Angewandte Essays

Carbon Complexes

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Coordination Chemistry at Carbon: The Patchwork Family Comprising $(Ph_3P)_2C$, $(Ph_3P)C(C_2H_4)$, and $(C_2H_4)_2C$

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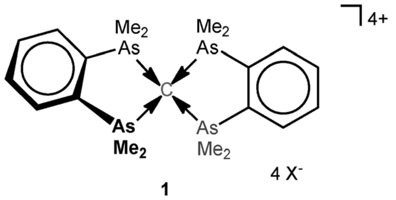
carbodiphosphoranes · cyclopropanes · olefin ligands ·
phosphorus ylides · spiropentane

1. Introduction and History

For about two centuries, coordination chemistry was a domain of main-group and transition-metal chemistry with metal atoms (as in tetracarbonyl nickel(0)) or ions (as in tetrafluoroberyllate(II) or dicyanoaurate(I)) serving as coordination centers for a large variety of neutral or anionic ligands. Typically, the metal centers were considered as positively charged or otherwise electron-deficient acceptors keen to accommodate any electron-rich donors with the resulting types of bonding ranging from purely electrostatic (ion–ion or ion–dipole) to covalent electron-sharing. Concepts such as the rare-gas rules or simply excessive charge accumulation and steric crowding were established to explain the structures and the limits for the population of the coordination spheres.[1–4]

Non-metal and metalloid atoms were rarely considered as acceptor centers of complexes, except for cases where a notorious electron deficiency of an element, or a large difference in electronegativity between non-metal elements as donor and acceptor sites, suggested similar polar bonding characteristics, as in BF_4^- or SbF_6^-, TeF_6 and IF_6^+. For combinations with a small difference in electronegativity and for low coordination numbers the model of a complex had less attraction and no obvious heuristic value. A carbon atom in particular was not considered a "coordination center" in molecular chemistry, but was rather the epitome of the world of conventional covalent bonds. Carbides were generally taken as either interstitial compounds of metals (WC)[4] and of polynuclear metal complexes as in $[Fe_5C(CO)_{15}]$[5] and $[(LAu)_6C]^{2+}$,[6] or as salt-like solids (Al_4C_3), in which the carbon atoms donate their valence electrons to the metal or cluster matrix, or accept electrons therefrom, to become intercalated as tetracations C^{4+} or tetraanions C^{4-}. The same applies to dicarbides such as CaC_2, with its acetylide dianions $[|C{\equiv}C|]^{2-}$,[7] or to dicarbido-centered silver clusters.[8]

In 1964, Nyholm had published a note in *Nature* entitled "Four-coordinate Complexes of Carbon" describing the products of the reaction of CBr_4 or CI_4 with phenylene-1,2-bis(dimethylarsine) in a sealed tube. The compounds were formulated as shown in formula **1** (X = Br, I, ClO_4) and characterized by elemental analysis, melting point, and electrical conductivity in water, the latter approaching the values for a 1:4 electrolyte. Structural work by Pauling was announced to be under way, but to our knowledge the results were never published.[9,10] The "complexation of carbon" referred to C^{4+} as the acceptor center for four arsine donors in analogy to the role of Ti^{4+} in the previously structurally characterized titanium complexes (**2**).[11,12] The relation drawn by Nyholm therefore referred to a carbon atom stripped of its valence electrons and functioning as a positively charged spiro center with four dative bonds $C^{4+}\leftarrow As$ in a standard tetrahedral geometry.



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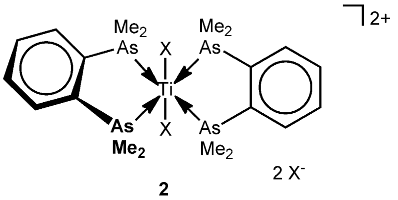

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A decade later, "complexation of carbon" was seen from a very different perspective,[13] mainly through the development of carbanion chemistry, dealing with compounds where carbon atoms bear a negative charge in general,[14] and of

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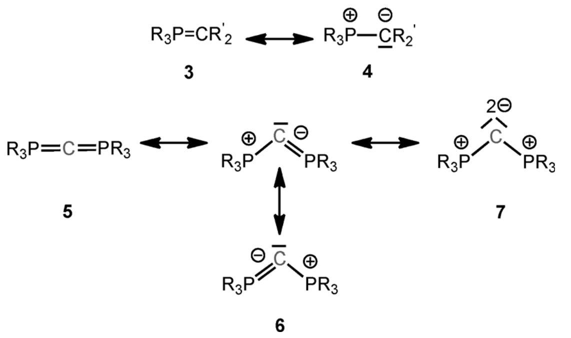
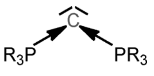
ylide chemistry in particular.[15] While the bonding situation in mono-ylides of phosphorus[15–18] or sulfur[19] could be represented with straightforward canonical forms **3** and **4** with the ylidic carbon atom next to the onium center featuring a maximum charge of 1−, the corresponding bis-ylides required formulae with a 2− charge for the carbon atom flanked by two onium centers (**5**–**7**). The formula **7** appeared



for the first time in the Communication by Ramirez et al. reporting the synthesis of the double-ylide with six phenyl groups (R = Ph), which was named “hexaphenylcarbodiphosphorane”, but not drawn or explicitly designated as a complex of carbon.[20,21] The cumulene or ylide formulae **5** and **6** were used exclusively in most early Reviews, leaving out form **7** for the time being.[22]

