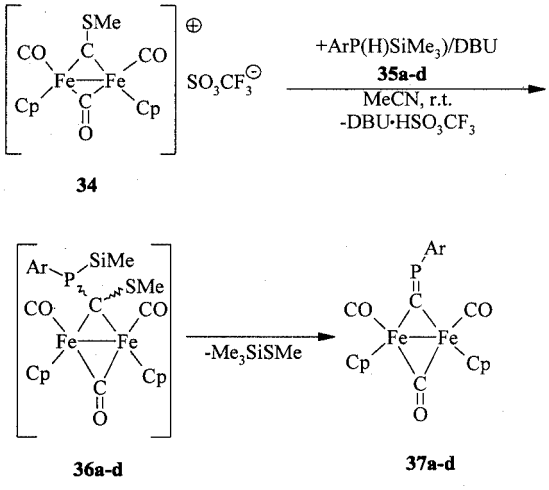
In contrast to the reaction in Scheme 17 with PPh_3 as a ligand in the nickel complex precursor, the treatment of a 1:2 mixture of $[Ni(cod)_2]$ and PEt_3 with $Cl_2C{=}PN(SiMe_3)_2$ afforded the nickeliophosphaalkene **32**, which is formally analogous to the *Pt*-functionalized species **24**. This compound did not rearrange to an analog of **30**, and it did not react further with an excess of Ni^0 complexes to molecules like **31** or to μ-isophosphaalkene complexes. In solution, compound **32** decomposed to nontractable materials within 1 d. In contrast to this finding, the dihalophosphaalkenes $X_2C{=}P{-}Mes^*$ (X = Cl, Br) were dehalogenated by 2 equiv. of $[Ni(cod)_2]/2PR_3$ mixtures to give the metalloheterocycles **33** in moderate yields (Scheme 18).



33	X	R
a	Cl	Ph
b	Br	Ph
c	Br	Cy

Scheme 18. Preparation of metalloheterocycle **33**

A completely different approach to dinuclear complexes with bridging μ-isophosphaalkyne ligands **37a−c** made use of the condensation of the cationic (μ-carbyne)diiron complex **34** with the secondary aryl(silyl)phosphanes **35a−d** in acetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 19).[19a,19b]



35-37	Ar
a	2,4,6-$Me_3C_6H_2$
b	2,4,6-$i Pr_3C_6H_2$
c	2,4,6-$t Bu_3C_6H_2$
d	2,4,6-$(CF_3)_3C_6H_2$

Scheme 19. Synthesis of (μ-isophosphaalkyne)diiron complexes **37a−d**

Complexes **37a−c** were isolated in moderate yields as dark-red, air-stable crystals after column chromatography. Thermolabile derivative **37d**, however, had to be converted into its stable $[Cr(CO)_5]$ adduct **38d** by treatment with (cyclooctene)$Cr(CO)_5$ immediately after isolation.[19b] It is conceivable that the generation of **37a−d** was initiated by the nucleophilic attack of phosphanes **35a−d** at the bridging carbyne carbon atom, with subsequent deprotonation of the resulting phosphonium salt. Alternatively, the nucleophilic attack of anions $[P(SiMe_3)Ar]^-$ is also possible. Evi-

dence for the intermediates **36** is given by ^{31}P NMR spectroscopic signals at δ = 8.3 (**36a**) and 2.1 ppm (**36c**) at the beginning of the process. Elimination of Me_3SiSCH_3 from **36a–d** afforded the final products. The presence of P=C double bonds was indicated by ^{31}P NMR spectroscopic resonances at δ = 200–258 ppm and doublets in the $^{13}C\{^1H\}$ NMR spectra at very low field (δ = 333.8–345.8 ppm).

The X-ray structure analysis of **37a** shows a dinuclear complex, the Fe–Fe bond of which [2.527(5) Å] is symmetrically bridged by a μ-CO ligand [Fe(1,2)–C(12) = 1.954(16), 1.927(15) Å] and a μ-C=P–Mes* ligand [Fe(1,2)–C(13) = 1.903(16), 1.927(16) Å] (Figure 3). The P–C bond length of 1.683(17) Å is consistent with a double bond. The angles Fe(1)–C(13)–P(1) [147.2(10)°] and Fe(2)–C13)–P(1) [129.7(9)°] differ significantly, but not as much as in the diplatinum complex **18a** [164.1(6)° and 112.0(5)°]. The condensation discussed here for the construction of the P=C bond of an μ-isophosphaalkyne complex is independent from the existence of a phosphaalkene precursor. This method, however, also lacks generality. Thus, reaction of **34** with an equimolar amount of *t*BuP(H)$SiMe_3$ in acetonitrile in the presence of DBU afforded complex **40** within 2 d at room temperature[19c] (Scheme 20).

