Carbones and Carbon Atom as Ligands in Transition Metal Complexes

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Abstract: This review summarizes experimental and theoretical studies of transition metal complexes with two types of novel metal-carbon bonds. One type features complexes with carbones \textit{CL}$_2$ as ligands, where the carbon(0) atom has two electron lone pairs which engage in double (\(\sigma\) and \(\pi\)) donation to the metal atom \([M] \equiv \text{CL}_2\). The second part of this review reports complexes which have a neutral carbon atom \textit{C} as ligand. Carbido complexes with naked carbon atoms may be considered as endpoint of the series \([M]\text{-CR}_3 \rightarrow [M]\text{-CR}_2 \rightarrow [M]\text{-CR} \rightarrow [M]\text{-C}\).

Keywords: Carbone complexes; carbido complexes; transition metal complexes; chemical bonding
1. Introduction

Transition metal compounds with metal-carbon bonds are the backbone of organometallic chemistry. Molecules with M-C single bonds are already known since 1849 when Frankland reported the accidental synthesis of diethylzinc while attempting to prepare free ethyl radicals [1,2]. Molecules with a [M]=CR₂ double bond (carbene complexes) or a [M]=CR triple bond (carbyne complexes) were synthesized much later [3-6]. Two types of compounds with metal-carbon double or triple bonds having different types of bonds are generally distinguished, which are named after the people who isolated them first. Fischer-type carbene and carbyne complexes are best described in terms of dative bonds following the Dewar-Chatt-Duncan (DCD) model [7,8] [M]=CR₂ and [M(−)]≡CR(+) whereas Schrock-type alkylidenes and alkylidyynes are assumed to have electron-sharing double and triple bonds [M]=CR₂ and [M]=CR [9-11].

This review deals with transition metal complexes with metal-carbon bonds to two types of ligands, which have only recently been isolated and theoretically studied. One type of ligand are carbones CL₂ [12], which are carbon(0) compounds with two dative bonds to a carbon atom in the excited 1D state L→C←L where the carbon atom retains its four valence electrons as two lone pairs that can serve as four-electron donors [13,14]. Thus, carbones CL₂ are four-electron donor ligands whereas carbenes CR₂ are two-electron donors. Carbenes have a formally [15] vacant p(π) orbital that can accept electrons in donor-acceptor complexes M=CR₂ whereas carbones are double (σ and π) donors in complexes [M]=CL₂. A good Lewis acid acceptor fragment A for a carbene complex has a vacant σ orbital and an occupied π orbital whereas a suitable acceptor for a carbone is a double Lewis acid with vacant σ and π orbitals as shown in Figure 1a and 1b. If the Lewis acid A has an occupied π orbital it would lead to π repulsion with the π lone pair of the carbene CL₂, whereby the repulsive interaction is reduced if L is a good π acceptor (Figure 1c). The two electron lone pairs of a carbone may bind to one or two monodentate Lewis acids A or protons or to a single bidentate Lewis acid as shown in Figure 1. The large second proton affinity is a characteristic feature of carbones, which distinguishes them from carbenes [16]. Examples of all cases are known and are described below.
Figure 1. Schematic representation of the most important orbital interactions between carbene ligands CR₂ and carbones CL₂ with Lewis acids A. (a) Carbene complex with a monodentate Lewis acid; (b) Carbone with a bidentate Lewis acid; (c) Carbone with a monodentate Lewis acid; (d) Carbone with two monodentate Lewis acids.

It is important to realize that the two electron lone-pairs of a carbone CL₂ may additionally engage in π-backdonation to the ligands L whose strength depends on the availability of vacant π orbitals of the ligands L. Stronger π acceptor ligands L enhance the π-backdonation L←C→L which leads to wider bending angles at the carbon atom (Figure 2). The significant bending of free C(CO)₂ [17,18] can straightforwardly be explained in terms of dative bonding in carbon suboxide C₃O₂ [19,20]. The π-acceptor strength of ligands L thus modulates the donor interaction of the carbone CL₂.

Figure 2. Calculated and (in parentheses) experimental bond angles of carbones CL₂ with different ligands L and partial charges Δq of the central fragments. The data are taken from ref. 20.
The following list gives some essential features of carbones and their differences to carbenes. At the same time we want to stress that the distinction between carbenes and carbones are just a useful classification of compounds, which are a helpful model to explain the structures and reactivity of molecules. Nature does not exhibit a strict distinction line and there are complexes with electronic structures that have intermediate features between both classes of compounds. Carbenes and carbones are two ordering principles like ionic and covalent bonding. Intermediate cases are common and yet, the two concepts are essential ingredients of chemistry. The first part of this review summarizes experimental and theoretical work about transition metal complexes with carbone ligands [M]-CL₂.

1. Carbones are neutral carbon(0) compounds of the general formula CL₂, which possess two electron lone pairs of electrons of σ and π symmetry, respectively.
2. Carbones CL₂ have dative σ bonds L→C←L and weaker π backdonation L←C→L which resemble donor-acceptor bonds in transition metal complexes.
3. The carbon atom of carbones has very large electron densities and thus, unusually large negative partial charges.
4. In contrast to carbenes, carbones exhibit high first and second proton affinities (PAs) in the region of about 290 and 150 - 190 kcal/mole, respectively; the second PA is a sensitive probe for the divalent C(0) character of a CL₂ molecule. Carbones can take up one and two protons with formation of [HCL₂]⁺ cations or [H₂CL₂]²⁺ dications, respectively.
5. Carbones have a bent equilibrium geometry where the bending angle becomes wider when the ligand L is a better π acceptor.
6. Carbones can take up one or two monodentate Lewis acids A building the complexes A←C(L₂) and A←C(L₂)→A or one bidentate Lewis acid A≡C(L₂).

The second type of transition metal complexes with a carbon ligand features species with a naked neutral carbon atom as a ligand [M]-C, which can be considered as endpoint of the series [M]-CR₃ → [M]-CR₂ → [M]-CR → [M]-C. Complexes with negatively charged carbon ligands [M]-C⁻, which are isoelectronic to nitride complexes [M]-N and are termed as carbides, were synthesized in 1997 by Cummins [21]. The first neutral carbon
complex [M]-C, which was prepared and structurally characterized was reported in 2002 by Heppert and co-workers [22]. They isolated the diamagnetic 16 valence electron ruthenium complexes [(PCy₃)Cl₂Ru(C)] (L=PCy and 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; Cy = Cyclohexyl) by a metathesis facilitated reaction. Quantum chemical calculations of model compounds suggested that the Ru-C bond in the complexes is best described by an electron-sharing double bond like in Schrock carbenes, which is reinforced by a donor bond [Ru]=C [23]. The field of neutral carbon complexes was systematically explored in recent years by Bendix [24]. This review summarizes in its second part the research in transition metal complexes with a naked carbon atom as ligand [M]-C that has been accomplished since 2002.