Unexpected observations, for example, that the bis-ylides of the formula R_3PCPR_3 had a strongly bent structure, with P-C-P angles of approximately 140°,[23] and could serve as ligands to metal atoms, led Kaska et al. to recognize Ramirez’ compound as “a prime example of a bis-phosphine carbon complex” written for the first time with dative bonds (→) as $(R_3P)\rightarrow\underline{\overline{C}}^0\leftarrow(PR_3)$ (**8**) with the carbon atom in its zero oxidation state.[13] It is an interesting observation that Kaska made reference not only to the report of Ramirez, but also to the paper of Nyholm, but Nyholm had not paid any attention to the discovery of Ramirez, which had appeared three years earlier. Ironically, in phosphonium ylides the difference in electronegativity between C as an acceptor and P as a donor center is particularly small, showing that extended concepts were required going beyond those on which traditional coordination chemistry was built.[24]



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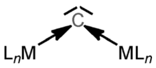

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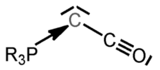
As early as 1983, H. Werner considered the new concept of “coordination at a carbon atom”[25] in attempts to use a carbon atom also as an acceptor of two metal bases $[ML_n]$ that would lead to dinuclear complexes with a “carbido bridge” $[L_nM]\rightarrow\underline{\overline{C}}\leftarrow[ML_n]$ (**9**).[26] Many of the attempted preparations gave products of extensive rearrangements involving the auxiliary ligands L, but several compounds of this type have later been realized,[5,26] also referring frequently to the formal analogy with carbodiphosphoranes.[27]

In a later Section the structural and coordination chemistry of carbodiphosphoranes is briefly summarized.

Historically, it was then only a small step to recognize that within the new concept of “coordination at carbon” the ketene-type compounds of the formula R_3PCCO (or $R_3P{=}C{=}C{=}O$)[28] can be described as mixed-ligand carbon complexes $(R_3P)\rightarrow\underline{\overline{C}}\leftarrow(CO)$ (**10**) with a tertiary phosphine and carbon monoxide as the donors. This picture was corroborated by a molecular structure showing a bend at the ylidic C-atom (P-C-C 145.5° for R = Ph).[29] Accordingly, isocyanides RNC were shown to form “complexes” $(R_3P)\rightarrow\underline{\overline{C}}\leftarrow(CNR)$ (**11**) with analogous characteristics.[22,29] It was noticed, however, that both CO and CNR ligands exert a strong π-acceptor effect which reduces the nucleophilic character and the donor capacity of the central carbon atom.[30a] This effect becomes most obvious for the classical textbook molecule, carbon suboxide C_3O_2 which it is now tempting to write not only as $O{=}C{=}C{=}C{=}O$, but also as $(OC)\rightarrow\underline{\overline{C}}\leftarrow(CO)$:. Its structure was initially taken as linear or quasi-linear[30b,c] but is now known to have a bent equilibrium structure in the gas phase (CCC ca. 156°) with an extremely flat energy profile of bending.[30d,e] Yet it can function as a donor at its central carbon atom, for example in the addition of AuCl.[30f]



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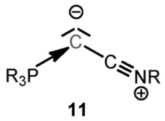

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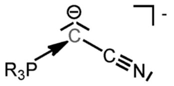

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Bestmann et al. have also prepared the anionic species $[(Ph_3P)\rightarrow\underline{\overline{C}}\leftarrow(CN)]^-$ (**12**) by deprotonation of the corresponding ylide $Ph_3P{=}CHCN$ and found that it features a highly increased nucleophilic reactivity compared to its precursor.[31] Its structure and the coordination chemistry are unknown, but it can be assumed that they follow the examples of the analogues described above. The ν(C≡N) stretching frequency is shifted from 2130 in the precursor to 2000 cm^{-1} in the deprotonated form, and the chemical shift δ(P) shows a difference of 21 ppm, both reflecting the strong σ and π interactions of the CN^- ion with the central carbon atom. Bestmann already proposed a canonical formula with two lone pairs of electrons at the central carbon to represent this high nucleophilicity and donor capacity.

The family of carbon complexes was finally extended including carbenes R_2C**:** as the donors for the carbon atom.[32–38] In this approach, not only tetrasubstituted allenes $R_2C{=}C{=}CR_2$ are considered as homoleptic complexes $(R_2C)\rightarrow\underline{\overline{C}}\leftarrow(CR_2)$, but also several heteroleptic, mixed-ligand systems have been included.[38] One of these compounds, $Ph_3P{=}C{=}C(OEt)_2$, now formulated as $(Ph_3P)\rightarrow\underline{\overline{C}}\leftarrow[C(OEt)_2]$,[28,38,39] was also found to have a bent structure.[38] Subsequently it was shown to be a ligand of which stable 1:1 and 1:2 complexes with AuCl could be obtained: $[(Ph_3P)C(AuCl)_n[C(OEt)_2]]$, $n = 1$ or 2, resembling the analogous gold complexes of carbodiphophoranes[38] (see below). This result supports the idea that the carbene [**:**$C(OEt)_2$] is a weaker π-acceptor than CO and CNR, leaving the central carbon atom with a high donor capacity. Tetraaminoallenes $(R_2N)_2C{=}C{=}C(NR_2)_2$ or $[(R_2N)_2C]\rightarrow\underline{\overline{C}}\leftarrow[C(NR_2)_2]$ afford only 1:1 complexes with AuCl at the central carbon atom,[35] probably owing in part to steric effects, since a double protonation at

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the central carbon atom is possible. A special case of singlet carbenes obtained from the combination of a phosphine and a strong π-acceptor, such as a fluorenyl unit, at a given carbon atom is an example of the broad range of opportunities offered by this concept.[38b]

This new and rapidly growing area of carbene complexes of carbon is not within the scope of the present article (see title).