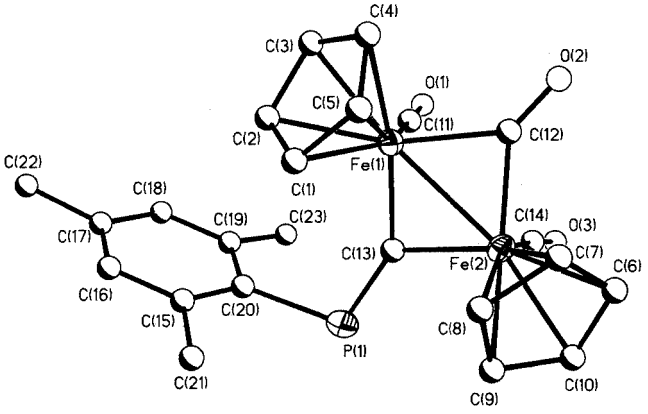
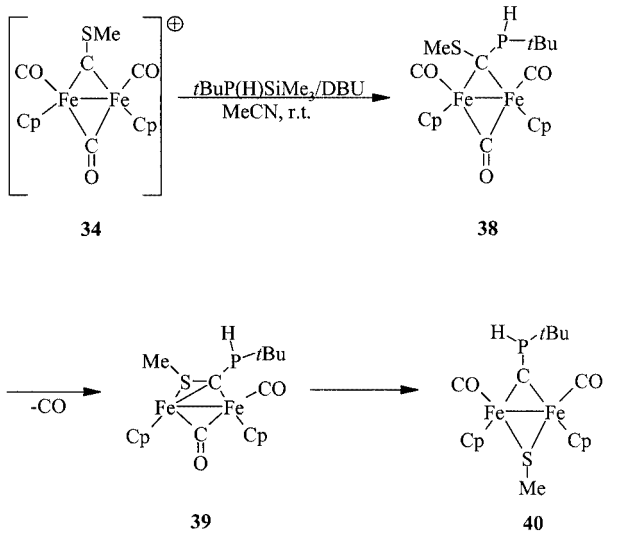


Figure 3. Molecular structure of **37a**; selected bond lengths [Å] and angles [°]: Fe(1)–Fe(2) 2.527(5), Fe(1)–C(12) 1.954(16), Fe(2)–C(12) 1.927(15), Fe(1)–C(13) 1.903(16), Fe(2)–C(13) 1.927(16), P(1)–C(13) 1.683(17); Fe(1)–C(13)–P(1) 147.2(10), Fe(2)–C(13)–P(1) 129.7(9), Fe(1)–C(12)–O(2) 138.3(13), Fe(2)–C(12)–O(2) 140.4(13), C(13)–P(1)–C(20) 104.5(7)

The reaction of **34** with *i*$PrPH_2$ or $(Me_3Si)_3CP(H)SiMe_3$ did not yield tractable products. The identity of **40** was deduced from elemental analyses and spectroscopic evidence. The ^{31}P NMR spectrum revealed a doublet of decets at δ = −6.0 ppm ($^1J_{PH}$ = 265, $^3J_{PH}$ = 14 Hz), whereas in the $^{13}C\{H\}$ NMR spectrum a doublet at δ = 420.0 ppm ($^1J_{PH}$ = 83 Hz) is diagnostic of a μ-phosphanylcarbyne ligand. Monitoring of the course of the reaction by $^{31}P\{H\}$ NMR spectroscopy showed, before DBU was added, only the resonance of *t*BuP(H)$SiMe_3$ at δ = −85.5 ppm. After the addition of the base, this resonance was replaced by a singlet at δ = 20.6 ppm, which in the proton-coupled experiment became a doublet of multiplets ($^1J_{PH}$ = 383.1 Hz). This signal is attributed to intermediate **38**. After 14 h at 20 °C, the spectrum displayed two singlets at δ = −7.9 and −17.4 ppm in addition to the resonance for **38**. After 2 d, only the singlet at δ = −7.9 ppm of the final product **40** remained. The signal at δ = −17.4 ppm was due to intermediate **39**, which was isolated after 2 h of reaction and fully characterized by an X-ray diffraction study (Figure 4).[19c]