2. Transition metal complexes with carbone ligands [M]-CL₂

2.1. Transition metal addition compounds of symmetrical carbones C(PR₃)₂

Among the existing carbones with a symmetric P-C-P skeleton, five species (1a to 1e) are known today as donor ligands to various transition metal fragments as outlined in Figure 3. From other linear or bent carbones with this skeleton, no transition metal complexes are described so far.

![Figure 3. Symmetric carbones 1a – 1e as ligands for transition metal complexes.](image-url)
1a was detected by Ramirez in 1961 [25] and 1b - 1d stem from the laboratory of Schmidbaurs group [26]. Later on a series of related carbones were synthesized, but for which transition metal complexes are unknown so far. Quite recently the new amino substituted carbone 1e was published together with Zn and Rh addition compounds [27]. In the $^{31}$P NMR spectra singlets at about -4.50 ppm (1a), -6.70 (1b), -29.6 (1c) -22.45 (1d), and 12.5 pm (1e) confirm the symmetric array of the compounds. All carbones have a bent structure but a linear form of 1a is realized if crystallized from benzene [28]. 1a has a short P-C distance of 1.633(4) Å and the P-C-P angle amounts to 130.1(6)$^\circ$ [29]. The carbone 1b exhibits a slightly longer P-C distance of 1.648(4) Å and the introduction of two less bulky methyl groups allows a more acute P-C-P angle of 121.8(3)$^\circ$ [30]. 1d has similar P-C bond distances of 1.645(12) Å 1.653(14) Å and the shortest P-C-P angle in this series of 116.7(7)$^\circ$ [31,32]. For 1e, gas phase electron diffraction studies result in a P-C distance of 1.594(3) Å and a P-C-P angle of 147.6(5)$^\circ$ assuming an apparent non-linearity but linearity in the average structure [31]. All structural parameters of 1e are close to those of 1a (P-C = 1.632(2) Å, P-C-P angle = 136.5(3)$^\circ$ [27].

Scheme 1: Selected transition metal compounds with the carbone 1a as two electron donor ligand; a) Ml, b) CdI$_2$, c) UCl$_4$, d) Fe(N{SiMe$_3$})$_2$, e) Znl$_2$. 

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**Scheme 2**: Selected transition metal compounds with the carbone 1a as four electron donor ligand.

\[2 [1aH]^+ \rightarrow \text{AgCl} \rightarrow \]

\[\begin{align*}
\text{Ph}_3\text{P} & \quad \text{H} \\
\text{C} & \quad \text{Ag} \\
\text{C} & \quad \text{H} \\
\text{Ph}_3\text{P} & \quad \text{PPh}_3
\end{align*}\]

\[[1aH-Ag-1aH]^3^+\]

\[\begin{align*}
\text{Ph}_3\text{P} & \quad \text{C} \\
\text{PPh}_3 & \quad \text{Au} \\
\Au & \quad \text{Au} \\
\text{Cl} & \quad \text{Cl}
\end{align*}\]

\[1a(AuCl)_2\]

**Scheme 3**: Selected transition metal complexes with the carbone 1b as two and four electron donor ligand. a) Ni(CO)$_4$, b) Ni(CO)$_4$ under CO atm, c) Fe(N{SiMe$_3$})$_2$, d) AuX(tth).

\[\begin{align*}
\text{MePh}_2\text{P} & \quad \text{C} \\
\text{H} & \quad \text{PPh}_2\text{Me}
\end{align*}\]

\[1b\text{AuX, } X = \text{Cl, C}_6\text{F}_5\]

\[\begin{align*}
\text{MePh}_2\text{P} & \quad \text{OC} \\
\text{CO} & \quad \text{Ni} \\
\text{MePh}_2\text{P} & \quad \text{OC}
\end{align*}\]

\[1b\text{Ni(CO)}_3\]

\[\begin{align*}
\text{MePh}_2\text{P} & \quad \text{C} \\
\text{PPh}_2\text{Me}
\end{align*}\]

\[1b\text{Fe[N(SiMe$_3$)$_2$]}_2\]

\[\begin{align*}
\text{MePh}_2\text{P} & \quad \text{C} \\
\text{PPh}_2\text{Me}
\end{align*}\]

\[1b\text{Ni(CO)}_3\]
Scheme 4: Transition metal complex with the carbone 1c as two and four electron donor ligand. a) [Tp*(CO)₂W≡CPMe₃]⁺/PMe₃, b) 1c/2 MeAuPMe₃.

Scheme 5: Selected transition metal complex with the carbone 1e as two electron donor ligand.

In Table 1 transition metal addition compounds between carbones with the P-C-P core are collected. All compounds show longer P-C bonds than the basic carbones as consequence of the competition of the occupied p orbital at C(0) between the two P-σ* orbitals and those of A.

Occupied d orbitals of Ni in the 1a-Ni(CO)₃ complex elongate the C-Ni bond to a carbone (2.110 Å) [36] but leads to relative short bond length to a NHC (1.971 Å) moiety [33]. In contrast, UCl₄ leads to a short bond to a carbone (2.411 Å) [48] indicating an appreciable U-C double bond character and a long one to a NHC base (2.612 Å) [34,35].
Table 1. Transition metal complexes with the carbone 1a to 1e including C-M and P-C bond lengths and P-C-P angles and $^{31}$PNMR shifts in ppm.