All examples put together in this introductory summary are complexes of carbon with σ-donor ligands with a varying π-acceptor character. In the present account an attempt is made to propose a heuristic extension of the "coordination at carbon" concept by including π-complexation of hydrocarbons such as ethene and even cyclopropane.

2. Homo- and Heteroleptic σ- and π-Coordination at a Carbon Atom

2.1. Coordination of Two Tertiary Phosphines at a Carbon Atom: Carbodiphosphoranes

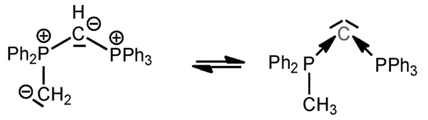
After the first synthesis of the parent molecule fully substituted by phenyl groups,[20] an increasing number of carbodiphosphoranes $(R_3P)C(PR_3)$ with various substitution patterns were prepared and structurally characterized (Table 1).

Table 1: Prototypical carbodiphosphorane molecules.

Compound	Reference
$(Me_3P)C(PMe_3)$	[40,41]
$(MePh_2P)C(PPh_2Me)$	[42–45]
$[Me(o\text{-}Tol)_2P]C[P(o\text{-}Tol)_2Me]$	[46]
$[Ph_2(ArCH_2)P]C[P(CH_2Ar)Ph_2]$	[47]
$(Ph_3P)C(PR_3)$ R = Me, Et, Pr, Bu	[48,49]
$(Ph_3P)C(PPhMe_2)$	[48]
$(Ph_3P)C(PPh_2Me)$ [Eq. (2)]	[48]
$(MePh_2P)C(PPh_2iPr)$ [Eq. (1)]	[50,51]
$(MePh_2P)C[Ph_2(c\text{-}C_3H_5)]$ [Eq. (1)]	[52]
$[(CH_2)_3(PPh_2)_2]C$ (**16**)	[53,54]
$[(H_2C)_4(PPh_2)_2]C$ (**17**)	[55]
$[(Me_2N)_3P]C[P(NMe_2)_3]$	[56]
$(Ph_3P)C(PPh_3)$	[20,21,57]
$1,2\text{-}C_6H_4(PPh_2)_2C$ (**15**)	[58,59]
(**20**, R = N*i*Pr$_2$)	[60]
$[(MePh_2P)C(PPh_2CH_2CH_2)]_2$ (**19**)	[55]
$[Me(Me_2N)_2P]C(SPh_2)$	[61]
$(Ph_3As)C(AsPh_3)$	[62]

Against original expectations, the list now also includes several compounds with alkyl substituents R bearing acidic hydrogen atoms in one or more of the α-positions for which a conjugated isomer (with alternating electrical charges) **13** could be envisaged. However, in all cases the prototropy was found to rest at the cumulated form **14** (with a remarkable charge accumulation at the central C atom).

When the fully methylated homologue became available, it could be shown by electron diffraction that this volatile compound $(Me_3P)\rightarrow\overline{C}\leftarrow(PMe_3)$ has a bent gas-phase structure.[40,41] The results also allowed a comparison with the gas phase data of the simplest mono-ylide Me_3PCH_2.[63,64] Even cyclic systems where the bending of the P-C-P unit is enforced by ring strain were found to exhibit the cumulated form. The examples include five-, six-, and seven-membered diphosphacycles with or without annelated rings (**15**–**17**).[46,53–55]



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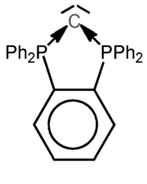

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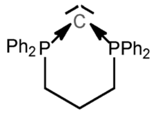

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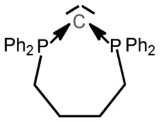

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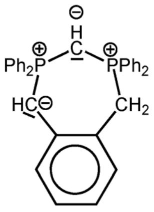

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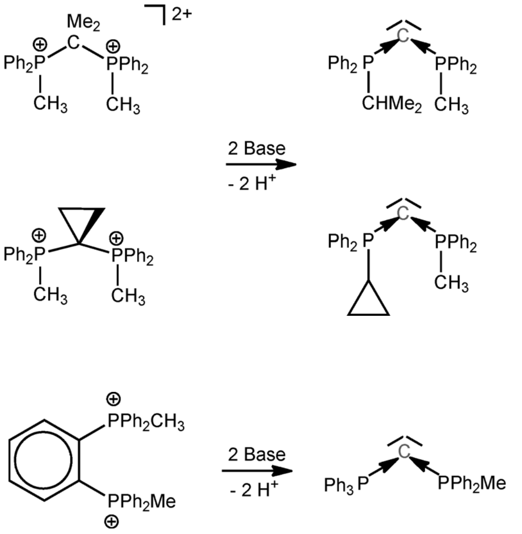
It was only in the case of benzyl substitution, that the conjugated isomer **18** was more stable than the cumulated isomer (i.e., the carbodiphosphorane). In several other examples, intramolecular rearrangements leading from molecules with two "isolated" ylide functions to the corresponding carbodiphosphoranes have been observed [Eq. (1a), (1b), (2)].[50,52,53,65]



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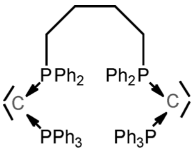
In another case, two carbodiphosphorane units could be linked by a 1,4-butane bridge (**19**) without any isomerization.[55]



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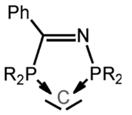