Scheme 20. Synthesis of μ-phosphanylcarbyne complex **40**

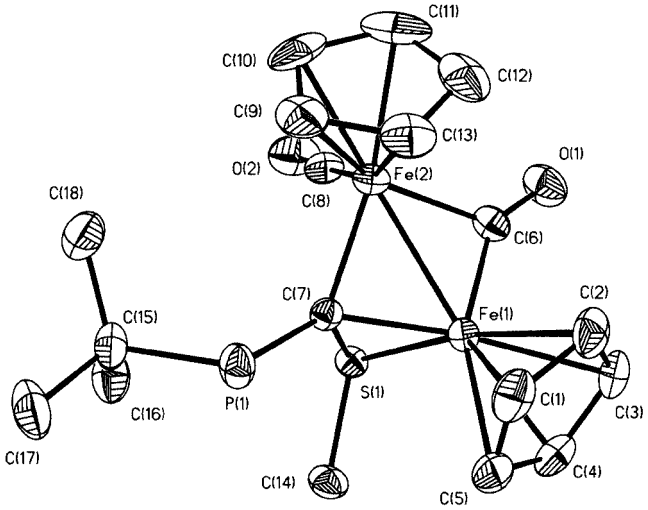
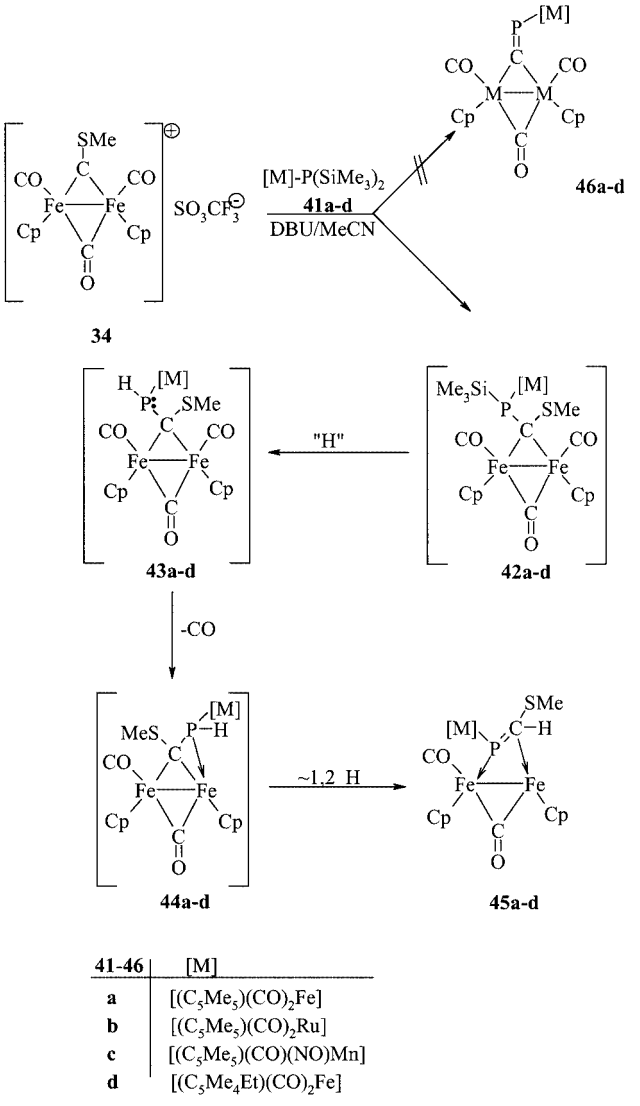


Figure 4. Molecular structure of **39** in the crystal; selected bond lengths [Å] and angles [°]: Fe(1)–Fe(2) 2.5015(7), Fe(1)–C(7) 1.910(3), Fe(2)–C(7) 1.975(3), Fe(1)–S(1) 2.2309(8), S(1)–C(7) 1.800(3), P(1)–C(7) 1.807(3), P(1)–C(15) 1.885(3); Fe(2)–C(7)–P(1) 124.34(14), C(7)–P(1)–C(15) 108.37(14), S(1)–C(7)–P(1) 125.4(2), Fe(1)–C(7)–P(1) 126.8(2), Fe(1)–C(7)–Fe(2) 80.14(10)

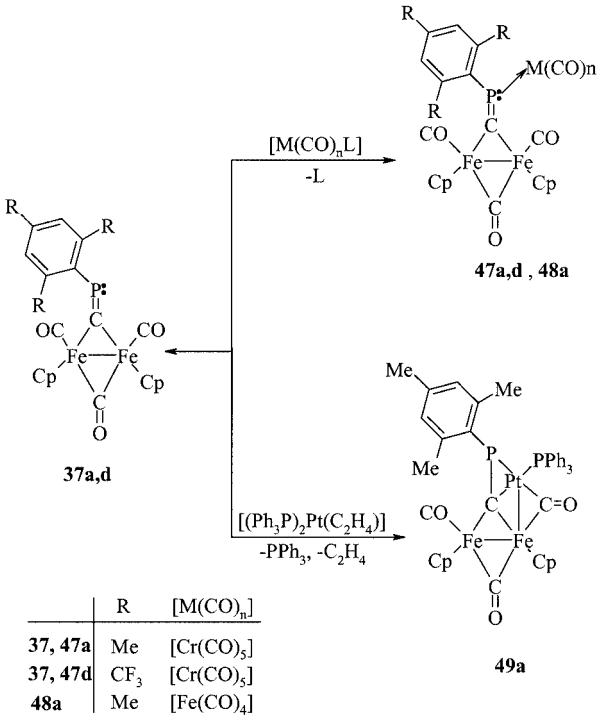
The most interesting feature of the molecule is that the *tert*-butylphosphanyl(methylthiolato)methylidene ligand bridges the Fe–Fe unit via the distorted tetrahedral carbon atom C(7) [Fe(1,2)–C(7) = 1.910(3), 1.975(3) Å]. In addition, the sulfur atom of the thiolato substituent is coordinated to Fe(1) [Fe(1)–S(1) = 2.231(1) Å]. The distances

P(1)−C(7) [1.807(3) Å] and S(1)−C(7) [1.800(3) Å] are consistent with single bonds. The attempted condensation of the metallodisilylphosphanes **41a−d** with μ-carbyne complex **34** resulted in the formation of the dinuclear complexes **45a−d** featuring μ-η^1-*P*:η^2-*C*,*P*-metallophosphaalkene ligands instead of the anticipated trinuclear C≡P complexes **46** (Scheme 21).[19d]