| Nr. | $^{31}$P NMR | C-M     | P-C     | P-C-P     | Ref   |
|-----|-------------|---------|---------|-----------|-------|
|     |             |         |         |           |       |
| 1a→Ni(CO)$_2$ | 19.20     | 1.990(3) | 1.677(3) | 1.676(3) | 132.13(16) | [36] |
| 1a→Ni(CO)$_3$ | 9.92      | 2.110(3) | 1.681(3) | 1.674(3) | 124.58(19) | [36] |
| 1a→ZnI$_2$   | 17.8      | 2.000(9) | 1.691(9) | 1.703(8) | 128.3(6)   | [37] |
| 1a→CdI(μ-I)$_2$CdI←1a | 18.5 | 2.25(1) | 1.700(9) | 1.68(1) | 124.8(7) | [37] |
| [1a→Hg←1a][Hg$_2$Cl$_6$] | 21.2 | 2.057(6) | 1.731(6) | 1.706(6) | 124.2(4) | [38] |
| [1a→Ag←1a]I | 13.6      | 2.115(8) | 1.656(7) | 1.690(7) | 128.5(5) | [39] |
| [1a→Cu←1a]I | 15.8      | 1.944(5) | 1.683(6) | 1.688(6) | 125.6(3) | [38] |
| [1a→ReO$_3$][ReO$_4$] | 29.5 | 1.997(7) | 1.771(8) | 123.1(4) | [40] |
| 1a→CuCl     | 16.5      | 1.906(2) | nr       | 123.8(1) | [41] |
| 1a→Cu-C$_5$H$_5$ | 8.5 | nr       | nr       | nr       | 123.8(1) | [42] |
| 1a→Cu-C$_5$Me$_5$ | 7.5 | 1.922(6) | 1.668(5) | 1.660(6) | 136.0(4) | [42] |
| 1a→CuPPh$_3$ | 3.7       | nr       | nr       | nr       | 123.8(1) | [42] |
| 1a→AgCl     | 16.5      | nr       | nr       | nr       | 123.8(1) | [42] |
| 1a→AgCp*    | 6.5       | nr       | nr       | nr       | 123.8(1) | [42] |
| 1a→Au-C≡C-R | nr        | 2.082(2) | 1.688(2) | 1.682(2) | 133.64(13) | [43] |
| R = C$_6$H$_4$NO$_2$-p |         |         |         |         |       |
| 1a→Au-CH(COMe)$_2$ | nr | nr       | nr       | nr       | 123.8(1) | [43] |
| 1a→AuCl     | 13.7      | 14.4     | nr       | nr       | 123.8(1) | [41] |
| [1a→Ir(COD)]PF$_6$ | nr | nr       | nr       | nr       | 123.8(1) | [44] |
| 1a→VCl$_3$  | 21.13     | 2.050(3) | 1.712(2) | 1.722(2) | 123.6(2) | [45] |
| 1a→FeCl(μ-Cl)$_2$FeCl←1a | par | 2.043(7) | 1.689(7) | 1.712(7) | 121.3(4) | [46] |
| 1a→Fe[N(SiMe$_3$)$_2$]$_2$ | par | 2.147(2) | 1.702(2) | 1.720(2) | 120.0(1) | [47] |
| 1a→FeCl$_2$ | par       | 2.055(8) | 1.709(7) | 1.702(7) | 122.7(5) | [46] |
| 1a→Fe(CH$_2$Ph)$_2$ | par | 2.097(5) | 1.694(5) | 1.671(5) | 124.5(3) | [46] |
The cation \([\text{1a-ReO}_3]^+\) holds the longest one with 1.771(8) Å indicating an appreciable C=Re double bond character. This feature applies also in part to \(\text{1a-UCl}_4\) and \(\text{1c-W(CO)}_2\text{N}_3\) with elongated P-C bonds; a partial C-U double bond is confirmed by theoretical calculations. Similar long P-C bonds are found in the trication \([\text{1aH-Ag-1aH}]^{3+}\), in \(\text{1a-(AuCl)}_2\), and in \(\text{1b-Ni}_2\text{(CO)}_5\), where the carbone provides each two electrons to two accepting Lewis acids as depicted in Figure 1d. The P-C-P angles are in the range between 115° and 132° reflecting the

|       | Angle 1 | Angle 2 | Angle 3 | Angle 4 | Angle 5 | Angle 6 |
|-------|---------|---------|---------|---------|---------|---------|
| 1a→FeCl[N(TMS)]_2 | par | nr | nr | nr | [46] |
| 1a→FeOTf[N(TMS)]_2 | par | 2.040(3) | 1.701(3) | 1.704(3) | 122.1(2) | [46] |
| 1a→UCl_4 | nr | 2.411(3) | 1.705(3) | 1.719(3) | 125.05(16) | [48] |
| 1a→(AuCl)_2 | 21.2 | 2.078(3) | 1.776(3) | 1.776(3) | 117.30(15) | [43] |
| [1aH-Ag-1aH]^{3+} | 23.6 | 2.221(5) | 1.770(7) | 1.779(7) | 119.9(4) | [49] |
| [1aH-Au-1aH]^{3+} | 26.1 | nr | nr | nr | [43] |
| [1aH→AuCl]^+ | 22.1 | nr | nr | nr | [43] |

Transition metal complexes with the carbone 1b

|       | Angle 1 | Angle 2 | Angle 3 | Angle 4 | Angle 5 | Angle 6 |
|-------|---------|---------|---------|---------|---------|---------|
| 1b→Fe[N(SiMe_3)]_2 | par | 2.100(2) | 1.694(2) | 1.696(1) | 120.8(9) | [47] |
| 1b→Ni(CO)_3 | 2.6 | 2.091(2) | 1.683(2) | 1.673(2) | 122.3(1) | [50] |
| 1b→Ni_2(CO)_5 | 12.1 | 2.080(5) | 1.742(5) | 1.743(5) | 117.1(3) | [50] |
| [1bH→AuC_6F_5]^+ | 22.7 | 2.029(6) | 1.781(2) | 1.792(2) | 119.1 | [51] |
| [1bH→AuCl]^+ | 22.1 | nr | nr | nr | [51] |

Transition metal complexes with the carbone 1c

|       | Angle 1 | Angle 2 | Angle 3 | Angle 4 | Angle 5 | Angle 6 |
|-------|---------|---------|---------|---------|---------|---------|
| 1c→W(CO)_2(Tp*][PF_6] | 36 | 2.11(1) | 1.75(2) | 1.77(1) | 114.5(8) | [52] |
| 1c→(AuMe)_2 | nr | nr | nr | nr | [124] |

Transition metal complexes with the carbone 1d

|       | Angle 1 | Angle 2 | Angle 3 | Angle 4 | Angle 5 | Angle 6 |
|-------|---------|---------|---------|---------|---------|---------|
| 1d→Ni(CO)_3 | 3.5 | 2.0661(9) | 1.712(2) | 1.722(2) | 117.19(9) | [45] |

Transition metal complexes with the carbone 1e

|       | Angle 1 | Angle 2 | Angle 3 | Angle 4 | Angle 5 | Angle 6 |
|-------|---------|---------|---------|---------|---------|---------|
| 1e-ZnCl_2 | 28.9 | 1.994(2) | 1.686(2) | 125.3(1) | [27] |
| 1e-Rh(CO)(acac) | 32.9 | 2.092(3) | 1.685(3) | 128.56(17) | [27] |
required space of the appropriate Lewis acid. The $^{31}$P NMR shift of the carbone $1a$ amounts to about -5 ppm and those of the related addition compounds are shifted to lower fields and range between 4 ppm and 30 ppm. All iron(II) complexes of $1a$ and $1b$ are paramagnetic and $^{31}$P NMR spectra could not be obtained.

For the $^{31}$P NMR spectrum of the carbone $1b$, a shift of -6.70 ppm was recorded [26]. With exception of $1b\rightarrow$Ni(CO)$_3$ which resonate at 2.6 ppm, low field shifts between 12 and 22 ppm were found when $1b$ act as a four electron donor [50].

$1e$-ZnCl$_2$ [27] and $1a$-ZnI$_2$ [37] have closely related structural parameters but exhibit shorter C-Zn bond lengths than to related NHC-addition compounds ($\Delta = 0.051$ Å) [53]. In both compounds a nearly perpendicular array of the ZnX$_2$ and the PCP plane are found. No tendency for an additional N-coordination to the amino ligand of $1e$ is recorded for the ZnCl$_2$ addition compound. In contrast the Rh-C distances in $1e$-Rh(CO)$_2$(acac) are longer ($\Delta = 0.117$ Å) than in the corresponding NHC compound [54] and a partial $\pi$ interaction was found by DFT calculation; Rh shows also no tendency for coordination of the adjacent amino groups [27].