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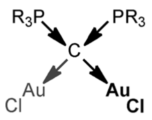
Where structures have been determined for the compounds listed in Table 1, the variations of the key data (i.e., the P−C distances and the P-C-P angles) are found in a rather narrow range except for the cyclic compounds (**15**–**17**), where angles as low as 104.82(10)° are encountered. This narrow angle in a five-membered ring leads to reduced stability and to isomerization, but with protective substituents a stable situation can be achieved (**20**; $PR_2 = P[N(i\text{Pr})CH_2]_2$).[58–60]

Table 1 also contains an example of a mixed ylide with a central P=C=S unit[61] and of a carbodiarsorane,[62] but their structures have not been determined. By contrast the Ramirez compound $(Ph_3P)C(PPh_3)$ was found to have a particularly rich structural chemistry. It crystallizes in several polymorphs in which the molecules show a variation of P-C-P angles owing to packing forces. The slight energy differences associated with the conformational changes lead to triboluminescent behavior.[57]

Since both the structure and the reactivity pattern observed in organic reactions[15–17] suggested a highly nucleophilic character of the central carbon atom of carbodiphosphoranes, the donor capacity of this function was also investigated starting as early as 1974.[13] A selection of early-transition-metal complexes were used in the synthesis of the corresponding ylide complexes in which one discrete C→M donor–acceptor bond was established. In this early work, no dimetallated examples were yet considered.[15–17,40,41,66–69] Because investigations of the coordination chemistry of gold(I) with simple mono-ylides R_3PCH_2 had produced a large variety of mono- and polynuclear ylide complexes,[70,71] experiments with carbodiphosphoranes were also initiated. With Me_3PCPMe_3 as the ylide and $[Me_3PAuMe]$ as the gold component, a 1:2 complex $[(Me_3P)_2C(AuMe)_2]$ was obtained as the first example of a dimetallated carbodiphosphorane.[72] This result suggested that two lone pairs of electrons are available for dative bonding in carbodiphosphoranes and that consequently these compounds could be described as phosphine complexes of carbon. The tetrahedral configuration at the central carbon atom was later confirmed by X-ray diffraction analysis of the chloro compound $[(Ph_3P)_2C(AuCl)_2]$ (**21**).[73] According to quantum chemical calculations, both the mono- and the di-auration of the carbodiphosphorane using $[(Me_2S)AuCl]$ are exothermic processes.[38,74] In subsequent studies, several other metals from various parts of the Periodic Table were also used for dimetallation of carbodiphosphoranes, including aluminum, zinc, cadmium, and silver.[54,75,76a] Among the main-group elements, boron in particular has been demonstrated to form 1:1 and 1:2 complexes, such as $[(Ph_3P)_2CBH_3]$ and $[(Ph_3P)_2C(BH_2)_2H]^+$.[76b]



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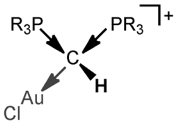

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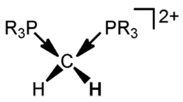

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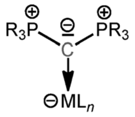
These results correspond to the known double protonation of carbodiphosphoranes with acids HX which affords the parent bis-phosphonium salts $[R_3PCH_2PR_3]^{2+}\,2X^-$ (**23**). The reverse process, treatment of these salts by base, represents the most convenient access to carbodiphosphoranes.[15–18,20,21] The analogy between $[LAu]^+$ or [XAu] and the proton $[H]^+$ is in line with the isolobal concept.[77] Accordingly, mixed complexation of a proton and an AuX unit has been observed in the cation $[(Ph_3P)_2C(AuCl)H]^+$ (**22**).[77] In another short description, the central carbon atom in complexes $[(R_3P)_2C(AuX)_2]$ and related compounds is involved in "push–pull" or "capto–dative" bonding with two donors and two acceptors (**21**).[24,38]

In the gold(I) complexes of carbodiphosphoranes the metal atoms with their d^{10} electronic configuration are assumed to be only 2-electron acceptors (**24**).[16–18] For a growing number of 1:1 complexes with highly electron-deficient metal centers, the $M \leftarrow C(PR_3)_2$ dative bonding is ascribed double bond character with the ylidic carbon atom and the metal atom serving as a 4-electron donor and acceptor, respectively. In the hybrid description, the two filled lone-pair orbitals at the carbon atom act as σ and π donor functions (**25**). This mode of interaction has recently been proposed mainly for complexes of U^{VI} with di-functionalized carbodiphosphoranes (**26**).[78a] However, there are also similar discoveries and developments with main-group-element acceptors, in particular boron, as demonstrated in species such as $[(Ph_3P)_2C{=}BH_2]^+$.[78b,c]



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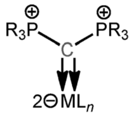

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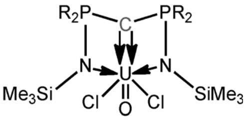

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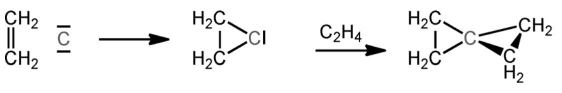
2.2. Coordination of Two Ethene Molecules at a Carbon Atom: Spiropentane

Homoleptic π-coordination of two molecules of the simplest olefin, ethene, to a carbon atom leads to the smallest possible spiro-alkane, spiropentane $C_5H_8 \equiv (C_2H_4)C(C_2H_4)$ (**27**). The two steps of this process represent oxidative additions at carbon $C^0 \rightarrow C^{II} \rightarrow C^{IV}$ rendering first the smallest cyclic carbene $:C \leftarrow (C_2H_4)$ and then the bicyclic hydrocarbon with the central atom in its conventional tetravalent state [Eq. (3)]. A formal equation for this double addition was first presented in a paper by Gleiter et al. in an approach to the molecular orbital diagram for spiropentane starting from the orbitals of two ethene molecules and a carbon atom [Eq. (4)].[79] The result was shown to be in accord with data obtained from photoelectron spectroscopy experiments.