Scheme 21. Synthesis of μ-η^1:η^2-metallophosphaalkene complexes **45a−d**

It is reasonable to propose that the synthesis of compounds **45** is initiated by the nucleophilic attack of metallo(-silyl)phosphide {P[M](SiMe$_3$)}$^-$ at the carbyne bridge of **34** to give the μ-alkylidene complex **42**. The replacement of the Me$_3$Si group in **43** by a hydrogen atom was unexpected. Since traces of moisture are excluded from the reaction, the source of the hydrogen atom might be DBU itself. An intramolecular replacement of CO by the phosphane function in **43** results in intermediate **44**. A 1,2-hydrogen shift and a second Fe−P contact leads to the final product **45**. It is worth mentioning that the preparation of **45** failed when NEt$_3$ was used as the base instead of DBU. In a control experiment, (η^5-C$_5$Me$_5$)(CO)$_2$FePH$_2$, **34**, and DBU afforded **45a** with a slightly improved yield (39%, cf. 28%). The difference in reactivity between aryl−PH(SiMe$_3$) or aryl−PH$_2$ and [M]PH(SiMe$_3$) or [M]PH$_2$ towards **34** may be rationalized by regarding the common intermediate **42**. Obviously, activation by the aryl group at the phosphorus atom promotes the 1,2-eliminations of Me$_3$SiSMe or HSMe to give **37**, whereas the electron-releasing metallo group enhances the phosphane's nucleophilicity, favoring the intramolecular CO displacement instead of the 1,2-elimination. The chemistry of the (μ-isophosphaalkyne)diiron complexes **37** largely resembles that of classical phosphaalkenes. Thus, the synthesis of the pentacarbonylchromium complexes **47a**,**d** and of the [Fe(CO)$_4$] adduct **48a** was accomplished by reaction of **37a**,**d** with pentacarbonyl(cyclooctene)chromium or nonacarbonyldiiron, respectively, with the organophosphorus moiety acting as an η^1-ligand through the lone pair of electrons at the P atom (Scheme 22).[19b]



Scheme 22. Preparation of the trinuclear complexes **47a**,**d**, **48a**, and **49a** featuring bridging isophosphaalkyne ligands

The η^1-ligation of the phosphorus atom of **37a**,**d** to an [M(CO)$_n$] fragment in **47c**,**d** and **48a** was accompanied by the typical shielding of the ^{31}P NMR spectroscopic signal ($\Delta\delta^{31}$P = 25.0−74.3 ppm). The black crystalline complex **49a**, isolated from the reaction between **37a** and [(Ph$_3$P)$_2$Pt(C$_2$H$_4$)] displayed, in the ^{31}P NMR spectrum, two doublets at δ = 129.9 and 44.15 ppm ($^2J_{P,P}$ = 9.8 Hz) for the ^{31}P nuclei of the isophosphaalkyne and PPh$_3$ ligands. The increased high-field shift upon coordination (Δδ = 125.6 ppm) and the $^1J_{P,Pt}$ coupling constant of only

63 Hz suggest a π-interaction between the platinum atom and the P−C unit.[19b]

The X-ray diffraction study of **47a** (Figure 5) shows a pentacarbonylchromium complex that is attached to ligand **37a** via the lone pair of electrons at the P atom [Cr(1)−P(1) = 2.412(8) Å]. The geometry of **37a** is not significantly perturbed by the [$Cr(CO)_5$] fragment. The bonds and angles of the [Fe_2(μ-CO)(μCPMes)] unit of **47a** are shorter and smaller than those in the precursor molecule. Atoms C(15) and P(1) have trigonal-planar geometries. The exocyclic angles Fe(1)−C(15)−P(1) [139.0(13)°] and Fe(2)−C(15)−P(1) [140.3(14)°] in **47c** are nearly identical, whereas in **37a** they differ markedly [147.2(10) and 129.7(9)°, respectively].[19b]

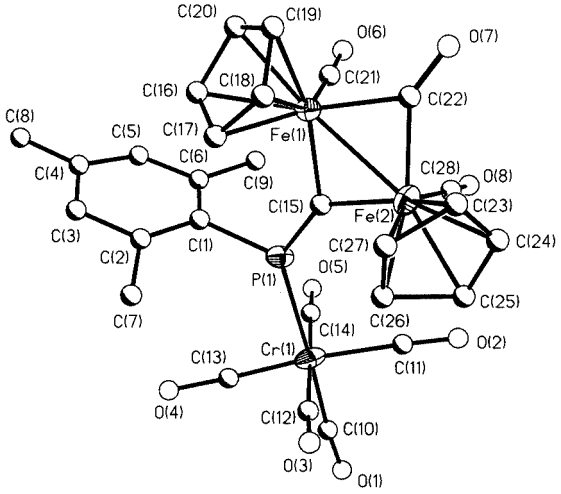


Figure 5. Molecular structure of **47a** in the crystal; selected bond lengths [Å] and angles [°]: Fe(1)−Fe(2) 2.500(6), Fe(1)−C(15) 1.958(21), Fe(2)−C(15) 1.908(21), Fe(1)−C(22) 1.953(26), Fe(2)−C(22) 1.912(25), P(1)−C(15) 1.632(21), P(1)−C(1) 1.836(23), P(1)−Cr(1) 2.412(8); Fe(1)−C(15)−P(1) 139.0(13), Fe(2)−C(15)−P(1) 140.3(14), C(15)−P(1)−Cr(1) 132.7(9), Cr(1)−P(1)−C(1) 118.1(7), Fe(1)−C(15)−Fe(2) 80.6(8)