2.2. Transition metal addition compounds of carbones C(PR$_3$)$_2$ with an additional pincer function

Starting material for $2a$ is not the free carbone Ph$_2$P-CH$_2$-PPh$_2$-C-PPh$_2$-CH$_2$-PPh$_2$ which could not be prepared so far, but the dication [Ph$_2$P-CH$_2$-PPh$_2$-CH$_2$-PPh$_2$-CH$_2$-PPh$_2$]$^{2+}$ as reported by Peringer [55]; the basic pincer ligand $2b$ was presented by the group of Sundermeyer in 2019 and the $^{31}$P NMR shift $\delta = -5.6$ ppm. The P-C-P angle in $2b$ amounts to 133.76(13)$^\circ$, P-C = 1.633(2), 1.642(2) [56].

![Figure 4](image-url). Tripodal basic pincer ligand $2a$ and $2b$. 

Figure 4. Tripodal basic pincer ligand $2a$ and $2b$. 

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Table 2. Transition metal complexes with the phosphine based pincer ligands 2a and the pyridyl based pincer ligand 2b; C-M and P-C distances are included and $^{31}$P NMR shifts in ppm.

| Nr. | $^{31}$P NMR | C-M | P-C | P-C-P | Ref |
|-----|--------------|-----|-----|-------|-----|
|     | Transition metal complexes with the tripodal carbone 2a |
| [2a(PdCl)]Cl | 34.5 | 2.062(2) | 1.694(3) | 124.9(2) | [55,57] |
| [2a(NiCl)]Cl | 36.4 | 1.942(4) | 1.6925(18) | 125.1(2) | [57] |
| [2a(NiCl)]NiCl₄ | nr | 1.930(7) | 1.696(7) | 126.3(4) | [57] |
| [2a(PtCl)]Cl | 35.7 | 2.06(4) | 1.692(5) | 124.86(15) | [57] |
| [2a(NiMe)][AlCl₂Me₂] | 31.8 | 1.959 | 1.697 | 120.9 | [58] |
| [2a(AuCl)]TiF₂ | 40.8 | 2.060(3) | 1.721(3) | 125.1(2) | [59] |
| [2a(AuI)](TiF₂)₂ | 41.1 | 2.082(8) | 1.723(8) | 124.5(5) | [59] |
| [2aH-PdCl]²⁺ | 42.4 | 2.102(3) | 1.803(3) | 121.9(2) | [55] |
| [2aH-PtCl]²⁺ | 44.4 | 2.106(4) | 1.811(4) | 120.4(2) | [57] |
|     | [2aH-NiCl]²⁺ | 32.7 | 1.990 | 1.801 – 1.834 | 121.1 | [57,58] |
|     | Transition metal complexes with the tripod carbone 2b |
| [2b(CeBr₃)THF] | -10.2 | 2.597(6) | 1.672(6) | 122.5(4) | [60] |
| [2b(CeBr)₂]b | nr | 2.573(6) | 2.597(6) | 120.5(4) | [60] |
| [2b(UCl₄)] | nr | 2.471(7) | 1.696(7) | 121.3(4) | [48] |
| [2b(TiCl₃)] [57] | 18.24 | 2.144(6) | 1.670(3) | 129.9(4) | [56] |
|     | 18.24 | 2.144(6) | 1.670(3) | 129.9(4) | [56] |
| [2b(Cr(CO)₃)] | 6.97 | 2.212(2) | 1.651(3) | 133.6(2) | [56] |
|     | 6.97 | 2.212(2) | 1.650(3) | 133.6(2) | [56] |
| [2b(MnCl₂)] | par | 2.1843(14) | 1.6671(17) | 127.70(9) | [56] |
| [2b(MnCl₂)] | par | 2.1843(14) | 1.6636(17) | 127.70(9) | [56] |
| [2b(CoCl₂)] | par | 2.015(6) | 1.680(7) | 127.5(3) | [56] |
|     | 2.015(6) | 1.681(7) | 127.5(3) | [56] |
| [2b(Mo₂(CO)₇)] | 9.49 | 2.355(4) | 1.722(4) | 120.4(2) | [56] |
|     | 9.49 | 2.355(4) | 1.724(4) | 120.4(2) | [56] |
| [2b(PdCl)]Cl | 31.6 | 2.004(4) | 1.689(4) | 132.4 | [56] |
|     | 31.6 | 2.004(4) | 1.676(4) | 132.4 | [56] |
| [2b(Ni₂(CO)₄)] | 34.20 | 2.0635(18) | 1.7142(18) | 121.1 | [57,58] |
|     | 34.20 | 2.0912(18) | 1.7146(18) | 121.1 | [57,58] |
Scheme 6. Selected compounds with the pincer ligands 2a and 2aH. a) MCl₂ with a mixture of dppm and 2 eq. of CS₂, b) AuCl(tht)/HNO₃, c) HCl.

Scheme 7. Selected compounds with the pincer ligand 2b as two and four electron donor. a) CeBr₃ in THF, b) UCl₄, c) 2 eq Mo(CO)₃(NCMe)₃, d) 2 eq Ni(CO)₄.
Various cationic complexes where reported with the pincer ligand \(2a\) and group 10 metal halides and one dication with the group 11 metal Au. The \(^{31}\)P NMR shifts range between 32 and 41 ppm. As with \(1a\) the carbone carbon atom of \(2a\) is basic enough to accept a proton to generate complexes of the type \(2a\,H\)-MCl dications with all group 10 elements.

A series of complexes with the N,C,N pincer ligand \(\text{sym-bis(2-pyridyl)tetraphenylcarbodiphosphorane} \ (2b)\) were reported recently by the group of Sundermeyer. Remarkable is the molybdenum complex \(2b\)-Mo\(_2\)(CO)\(_7\) in which \(2b\) provides four pairs of electrons for donation to a \(\text{Mo}_2\) unit with an Mo-Mo separation of 3.0456(5) Å [56].