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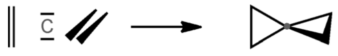

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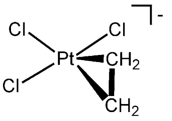
(4)

Spiro[2.2]pentane (**27**) has a molecular structure with D_{2d} point group as maximum symmetry. Its molecular dimensions were determined by electron diffraction (ED) in the gas phase,[80] by NMR spectroscopy in at least two liquid crystalline phases (LC),[81–83] and by low-temperature single-crystal X-ray diffraction (m.p. of spiropentane −115 °C).[84] The four radial (vicinal) C−C bonds are 1.469 Å long and shorter than the two peripheral (distal) C−C distances of 1.519 Å, with the exo- and endocyclic C-C-C angles at the central carbon atom at 137.2° and 62.8°, respectively (determined by ED). These data have been reproduced quite closely by quantum chemical calculations at various levels of sophistication.[85–94] The dimensions show that upon addition to carbon, each ethene molecule loses its double bond character, and four new bonds are established which are shorter owing to a better orbital overlap at close contacts.

The differences between the data obtained for gaseous, nematic and crystalline phases with various techniques are surprisingly small. Crystal packing forces lead to only very minor distortions, and the molecule was therefore termed a "tensile spring".[84] However, the influence of substituents on the relative length of the vicinal and distal C−C bonds can be quite marked, and the effects can be rationalized by quantum chemical calculations.[84,88–91,94]

It is interesting to compare the nature of the coordinated ethene in spiropentane and in a classical ethene complex of a metal atom or cation, such as the anion $[Cl_3Pt(C_2H_4)]^-$ of Zeise's salt. In this complex the C−C bond length was found to still be 1.375 Å by single-crystal X-ray and neutron diffraction, only about 4 % longer than in free ethene (1.337 Å, determined by ED). However, the hydrogen and carbon atoms are no longer coplanar (as in ethene), the two CH_2 planes of the complex forming a dihedral angle of 146° (**28**).



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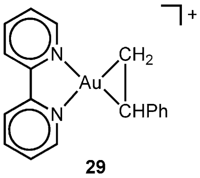
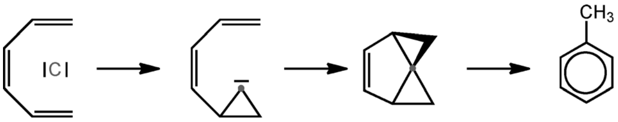


29

Upon addition of ethene to carbon [Eq. (3) or (4)] therefore the C=C bond order is much more strongly reduced towards a single bond than in common transition-metal complexes. The difference can be rationalized qualitatively by a strong π back-donation effect (from carbon into the antibonding π orbital of ethene), which is much weaker for metal atoms M with larger atomic radii, lower electronegativity, and largely complete electron shells. In other words, while in spiropentane the three-membered rings have true cyclopropane character, the nature of the three-membered ring in the Zeise's salt anion is far from that of a metallacyclopropane.[95,96]

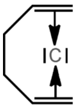
In contrast, in olefin complexes of gold(I) of the type $[LAu(RHC{=}CH_2)]$ (**29**), for L = 2,2′-dipyridyl and R = Ph, the C=C bonds of the coordinated styrenes are elongated to up to 1.48 Å.[97–99] These differences can be ascribed to the high electronegativity of gold, the extreme relativistic contraction of the gold orbitals, and the filled $5d^{10}$ electronic configuration. However, the bond lengthening may be also taken as evidence for a true oxidative addition of styrene to gold(I) which leads to an auracyclopropane unit with the metal atom in the oxidation state +3. For this reason the C−C bond length in the cation **29** is similar to that of the distal bonds in the molecule **27** where oxidative addition of two ethene molecules has led to the oxidation state +4 of the spiro carbon atom.

The second step of the formal addition of two ethylene donors to a carbon atom has been envisaged in the rearrangement of *cis*-1,3-butadienyl cyclopropylidene. The corresponding tricyclo[4.1.1.0^{1,3}]hept-4-ene is a metastable intermediate undergoing rapid rearrangement to toluene [Eq. (5)].[100]



(5)

Ansa-spiropentanes were also subjects of theoretical studies.[79] The molecules **30** and **31** are easily recognized as the analogues of cyclic carbodiphosphoranes **32** and **33** (**15**).



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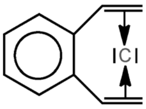

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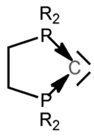

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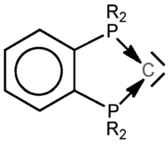

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In the present context (see above for the carbodiphosphoranes) the question arises if the central carbon atom of spiropentane shows any basicity or donor capacity that could indicate significant residual carbon(0) or carbon(II) character. Under the headline "tetracoordinate carbon as a nucleophile?", theoretical work has provided structural and proton affinity (PA) data for spiropentane as the conjugate base of the corresponding protonated species with a central hypercoordinate carbocation (carbonium ion). The gas-phase PA values indeed clearly show the exceptional basicity of the central carbon atom in its highly strained environment, which can be made even more strained with short ansa-linkers [Eq. (6)].[94]

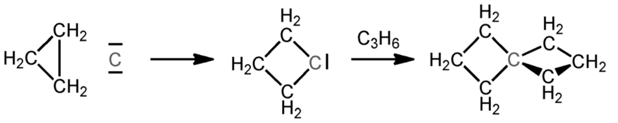
(6)

The proton affinity is much higher than that of cyclopropanes and even more so than in relaxed alkanes.[101] There is as yet no experimental evidence for any alkylation of spiropentane affording a stable salt with the cation featuring the central atom pentacoordinated by five carbon atoms, or for donor–acceptor complexation of spiropentanes at metal atoms or cations.