The molecular structure of **49a** (Figure 6) shows a μ-isophosphaalkyne complex acting as an η^3-ligand towards a [$Pt(PPh_3)$] fragment. Thereby, the skeleton of **37a** remains mainly unaffected. The trigonal-planar donor atom C(12) of the isophosphaalkyne bridges both iron atoms symmetrically [Fe(1)−C(12) = 1.915(9), Fe(2)−C(12) = 1.918(10) Å]. The Fe−Fe bond [2.519(4) Å] is similar to that in **37a** [2.527(5) Å]. The π-coordination to the Pt atom causes an elongation of the P=C bond to 1.737(10) Å, with a Pt−C bond of 2.162(9) Å and a relatively long Pt−P(2) contact of 2.471(2) Å. The Pt(1)−P(1) bond to the PPh_3 ligand has a length of only 2.240(2) Å. Compound **49a** may be regarded as either a [$Pt(PPh_3)$] complex of an η^3-1-ferra-3-phosphaallyl ligand or, in line with the Wade−Mingos rules, as an *arachno* cluster constructed of the atoms Pt(1), P(2), C(12), and Fe(1). The polyeder skeleton electron count gives only 40 valence electrons (v.e.) instead of the theoretically required 42. This agrees with the fact that Pt^0 complexes often acquire only 16 v.e. instead of the familiar 18 v.e. shell.

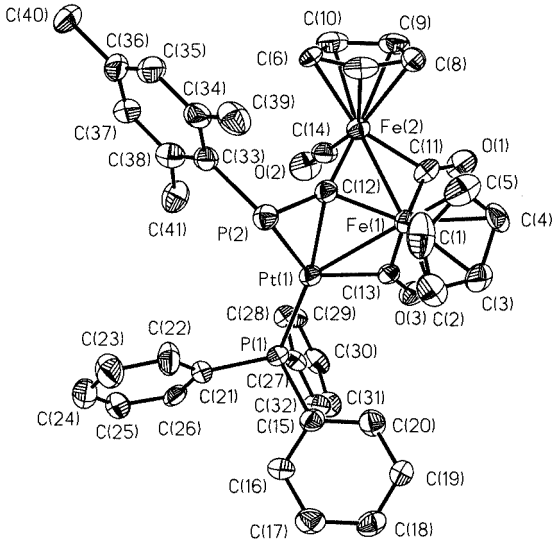
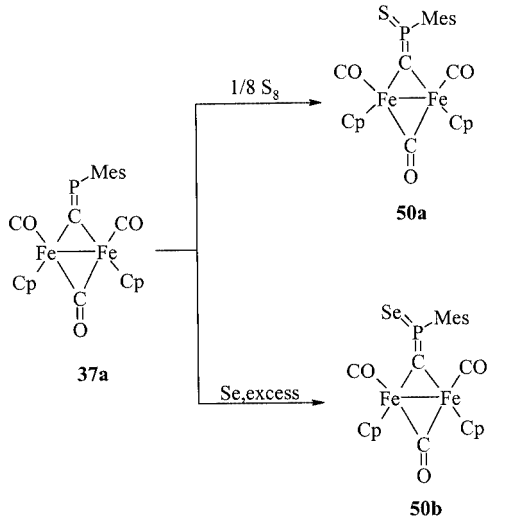


Figure 6. Molecular structure of **49a** in the crystal; selected bond lengths [Å] and angles [°]: Pt(1)−Fe(1) 2.577(2), Pt(1)−P(1) 2.240(2), Pt(1)−P(2) 2.471(2), Pt(1)−C(12) 2.162(9), Pt(1)−C(13) 1.997(2), Fe(1)−C(11) 1.879(10), Fe(1)−C(12) 1.915(9), Fe(1)−C(13) 1.951(9), Fe(1)−Fe(2) 2.518(4), Fe(2)−C(11) 1.952(9), Fe(2)−C(12) 1.918(10), P(2)−C(12) 1.737(10), P(2)−C(33) 1.862(10); Fe(1)−C(12)−Fe(2) 82.4(4), Fe(2)−C(12)−P(2) 146.5(5), Fe(1)−C(12)−P(2) 130.6(5), C(12)−P(2)−C(33) 105.9(4)