2.3. Transition metal addition compounds of Carbones C(PR\(_3\))\(_2\) with an additional ortho metallated pincer function

Source for the Rh complex \(3a\)-Rh(PMe\(_3\))\(_2\)H was the half pincer compound \(5a\)-Rh(C\(_6\)H\(_8\)) upon reacting with PMe\(_3\) under loss of cod. \(3a\)-Pt(SMe\(_2\)) forms upon reacting \(1a\) with [Me\(_2\)Pt(SMe\(_2\))]\(_2\) and loss of 4 molecules of CH\(_4\) [61]. PEt\(_3\) replaces the labile bonded SMe\(_2\) group of \(3a\)-Pt(SMe\(_2\)) to produce \(3a\)-PtEt\(_3\), which is transformed with P(OPh)\(_3\) into \(3a\)-Pt(PPh)\(_3\). The dication \([3a\,-\text{PtPEt}\(_3\)(\mu\,-\text{Ag})\,_2\text{EtPEt-Pt-3a}]^2+\) was obtained upon addition of AgOTf to \(3a\)-PtPEt\(_3\). According to the carbone C atom as four electron donor the Pt complexes with \(\mu\,-\text{Ag}\) functions show long Pt-C distances between 1.737 and 1.749 Å (mean values) and the \(^{31}\)PNMR shifts are in the narrow range of 33 and 36 ppm [63]. More complicated is the formation of \(3a\)-Pt(CO); it stems from hydrolysis of the related \(3a\)-Pt(CCl\(_2\)) complex (not isolated) [62].

The carbone complex \(3b\)-Pt(CO) was obtained from reacting the yldiide platinum complex (see Scheme 9) with 1 atm CO that inserts into the N-Si bond of the yldiide.
Figure 5. Bis-ortho metallated pincer complexes 3a and 3b.

Table 3. Transition metal complexes with ortho metallated tripodal pincer ligand 3a derived from 1a and the related pincer ligand 3b and $^{31}$P NMR shifts.

| Nr.            | $^{31}$P NMR | C-M  | P-C  | P-C-P | Ref  |
|----------------|--------------|------|------|-------|------|
| Transition metal complexes with the tripodal ligand 3a |
| 3a-Rh(PMe$_3$)$_2$H | 8.56         | 2.203(3) | 1.674(3) | 138.32(18) | [61] |
| 3a-PtSMe$_2$   | 30.42        | nr   | nr   | nr    | [61] |
| 3a-PtCO        | 41.5         | 2.037(5) | 1.706(3) | 128.4(3) | [62] |
| 3a-PtPEt$_3$   | 28.5         | 2.067(2) | 1.697(2) | 124.88(14) | [63] |
| 3a-PtP(OPh)$_3$| nr           | nr   | nr   | nr    | [63] |
| [3a-PtPEt$_3$(μ-AgPPh$_3$)$_3$]$^+$ | 32.5         | 2.130(4) | 1.737   | 126.0(2)  | [63] |
| [3a-PtP(OPh)$_3$(μ-AgPEt$_3$)]$^+$ | 36.0         | 2.105(3) | 1.743   | 122.9(2)  | [63] |
| [3a-PtPEt$_3$(μ-Ag$_2$)Et$_3$Ptt-3a]$^{2+}$ | 33.4         | 2.128(3) | 1.749   | 125.29(18) | [63] |
| 3aH-PtCl      | 27.9         | 2.077(6) | 1.796(6) | 123.4(4)  | [62] |
| Transition metal complexes with the tripodal ligand 3b |
| 3b-Pt(CO)     | 46.9         | 2.002(5) | nr      | 133.3(3)  | [64] |
Scheme 8. Selected addition compounds with the pincer ligand $3a$ and $3aH$ and those with the Ag-bridged cations or dication, respectively. a) from $3aH\text{-PtCl}$ via $3a\text{-Pt(CCl}_2\text{)}$ and $H_2O$, b) PMe$_3$, c) from $5a\text{-Pt(C}_8\text{H}_{11})$ (see Scheme 11) and CHCl$_3$, d) PPh$_3$, e) 2 AgOTf.
Scheme 9. Two mesomeric forms of 3b-Pt(CO); 3ba favors a tricarbene coordination at Pt(0) whereas 3bb is consistent Pt(II) forming two C-Pt s-bonds similar to 3a-Pt(CO). The short central C-Pt bond length of 2.002 Å indicates a partial doubly donation of the carbone C atom as shown in Figure x1b. The planar environment at Pt is typical for Pt(II) and supports this view [64].

2.4. Transition metal complexes with p-e-p five membered ring

The carbone 4 was obtained by deprotonation of the cation [4H]+. According to two P atoms in different chemical environments two doublets in the 31P NMR spectrum were recorded at δ = 60.0 and 71.5 ppm; 2JPP = 153 Hz. From X-ray determination stem the P-C(1) and P-C(2) distances of 1.644(19) and 1.657(17) Å, respectively, and the P-C-P angle amounts to 104.82(10)° [65]. The bond lengths are close to that reported for the carbone 1a.

Figure 6. Structure of compound 4.
Table 4. Transition metal complexes with the cyclic carbone 4, containing $^{31}$P NMR shifts and relevant structural parameters.

| Nr.   | $^{31}$P NMR | M-C  | $P^1$-C | $P^2$-C | Ref  |
|-------|--------------|------|---------|---------|------|
| 4-PdCl(π-C$_3$H$_5$) | 61.2 | 71.9 (225) | 2.120(2) | 1.673(2) | 1.694(2) | [65] |
| 4-RhCl(nbd) | 64.6 | 75.7 (230) | 2.115(18) | 1.676(18) | 1.702(18) | [65] |
| 4-Rh(CO)$_2$Cl | 68.2 | 75.6 (224) | nr | nr | nr | [65] |
| 4-AuOBu$^1$ | 64.1 | 60.4 (225) | 2.018(6) | 1.674(7) | 1.687(7) | [66] |
| 4-CuOBu$^1$ | 69.8 | 62.6 (195) | 1.8923(15) | 1.6763(15) | 1.6887(15) | [66] |
| 4-CuCl | 63.2 | 70.6 (186) | 1.8914(19) | 1.6700(19) | 1.6869(19) | [66] |

Scheme 10: Selected complexes with the cyclic carbone 4. R = iPr. a) [{PdCl(allyl)}$_2$], b) [{RhCl(nbd)}$_2$].

From the cyclic and asymmetric carbone 4 six transition metal complexes are known in which the ligand acts as two electron donor via the C atom. As in the starting compound 4 the $P^2$-C bond distances are slightly longer than $P^1$-C ones. Addition of CuCl and AuCl(SMe$_2$) to
4H\textsuperscript{+}/tBuOK generates the compounds 4-CuO\textsubscript{t}Bu and 4-AuO\textsubscript{t}Bu, respectively; in CH\textsubscript{3}Cl\textsubscript{2} or CHCl\textsubscript{3} 4-CuO\textsubscript{t}Bu is converted into 4-CuCl\textsuperscript{[66]}.

4-Rh(CO)\textsubscript{2}Cl stems from the reaction of 4 with [{RhCl(CO)\textsubscript{2}}\textsubscript{2}]\textsuperscript{[65]}. 4-CuO\textsubscript{t}Bu and 4-AuO\textsubscript{t}Bu catalyze the hydroamination or hydroalkoxylation of acrylonitrile\textsuperscript{[66]}.

2.5. Transition metal complexes with asymmetric P-C-P ligands

Several asymmetric carbones with orthometallation (5a-M, 5d-M), with an additional donor function (5c), or with a functionalized phenyl ring (5b) were reported that form TM complexes.