However, pentacoordination at carbon is supported by aurophilic bonding in multiaurated compounds of the types $[HC(AuL)_4]^+X^-$, $[C(AuL)_5]^+X^-$, or $[(Me_3Si)_2C(AuL)_3]^+X^-$.[102–105] Given the isoelectronic relation between C^0 and N^+ or P^+, it is further interesting to note that pentaaurated ammonium and phosphonium dications are known: $[N(AuL)_5]^{2+}$ and $[P(AuL)_5]^{2+}$ or $[RP(AuL)_4]^{2+}$ [106–109] all with pentacoordinated central atoms (R = aryl; L = *tert*-phosphine). Therefore, given the isolobal relationship of H^+ and $[AuL]^+$,[110] attempts to aurate spiropentane with strongly electrophilic $[LAu]^+$ agents may be a promising endeavor [Eq. (6)].

2.3. Addition of Two Cyclopropane Molecules to a Carbon Atom: Spiro[3.3]heptane

After introducing spiropentane as the 2:1 complex of ethene and a carbon atom [Eq. (3), (4)], spiro[3.3]heptane (**34**) can be recognized as the product of double oxidative addition of cyclopropane at C^0 via a carbene intermediate [Eq. (7), (8)].



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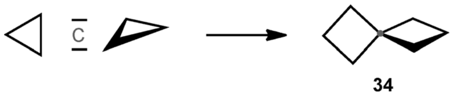

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(8)

The electronic structure of the hydrocarbon product can again be reached from linear combinations of the orbitals of the central carbon atom with the frontier orbitals of the cyclopropane molecule, that is, its Walsh orbitals which resemble those of ethene in their symmetry and energy (Figure 1).[111–113]

Spiro[3.3]heptane (**34**) is a liquid of boiling point 96–97 °C, first prepared by Weinstein et al. in 1965.[114] Its structure has been calculated to have a C_2 symmetric ground state with the four-membered rings folded by 11°.[112,113]

There is an intriguing parallel to be found in the oxidative addition of cyclopropane to platinum instead of carbon which yields a metallacyclobutane product: The dinuclear platinum(II) ethene complex $[\{(C_2H_4)PtCl_2\}_2]$ was found to react with cyclopropane in the presence of pyridine to afford a platinacyclobutane compound. In this reaction, the ethene ligand is replaced by the cyclopropane molecule which becomes part of a four-membered ring. Interestingly, cyclopropane can be liberated if the complex is treated with cyanide [Eq. (9)].[115] This sequence of reactions illustrates the similarity of ethene and cyclopropane in their affinity for a given element, where the elements may be as different as Pt or C. It also appears, however, that the interaction of Pt^{II} with cyclopropane is much stronger than with ethene (in Zeise's cation) and can also be interpreted as an oxidative addition to afford a platinacyclobutane with the metal atom in the +4 oxidation state.

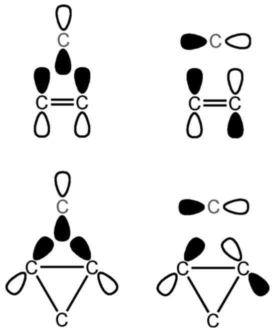
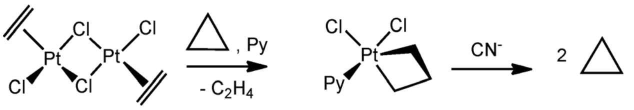
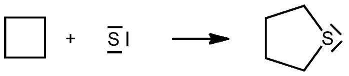


Figure 1.



(9)

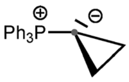
The question arises if cyclic hydrocarbons like cyclobutane or -pentane should still be considered in this context. It appears that for these cases where the ring strain is strongly reduced or absent, the energy gained in the oxidative addition to a carbon or a metal atom is greatly diminished. On the other hand it should be remembered that the insertion of a sulfur atom into cyclobutane to produce tetrahydrothiophene follows the same pattern [Eq. (10)].



(10)

2.4. Triphenylphosphonium Cyclopropylide and -Cyclobutylide

Solutions of a compound formulated as $Ph_3P{=}C(CH_2)_2$ with a three-membered ring (**35**) were first prepared by various authors using different routes, but the product was not isolated. Its identity was inferred from its reactivity pattern in organic reactions.[116–122] After some controversies about the NMR spectroscopy data,[123,124] the compound was isolated and its crystal structure determined.[125] The compound has



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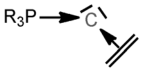