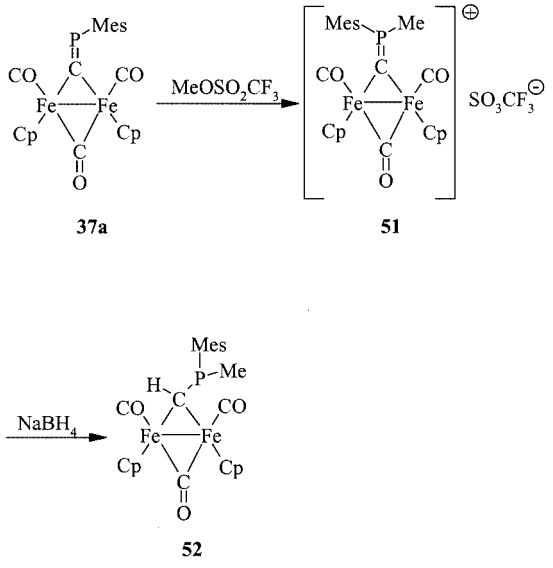
The oxidation of the μ-isophosphaalkyne complex **37a** with an equimolar amount of sulfur or an excess of grey selenium in benzene at 20 °C led to the formation of the methylene(thioxo)-λ^5,σ^3-phosphorane **50a** ($\delta^{31}P$ = 159.4 ppm) and the methylene(selenoxo)-λ^5,σ^3-phosphorane **50b** ($\delta^{31}P$ = 128.0 ppm) as orange-brown microcrystalline solids[19c] (Scheme 23). Methylation at the phosphorus atom of **37a** to give red microcrystalline **51** ($\delta^{31}P$ = 108.8 ppm) was effected by reaction with methyl triflate. The (μ-phosphanylalkylidene)diiron derivative **52** resulted from the subsequent reduction of salt **51** with $NaBH_4$ (Scheme 24).[19c]

Despite the existence of complexes with μ-isophosphaalkyne ligands, coordination compounds with terminal isophosphaalkyne ligands are still unknown and, thus, remain a challenge for the experimental chemist. A possible approach to these targets was stimulated by inspection of the electronic structures of aminocarbyne complexes, such as **53**,[20,21] or of the methanidocarbyne complex **54**,[22] where limiting structures such as **53′** and **54′** contribute significantly to the ground states of the molecules. In line with the diagonal relationship between C and P atoms, it is conceivable that structure **55′**, which features a terminal isophosphaalkyne ligand, also may be significant for the adequate description of the phosphidocarbyne complexes **55** (Scheme 25).

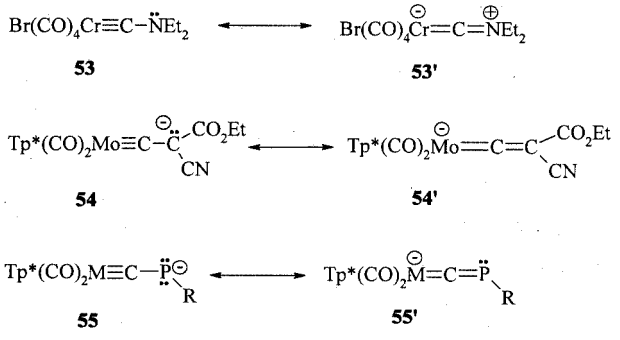
The chlorocarbyne complexes [Tp*$(CO)_2$M≡C−Cl] [**56**: M = Mo; **57**: M = W; Tp* = $HB(3,5\text{-}Me_2HC_3N_2)_3$][23] and inverse phosphaalkenes $Me_3SiP{=}C(NR_2)_2$ (**58a**: R=Me; **58b**: Et), the P−C bonds of which are strongly polarized ($P^{\delta-}C^{\delta+}$), were envisioned as suitable precursors for the



Scheme 23. Oxidation of μ-isophosphaalkyne complex **37a** by sulfur and selenium

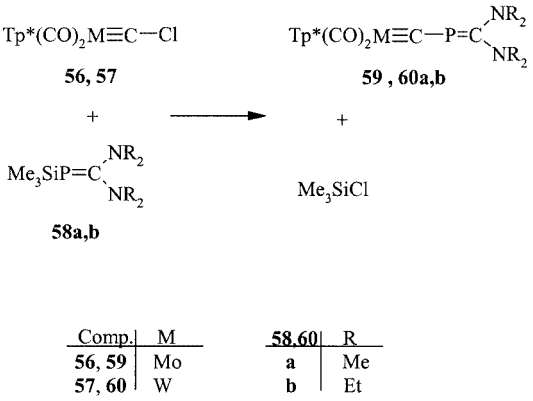


Scheme 24. Synthesis of μ-phosphanylcarbene complex **52**



Scheme 25. Limiting structures of the formally related carbyne complexes **53**, **54**, and **55**

synthesis of complexes **55**.[24] Reaction of the carbyne complexes **56** and **57** with 2 mol-equiv. of phosphaalkene **58a** in CH_2Cl_2 at 20 °C led to precipitation of the red compounds **59a** and **60a** within 2 h. The analogous conversion of **56** and **57** to the corresponding complexes **59b** and **60b** by treatment with $Me_3SiP{=}C(NEt_2)_2$ required 15−18 h to reach completion (Scheme 26).[25]