![Figure 7. Structures of compounds 5a-M, 5b, 5c and 5d-M.](image)

The neutral asymmetric carbone 5b (X = PPh\textsubscript{2}) has the structural parameters P\textsuperscript{1}-C = 1.642(2), P\textsuperscript{2}-C = 1.636(1) Å, and a P-C-P angle of 140.74(8)\textdegree; the P atoms resonate at δ = -6.9 and -3.4 ppm (\textsuperscript{2}J\textsubscript{PP} = 93 Hz)\textsuperscript{[67]}. Those of 5c are P\textsuperscript{1}-C = 1.6416(19) Å, P\textsuperscript{2}-C = 1.6398(29) Å, and P-C-P = 133.25(10)\textdegree\textsuperscript{[68]}. Three complexes in which the carbone 1a is half-side orthometallated forming 5a-M complexes are described\textsuperscript{[61,65,69]}. 
Table 5. Transition metal complexes with the unsymmetrical carbones 5a – 5d; $^3$P NMR shifts in ppm.

| Nr | $^3$P NMR ($^{2}J_{PP}$) | M-C | P$_1$-C | P-C-P | Ref. |
|----|-------------------------|-----|---------|-------|------|
|    |                         |     |         |       |      |
| 5a-Ptcod(C$_8$H$_{11}$) | 14.9 | 2.072(3) | 1.694(4) | 114.8(2) | [69] |
|    | 5.7 (59.8)              |     |         |       |      |
| 5a-Rhcod(p) | 10.15 | 2.165(2) | 1.693(2) | 124.50(13) | [61] |
|    | 12.40 (50.9)            |     |         |       |      |
| 5a-PdC$_3$H$_5$ | 39.8 9.9 (54) | nr | nr | nr | [65] |

Transition metal complexes with the carbones 5b

| Nr | $^3$P NMR ($^{2}J_{PP}$) | M-C | P$_1$-C | P-C-P | Ref. |
|----|-------------------------|-----|---------|-------|------|
|    |                         |     |         |       |      |
| 5b-AuCl (X=PPh$_2$) | 8.6 | 2.043 | 1.701(4) | 126.0(2) | [67] |
|    | 18.7 (52)               |     |         |       |      |
| 5b-AuCl (X=PPh$_2$-AuCl) | 20.2 | 2.037(3) | 1.690(3) | 131.4(2) | [67] |
|    | (X=PPh$_2$-AuCl)       |     |         |       |      |
| 5b-(AuCl)$_2$ (X=PPh$_2$-AuCl) | 25.4 | 2.089 | 1.774(5) | 123.6(3) | [67] |
|    | 26.9                    |     |         |       |      |
| 5b-PtMe$_2$ (X = Me) | 19.3 | nr | nr | nr | [70] |

Transition metal complexes with the carbones 5c

| Nr | $^3$P NMR ($^{2}J_{PP}$) | M-C | P$_1$-C | P-C-P | Ref. |
|----|-------------------------|-----|---------|-------|------|
|    |                         |     |         |       |      |
| 5c-UCl$_4$ | par | 2.461(5) | 1.699(5) | 120.6(3) | [48] |
| [5cAuPPh$_3$]$^+$ | 19.70 | 2.067(9) | 1.688(9) | 124.3(5) | [68] |
|    | 15.03 (30.7)            |     |         |       |      |
| [5c(CuCl)(AuPPh$_3$)]$^+$ | 39.7 | 2.111(4) Au | 1.732(5) | 120.2(3) | [68] |
|    | 26.2 (m)                |     |         |       |      |
| [5c(AuCl)(AuPPh$_3$)]$^+$ | 35.4 | 2.080(9) Au$^2$ | 1.756(9) | 119.3(5) | [68] |
|    | 27.5 (m)                |     |         |       |      |

Transition metal complexes with the carbones 5d

| Nr | $^3$P NMR ($^{2}J_{PP}$) | M-C | P$_1$-C | P-C-P | Ref. |
|----|-------------------------|-----|---------|-------|------|
|    |                         |     |         |       |      |
| 5d-Pt-5d | 19.3 | - | - | - | [70] |
Scheme 11: Selected structures of transition metal complexes with the carbene 5a; a) $\frac{1}{2}$ [PdCl(allyl)]; b) $\frac{1}{3}$ [Pt$_2$(cod)]; c) $\frac{1}{4}$ [RhCl(cod)]. All complexes are formed upon release of the cation [1aH]$^+$. As depicted in Scheme 11, three neutral complexes of 1a are known in which one of its phenyl group is orthometallated to produce the 5a-M core. The $^{31}$P NMR shift of the unchanged PPh$_3$ group range between about 6 and 13 ppm whereas for the orthometallated side shifts between 15 and 40 ppm where recorded. Both P-C distances do not differ markedly and amount to about 1.700 Å.

Scheme 12. Selected structures of transition metal complexes with the carbene 5b. a) [AuCl(tht)], b) 2 [AuCl(tht), 3 [AuCl(tht)].
All complexes shown in Scheme 12 have a further PPh₂ function at the ortho position of one phenyl group of 1a. In the complex 5b-(AuCl)₂ the carbone provides four electrons for donation with typical long P-C distances of about 1.770 Å [67].

Scheme 13. Selected structures of transition metal complexes with the mono pyridyl substituted carbone 5c.

The paramagnetic 5c- UCl₄ exhibits a short C-U distance indicative for a double dative bond of the carbone C atom as in 2b-UCl₄ and was obtained by reacting UCl₄ with the dication 5c-H₂/NaHMDS. Upon further coordination of the pyridyl group (U-N = 2.537(4) Å) the U atom attains the coordination number 6 [48].

[5c-AuPPh₃]⁺ was obtained from reacting the carbone 5c with [PPh₃AuCl]/Na[SbCl₆]. In the cationic complex [5c-(CuCl)((AuPPh₃))SbF₆, the carbone 5c acts as a six electron donor with a Cu-N distance of 2.267(6) Å and Cu-Au separation of 2.8483(10) Å. The Cu and Cl atoms are each disordered over two positions with occupancy of about 0.8 to 0.2. If CuCl is replaced by AuCl as in [5c-(AuCl)(AuPPh₃)]SbF₆ the C-AuPPh₃ distance is slightly elongated and no coordination of the pyridyl N atom is observed. The Au-Au separation is with 3.1274(6) Å too long for a metallophilic interaction. In both compounds, the carbone C atom constitutes a chiral center according to four chemical different substituents and acts as a four electron donor. The PPh₃ group resonates between 15 and 27 ppm [68]. In the related symmetric pyridyl-free
complex 1a-(AuCl)_2 slightly shorter C-Au (2.076(3) Å) were recorded accompanied by longer P-C (1.776(3) Å) bond lengths [43].