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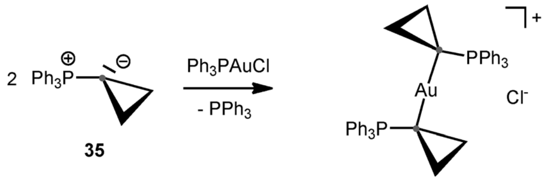
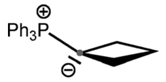
a molecular structure with a pronounced pyramidal configuration of the ylidic carbon atom and with an angle of 58° between the plane of the cyclopropyl ring and the P−C$_{ylide}$ bond. The cyclopropyl ring forms a triangle with almost equilateral distances, with the distal bond at 1.499(10) and the two vicinal bonds at 1.525(9) Å. The difference is significantly smaller than that found in the spiropentane structure **27** (1.469 vs. 1.519 Å, above), but considering the standard deviations, the variation shows a clear correspondence. The Ph$_3$P-C unit has a tetrahedral configuration at the P atom with bond lengths of 1.800(6), 1.814(5), and 1.816(6) Å for P−C$_{phenyl}$ and 1.696(6) Å for P−C$_{ylide}$. These data agree well with those of the two Ph$_3$PC units sharing the carbon atom in the carbodiphosphorane (Ph$_3$P)C(PPh$_3$).[23,57] The molecular and electronic structures of phosphonium cyclopropylides R$_3$PC-(CH$_2$)$_2$ were investigated in an early quantum chemical study for the model system with R = H. The bent structure has been reproduced and barriers to inversion and rotation have been estimated.[123,126,127] The ring strain in the cyclopropylide is clear from the isomerism observed in mixed methyl/cyclopropyl ylides, in which the simple methylide is clearly favored.[124,125]

In summary, the molecular structure of triphenylphosphonium cyclopropylide strongly supports the analogy of this molecule with both spiropentane on the one hand and with hexaphenylcarbodiphosphorane on the other. A formula (Ph$_3$P)→$\underline{\mathrm{C}}$←(C$_2$H$_4$) can thus be proposed to reflect this relationship (**35**). This formalism with lone pairs of electrons at the ylidic carbon atom is further supported by the formation of complexes with various metal compounds. In work carried out as early as 1982, the compound was shown to be a substrate for protonation and alkylation and to give 1:1 adducts not only with BH$_3$, AlMe$_3$, and GaEt$_3$, but also with [Ph$_3$PAuCl].[128] In the reaction with [Ph$_3$PAuCl], both the Cl and the Ph$_3$P ligands are replaced regardless of the employed ratio of reactants to produce a very stable 1:2 complex [Eq. (11)]. The reaction is evidence that the cyclopropylide is an even stronger donor for gold(I) than Ph$_3$P, which is generally considered one of the best donors for low-valent coinage metals.[18,70]



(11)

The homologous triphenylphosphonium cyclobutylide (Ph$_3$P)C(CH$_2$)$_3$[129,130] has also been structurally characterized and shown to have a pyramidal configuration at the ylidic carbon atom, but the pyramid is flat (with an inclination of only 19° instead of 58° for the cyclopropylide) and more readily inverted (**37**).[129] As shown for spiro[3.3]heptane **34** above, its skeleton may be seen as being generated in the addition of triphenylphosphine and cyclopropane to a carbon atom (**38**).



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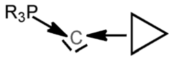

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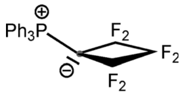
The structural characteristics of the cyclobutylidene part are indeed almost congruent, with a folding angle of the four-membered ring at 17°. Not surprisingly, in triphenylphosphonium hexafluorocyclobutylide (**37-F**) the ylidic carbon atom has an almost trigonal-planar environment PCC$_2$, and the cyclobutylidene ring is also flat.[131] This result reflects the extremely strong electron-withdrawing effect of the hexafluorocyclopropane part as compared with unsubstituted cyclopropane, leaving very little, if any lone-pair electron population at the ylidic carbon atom.



37-F

A sulfur analogue of the phosphorus compound **35**, diphenylsulfonium cyclopropylide (Ph$_2$S)C(CH$_2$)$_2$, has also been prepared and its activity in organic reactions carefully investigated. Although its molecular structure is not known, it has followed from the stereocontrol of the reactions that the configuration of the ylidic carbon atom must be pyramidal with a high barrier of inversion.[132]

In summary it appears that the seemingly unrelated compounds within the two patchwork families (Ph$_3$P)C-(PPh$_3$), (Ph$_3$P)C(C$_2$H$_4$), (C$_2$H$_4$)C(C$_2$H$_4$) and (Ph$_3$P)C(PPh$_3$), (Ph$_3$P)C(CH$_2$)$_3$, (CH$_2$)$_3$C(CH$_2$)$_3$ follow a consistent pattern in stoichiometry and structure which even has parallels in the complexes of dicarbon C$_2$ and tricarbon C$_3$. This chemistry is less well developed.

3. Coordination at Dicarbon C$_2$ and Tricarbon C$_3$

The analogous approach to complexes of "dicarbon" (C$_2$) has a much shorter history. This carbon dimer C$_2$ has a X$^1\Sigma_g^+$ ground state and a calculated bond energy larger than the triple bond in acetylene suggesting significant quadruple bonding [C≣C], with the fourth bond contributing about 13 kcal mol^{-1}.[133–136] In comparison to the acetylide dianion [|C≡C|]$^{2-}$, which appears in many carbides and carbide complexes, the role of neutral C$_2$ as an acceptor unit for donor molecules has generally not much been considered and investigated.