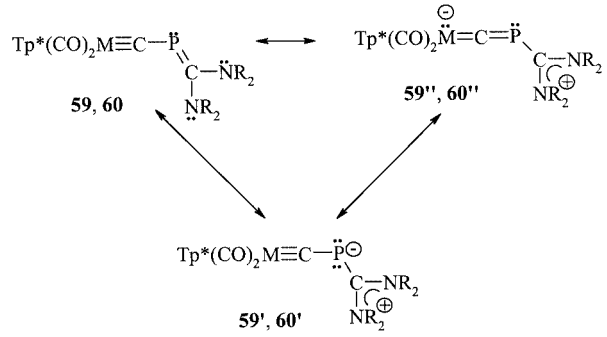


Comp.	M
56, 59	Mo
57, 60	W

58,60	R
a	Me
b	Et

Scheme 26. Synthesis of complexes **59a**,**b** and **60a**,**b**

On the basis of IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopic evidence, three resonance structures were chosen to fully describe the bonding situation in **59** and **60** (Scheme 27).



Scheme 27. Limiting structures of complexes **59** and **60**

Since the interpretation of the spectroscopic data is not unambiguous, however, an X-ray structual analysis of **60b** was carried out (Figure 7).

The most informative feature of the molecule is the geometry of the organophosphorus ligand. The bond length W(1)−C(3) of 1.838(6) Å compares well with that of the corresponding bond length in $[Tp^*(CO)_2W{\equiv}C{-}PMe_2Ph]PF_6$ [1.821(9) Å][26] and must be regarded as a metal−carbon triple bond. Accordingly, it is better to consider the ligand in **60b** as a phosphaalkenyl-functionalized methylidyne than as the anticipated terminal isophosphaalkyne ligand as depicted in structural formulas **59**′′ and **60**′′. The valence angle W(1)−C(3)−P(1) of 167.9(4)° deviates only slightly from linearity, which is in line with it having an sp-hybridized donor carbon atom. The bonds between the two-coordinate phosphorus atom and carbon atoms C(3) and C(4) are of equal length [1.759 Å]. Considering the different hybridizations at C(3) (sp) and C(4) (sp^2), and

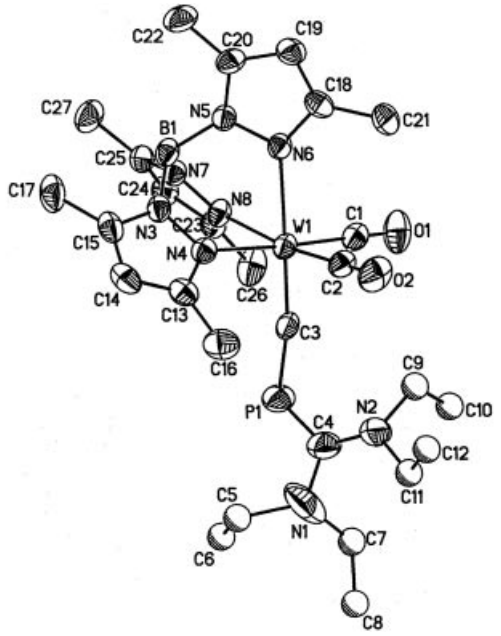
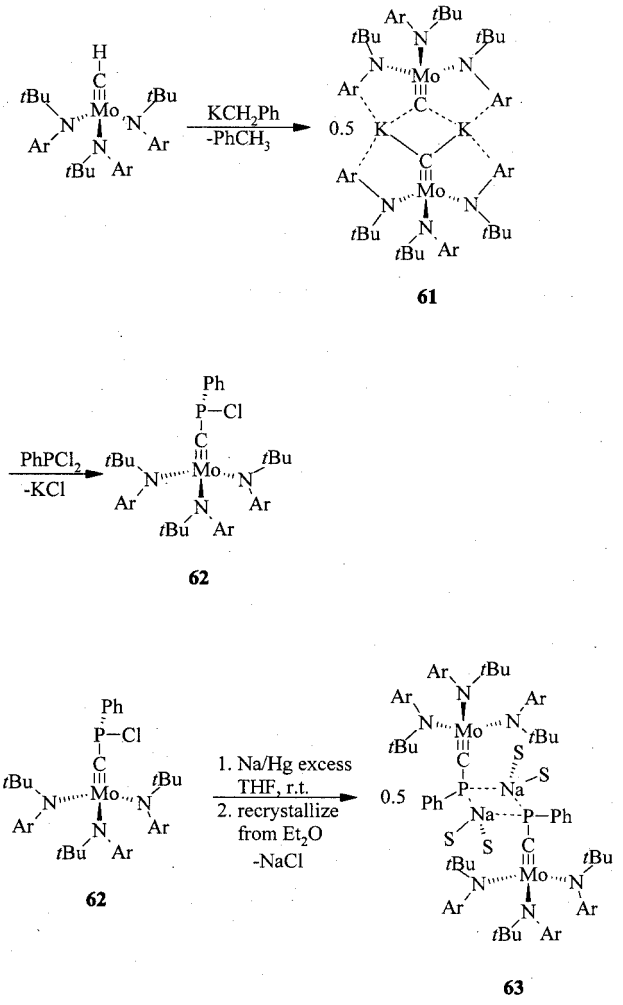