2.6. Transition metal complexes of carbones with cyclobutadiene

The carbones 6a and 6b can also be seen as an all-carbon four-membered ring bent allene (CBA); 6a is stable for several hours at -20º but decomposes when warmed up to -5º. The optimized geometry reveals a very acute allene bond angle of 85.0º and coplanarity of the ring carbon atoms including the two nitrogen atoms. The C=C bonds of the allene fragment amount to 1.423 Å and are significantly longer than in typical linear allenes (1.31 Å). Short CN bonds of 1.36 Å indicate some double bond character. The CCC carbon atom resonates in the ^13_C NMR spectrum at 151 ppm. The first and second proton affinities (PAs) are very high amounting to 307 and 152 kcal/mol [71].

![Figure 8. Structures of compounds 6a and 6b.](image)

The molecular orbitals show that the HOMO and HOMO-1 have clearly the largest coefficients at the central carbon atom and exhibit the typical shape of lone-pair molecular orbitals with σ (HOMO) and π (HOMO-1) symmetry; however, with reversed order with respect to CDPs and CDCs. To emphasize the proximity of 6 to CDP carbones, we use the same symbolism mimicking a metal.

The free CBA 6b could not be obtained only the cationic 6bH^+ and 6bH_2^2+ are known and used as starting compounds for the syntheses of the related transition metal complexes [72].
Table 6. Transition metal complexes with the all carbon ligand 6; $^{13}$C NMR shifts (in ppm) of the donating carbon atom. Distances in Å, angles inº.

| Nr. | $^{13}$C NMR | C-M | C-C | C-C-C | Ref. |
|-----|--------------|-----|-----|-------|------|
|     |              |     |     |       |      |
|     | Transition metal complexes with the carbene 6a   |     |     |       |      |
| 6a-RhCl(cod) | 136.6 (41)   | 2.038(5) | 1.405(6) | 88.4(3) | [71] |
| 6a-IrCl(cod) | 138.6        | nr   | nr   | nr    | [71] |
| 6a-RhCl(CO)$_2$ | 124.7 (32)   | nr   | nr   | nr    | [71] |
| 6a-IrCl(CO)$_2$ | 129.2        | nr   | nr   | nr    | [71] |
|     | Transition metal complexes with the carbene 6b   |     |     |       |      |
| 6b-W(CO)$_5$  | 130.1        | 2.319(3) | 1.419(4) | 88.0(2) | [72] |
| 6b-AuCl      | 123.6        | 2.001(4) | 1.409(5) | 90.5(3) | [72] |
| 6b-RhCl(CO)$_2$ | 131.2 (32)   | 2.0602(14) | 1.4102(19) | 89.73(11) | [72] |

Scheme 14. Selected structures of complexes with the cyclic carbones 6a and 6b. Preparation see text.
The $^{13}$C NMR shifts of the central carbon atom are shifted to higher fields relative to the starting free carbone ranging between 124 and 139 ppm.

All complexes of the CBA 6a where obtained by reacting the freshly prepared free carbone 6a at -20° with $\left\{ \text{MCl} (\text{cod}) \right\}_2$ with M = Rh, Ir. The cod ligand can be replaced by bubbling CO through solutions of 6a-MCl(cod) to produce the related 6a-MCl(CO)$_2$ compounds [71].

Transition metal complexes with 6b as ligand where obtained by reacting 1,1,2,4-tetrapiperidino-1-buten-3-yne with a) [(tht)AuCl], b) [RhCl(CO)$_2$], c) [(NMe$_3$)W(CO)$_3$]; during the reaction rearrangement of the starting buten-3-yne to 6b has occurred [72].

2.7. Cyclopropenylidene

Stephan described the first carbodicarbene stabilized by flanking cyclopropylidenes, named carbodicyclobutadiene 7.

Neither the neutral singlet 1,2-diphenylocyclopropenylidene as carbene ligand L in 7 nor the carbone tetraphenylcarbodicyclopropenyliden (CDC) 7 itself are stable compounds at room temperature. The free carbene L has only been observed in an argon matrix isolated at 10 K and 7 could be characterized in solution by low temperature NMR spectroscopy; for the central carbon atom a $^{13}$C NMR shift at $\delta = 133$ ppm was recorded at −60°C.
The first and second proton affinities of 7 were determined to be 283 and 153 kcal mol\(^{-1}\), respectively. Thus, the energy difference between the linear allenic structure and the bent arrangement is shallow amounting to 6.6 kcal mol\(^{-1}\) for a bending angle of 140 ° and 10 kcal mol\(^{-1}\) for 130°. The molecular structure of 7 was determined by computational methods. Calculations reveal that the central carbon atom is in a linear environment the C-C distances were calculated at 1.308 Å and the C-C-C angle to 180 °. The highest occupied molecular orbital (HOMO) and HOMO-1 of 2 are degenerate and incorporate the p orbitals of the C2-C1-C2a fragment.

The central C atom is more negatively charged (- 0.19 a.u.) than the adjacent C atoms suggesting nucleophilic character [73].

Table 7. Complexes with the carbene 7. \(^{13}\)C NMR shifts (in ppm) of the donating carbon atom.

| Nr        | \(^{13}\)C NMR | M-C          | C-C      | C-C-C  | Ref. |
|-----------|---------------|--------------|----------|--------|------|
| [7-AuNHC-Ad]\(^+\) | 92.7          | 2.071(6) 2.047(6) | nr       | nr     | [73] |
| [7-AuNHC-Dipp]\(^+\) | 98.0          | nr           | nr       | nr     | [73] |

Scheme 15: Selected structures of complexes with the cyclo propylidene stabilized carbene 7. a) KHMDS/ (NHC)AuOTf.

The addition compounds [7-AuNHC-Ad]OTf and [7-AuNHC-Dipp]OTf were prepared from reacting [7H]\(^+\) with KHMDS and the related (NHC)AuOTf at -45° [73].
2.8. Carbodicarbenes

Carbodicarbenes, CDCs, are neutral compounds, where a bare carbon atom with its four electrons is stabilized by two NHC ligands which plays the role of a phosphine group as in carbodiphosphoranes, CDPs. Theoretical studies have demonstrated that this class of compounds could be stable and their existence was predicted by Frenking [74] and short times later realized by the group of Bertrand [75].

Figure 10. Symmetrical CDCs from which transition metal complexes are known.

Structural and spectroscopic parameters of the following symmetric CDCs are available: 8a, C-C = 1.343(2) Å, C-C-C = 134.8(2)°, $^{13}$C NMR 110.2 ppm [75]. 8b, C-C = 1.333(2) Å and 1.324(2) Å, C-C-C = 143.61(15)° [76]. 8c, C-C = 1.335(5) Å, C-C-C = 136.6(5)° [77].

Figure 11. Unsymmetrical CDCs from which transition metal complexes are reported.
Structural parameters of the unsymmetrical CDCs are reported: 8e, C-C = 1.3401(16) Å and 1.3455(16), C-C-C 137.55(12)°. For 8f, no data are available [78].