3.1. Homoleptic Coordination of Tertiary Phosphines

A remarkable exception were the attempts by Stang et al. in 1999[137] to find evidence for the at least transitory existence of a cumulated compound Ph$_3$P=C=C=PPh$_3$ expressing the idea that this compound may be taken as a complex of dicarbon C$_2$, (Ph$_3$P)→C$_2$←(PPh$_3$), in analogy to the corresponding adduct of C$_1$ (**39**, **40**).[13,20,24] This study was preceded by work of Bestmann et al.[138] who prepared and formulated Ph$_3$P=C=C=BPh$_3$ as a push–pull adduct of C$_2$: (Ph$_3$P→C≡C→BPh$_3$), along with the corresponding butadiyne system R$_3$P-

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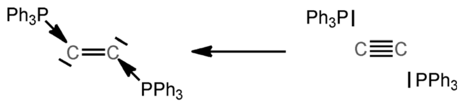
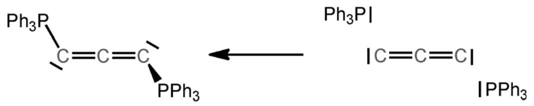
C≡C−C≡C-BR$_3$.[139] A very recent theoretical study of a model compound (Me$_3$P)C=C(PMe$_3$) gave a Z-type structure with C_i symmetry, a C−C bond length of 1.349 Å and C-C-P angles of 116.2°.[140a] Calculations were also carried out for the adducts with the heavier congeners E$_2$ with E = Si, Ge, Sn, Pb.[140b]



39 **40**

Dinuclear metal complexes of the type (L$_n$M)→C$_2$←(ML$_n$) with a C$_2$ unit bridging the two metal atoms have also been prepared in a number of varieties,[4,25,27,141] but these analogues are not within the scope of the present summary.

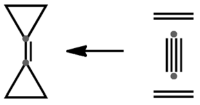


41 **42**

The cumulene Ph$_3$P=C=C=C=PPh$_3$ was first envisaged as a complex of C$_3$ with two tertiary phosphines: (Ph$_3$P)→C$_3$←(PPh$_3$) by Bestmann et al. in 1989.[138] The compound was finally prepared in 1993 from a racemic allene precursor by treatment with a base and obtained as an orange solid of m.p. 73 °C.[139] A structure with a linear C$_3$ unit and two C-C-P angles as shown in formula **41** was proposed (C_2 symmetry). Its existence, at least as an intermediate, had already been demonstrated by Stang et al. in 1991, and a similar structure had been formulated (**42**).[137] Dinuclear metal complexes with a linear C$_3$ unit between the two metal atoms have also been realized.[25,142]

3.2. Homoleptic Coordination of Ethene and Cyclopropane

Following the same concept, the double addition of ethene to dicarbon C$_2$ or tricarbon C$_3$ formally leads to bis(cyclopropylidene) (**43**) and bis(cyclopropylidene)methane (**44**), respectively.



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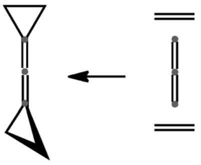

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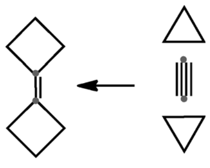
The hydrocarbon **43** and many of its derivatives have been prepared[143a–f] and the structures of some them have been determined.[144a,b,145] The length of the central C=C bonds is about 1.30 Å, and the C−C distances in the three-membered rings are 1.48 (vicinal) and 1.54 Å (distal). Unsubstituted **44** has also been prepared and fully characterized. Its electronic structure has been calculated and the results correlated with its PE spectrum. The molecular structure of the octamethyl derivative has been determined and shown to have approximately the usual D_{2d} allene geometry. The C=C and C−C bond lengths are 1.293 (central), 1.482 (vicinal) and 1.526 Å (distal), respectively.[146]

Cyclobutylidene cyclobutane (**45**) has been prepared by different routes,[147,148] one of which uses triphenylphosphonium cyclobutylide as a precursor.[148,149] Its structure has been determined by X-ray diffraction and shown to feature a central C=C bond length of 1.315 Å with the six core carbon atoms roughly in a common plane, but with puckered four-membered rings (14° as the dihedral angle).[150]

Bis(cyclobutylidene)methane (**46**) has been prepared from the precursor **45** by cyclopropanation of the C=C bond and subsequent ring opening.[147] Its molecular structure has been calculated by quantum chemical studies and was found to feature C=C bond lengths of around 1.30 Å.[151]



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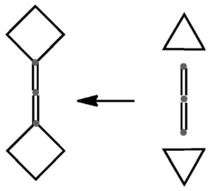

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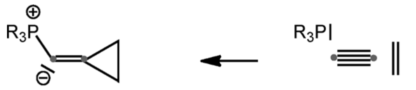
3.3. Heteroleptic Coordination

A literature survey has shown that the heteroleptic complexes of C$_2$ and C$_3$ with a tertiary phosphine and ethene or cyclopropane as ligands (**47–50**) have not yet been prepared, but simple "cumulenes" with two independent terminal substituents R are well established (**51**, **52**).[28]



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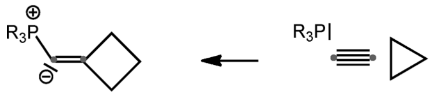

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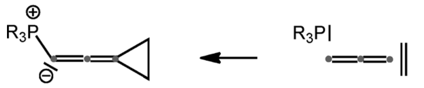

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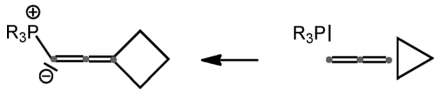

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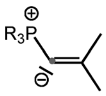

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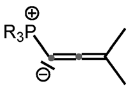

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It is interesting to note that compounds like **47** and **49** can be viewed as complexes of either C_1 or C_2 with phosphines and cyclopropylidene or ethene ligands.

4. Conclusions

Following the concept of "coordination at carbon" some interesting and even unexpected correlations can be detected which can make the investigator think differently about long established classes of compounds and their relationships. The role of olefins and cyclopropanes as ligands for carbon atoms or molecules, C_n, is not immediately obvious, because in general we think in different categories when dealing, for example, with standard organic compounds on the one hand and with coordination compounds on the other. Applying the conventional lines of thinking of one area to quite another one helps us to cross the borders between traditional realms, and opens the possibility to see things from a different perspective.

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