Figure 7. Molecular structure of **60b** in the crystal; selected bond lengths [Å] and angles [°]: W(1)−C(3) 1.838(6), P(1)−C(3) 1.759(7), P(1)−C(4) 1.759(9), N(1)−C(4) 1.362(11), N(2)−C(4) 1.354(10); W(1)−C(3)−P(1) 167.9(4), C(3)−P(1)−C(4) 105.7(3), P(1)−C(4)−N(1) 115.1(7), P(1)−C(4)−N(2) 127.9(7), N(1)−C(4)−N(2) 117.0(8)

in view of the P−C (sp) bond length in [Tp*$(CO)_2W{\equiv}C{-}PMe_2Ph]^+$ [1.741(9) Å], the bond P(1)−C(1) may be designated as a single bond, whereas the bond length P(1)−C(1) compares well with the P=C double bond in the inversely polarized phosphaalkene $HP{=}C(NMe_2)_2$ [1.740(1) Å].[27] Atom C(4) has a trigonal-planar environment with shortened carbon−nitrogen bonds N(2)−C(4) [1.354(10) Å and N(1)−C(4) [1.362(11) Å] because of π-conjugation.

In a more recent paper, another attempt was described at the synthesis of a molybdenum alkylidynephosphanide complex of type **55** (Scheme 25). In contrast to the synthesis of **59** and **60**, where the C−P bond was formed between a positively polarized alkylidyne carbon atom and a negatively polarized phosphorus atom, the approach to anion **63** was based on the reaction of anion **61** and $PhPCl_2$. Reduction of the phosphanylalkylidyne complex **62** with sodium amalgam afforded complex **63**, which features the MoCPPh arrangement expected for a complex with a terminal isophosphaalkyne (phosphoisocyanide) ligand (Scheme 28).

Inspection of the molecular structure obtained from an X-ray diffraction study showed a molybdenum−carbon distance Mo−C(1) of 1.762(5) Å, which has to be regarded again as a triple bond. The bond length P−C(1) of 1.771(5) Å in **63** is similar to that in **60b** [1.759(7) Å], but markedly longer than the P−C single bond in [Tp*$(CO)_2W{\equiv}C{-}PMe_2Ph]^+$ [1.741(9) Å]. Obviously, the P−C bond shortening is mainly the result of an sp-hybridized carbon atom, rather than resulting from a significant amount of C−P multiple bonding. The angles



Scheme 28. Synthesis of the dimeric sodium phosphanidocarbyne complex **63**; S = ether or THF

Mo−C(1)−P [171.0(3)°] and C(1)−P−C(41) [106.0(2)°] are similar to the corresponding values in **60b** [W−P−C = 167.9(4)°; C−P−C = 105.7(3)°].[28] In conclusion, the bonding situation in the anion of **63** is similar to those of the previously reported complexes **59** and **60**, and are better interpreted in terms of alkylidyne complexes that are functionalized at the sp-hybridized carbon atom by either a $[PPh]^-$ unit or a phosphaalkenyl group, and not, as claimed by the authors, as a P-analog **55** of complexes with terminal isocyanide ligands.

5. Conclusions

What have we learnt about isophosphaalkynes? Firstly, the rich chemistry displayed by organic isocyanides is not mirrored by their phosphorus analogs. All attempts to synthesize these molecules have met with failure. In many instances the more stable isomers, the well-known phosphaalkynes, were isolated instead. Moreover, all experiments attempting to trap these molecules to provide some evidence for their transient existence have been unsuccessful. From mechanistic work with (isophosphaalkyne)plati-

num complexes, it might even be concluded that the degradation of phosphavinylidene carbenoids of the type R−P=C(X)Li to phosphaalkynes RCP and lithium halide circumvents the occurrence of free isophosphaalkynes. Quantum-chemical calculations predict isophosphaalkynes as maxima on the energy surface in the system HPC/HCP with energies of ca. 80 kcal/mol above the ground state. In contrast to these findings, the chemistry of dinuclear and trinuclear complexes with bridging phosphaalkyne ligands seems to be more promising for their synthesis. Here, however, it must be stated that the successful preparation of these compounds lacks generality. Product formation is governed sensitively by the nature of the transition metal, its ancillary ligands and the substituents at the dicoordinate phosphorus atom.

To date, no coordination compounds featuring terminal isophosphaalkyne ligands are known. Recently prepared complexes with the required atomic array MCP−R display C−P bond orders of unity only.

In summary, the synthesis of free isophosphaalkynes still remains a challenge. Future approaches to a satisfactory solution may involve sterically encumbering substituents, such as *m*-terphenyl units, at the P atom that could prevent 1,2-P−C migrations and that enclose the C=P terminus in a protective environment. Another possible method to add stability to isophosphaalkynes involves employing highly electronegative substituents at the phosphorus atom. Likewise, the search for complexes with terminal isophosphaalkyne ligands still awaits a solution.

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