8g: C-C = 1.344(3) Å and, 1.318(3) Å, C-C-C = 146.11(19)° [78]. 8h was obtained at -60° by reacting 8hH + with KMDS, and characterized spectroscopically; on warming to room temperature, it dimerizes. 13C NMR: δ = 105.5 ppm [79].

Table 8. Collection of transition metal complexes with the CDCs 8a-8h. 13C NMR shifts of the central carbon atom (in ppm).

| Nr   | 13C NMR          | M-C          | C-C            | C-C-C          | Ref. |
|------|------------------|--------------|----------------|----------------|------|
| 8a-RhCl(CO)2 | 64.1             | 2.089(7)     | 1.398(10)      | 121.2(7)       | [75] |
| 8a-RuCl2(=CHPh)NHC | 73.01 mes    | 2.069(18)     | 1.352(3) 1.429(3) | 119.84(17)     | [80] |
| 8a-RuCl2(=CHPh)NHC | 73.4 iPr        | 2.210(7)     | 1.345(11) 1.439(9) | 116.9(6)       | [80] |
| [8b-PdCl]2 | nr              | 1.973(3)     | 1.369(5) 1.398(5) | 126.5(3)       | [76] |
| [8b-Fe0.5]2+ | 2.018(3)        | 1.374(3)     | 128.4(3)       | [81] |
| [8b-Fe0.5]3+ | 1.968(4)        | 1.387(6)     | 125.2(4)       | [81] |
| [8b-Fe0.5]4+ | 1.928(3)        | 1.407(4)     | 125.4(2)       | [81] |
| 8c-PdClC3H5 | nr              | 2.207(4)     | 1.404(5) 1.377(5) | 119.7(4)       | [77] |
| 8c-RhCl(CO)2 | 63.7             | 2.109(2)     | 1.4113 1.385(3) | 117.4(2)       | [77] |
| 8d--RhCl(CO)2 | 2.123(2)       | 1.416(3) 1.368(3) | 116.8(2)       | [77] |
| 8e-PdCl2(POR)3 | nr              | 2.039(18)    | 1.395(3) 1.328(3) | 119.20(16)     | [82] |
| 8e-PdCl2PPh3 | nr              | 2.063(2)     | 1.383(3) 1.409(3) tP | 115.63(19)     | [83] |
| 8e-PdCl2PTol3 | nr              | 2.049(4)     | 1.374(7) 1.412(8) tP | 117.7(4)       | [83] |
| 8e-PdCl2PCy3 | nr              | 2.111(2)     | 1.343(3) 1.415(4) tP | 123.6(2)       | [83] |
| 8f-RhCl(CO)2 | 67.1             | 2.117(2)     | 1.369(3) 1.424(3) | 117.8(2)       | [78] |
| 8g-RhCl(CO)2 | 63.2             | 2.1164(17)   | 1.374(2)NHC 1.420(3) | 118.77(16)     | [78] |
| 8h-IrCl(CO)2 | nr              | nr         | nr          | nr             | [79] |
| 8h-IrCl(cod) | 166.4           | nr         | nr          | nr             | [79] |
Scheme 16. Selected structures of transition metal complexes with symmetric CDCs 8a and 8b; a) Fe(OTf)2(MeCN)2

Scheme 17. Selected structural representation of 8e-PdCl2P(OiPr)3 a) PdCl2P(OiPr)3

8a-RhCl(CO)2 was prepared by addition of a suspension of 8a in benzene to a solution of [RhCl(CO)2]2 [75]. [8b-Fe0.5]2+ contains Fe2+ in octahedral environment coordinated by two molecules of 8b. Fe(II) can be successively oxidized to the corresponding tri-, tetra-, and pentacationic species [81].
The addition compounds 8c-RhCl(CO)$_2$ and 8d-RhCl(CO)$_2$ where obtained upon reacting the appropriate carbene 8c or 8d with [RhCl(CO)$_2$]$_2$; similarly addition of [Pd(allyl)Cl]$_2$ to 8c leads to the allyl complex 8c-PdCl(C$_3$H$_5$) [77].

As depicted in Scheme 17, introduction of PdCl$_2$(OiPr)$_3$ to 8e afforded the complex 8e-PdCl$_2$(OiPr)$_3$; it features a square planar Pd center with a short interatomic distance of one phosphite oxygen atom and the carbon atom of the NHC molecule of 2.890 Å that is smaller than the sum of van der Waals radii. This indicates strong attractive interaction between the atoms [82]. The three Pd complexes 8e-PdCl$_2$PPh$_3$, 8e-PdCl$_2$PTol$_3$, and 8e-PdCl$_2$PCy$_3$ were obtained by reacting the carbene 8e with the appropriate PdCl$_2$PR$_3$; between the NHC and the aromatic phosphine substituents (Ph or Tol) an unexpected $\pi$-$\pi$ interaction was detected. One Ph and Tol group are nearly parallel to the imidazole rings with centroid-centroid distances of 3.25 Å (Ph) and 3.30 Å (Tol), respectively [83].

8f –RhCl(CO)$_2$ and 8g-RhCl(CO)$_2$ stem from reacting the appropriate carbene with [RhCl(CO)$_2$]$_2$ [78]. The cod ligand of [Ir(cod)Cl]$_2$ was replaced by bubbling CO through a mixture with 8h to generate the complex 8h-IrCl(CO)$_2$ [79].

2.9. Tridentate cyclic diphosphino CDCs

The carbones 9a and 9b are functionalized carbodicarbene in which the donating carbon atom is part of a seven membered ring.

![Figure 12. Hypothetical free carbones 9a and 9b.](image)

The neutral 9a and 9b could not be isolated, source for transition metal complexes are the related cations 9aH$^+$ and 9bH$^+$ [84].
Table 9. Transition metal complexes with the carbones 9a and 9b; $^{13}$C NMR signal of the central donating carbon atom.

| Nr | $^{13}$C NMR | M-C | C-C | C-C-C | Ref. |
|----|-------------|-----|-----|-------|------|
| Transition metal complexes with the carbone 9a |
| 9a-RhCl | 73.0 | nr | nr | nr | [84] |
| [9a-RhNCMe]$^+$ | nr | 2.043 | 1.398 1.387 | | [84] |
| [9a-Rh(CO)]BF$_4$ | nr | nr | nr | nr | [84] |
| [9a-Rh(styrene)]BF$_4$ | nr | 2.075(2) | 1.404(3) 1.391(3) | 121.7(2) | [85] |
| [9aH-Rh(CO)](BF$_4$)$_2$ | nr | nr | nr | | [85] |
| Transition metal complexes with the carbone 9b |
| 9b-RhCl | 73.4 | nr | nr | nr | [84] |
| [9b-RhNCMe]BF$_4$ | nr | nr | nr | nr | [84] |
| [9b-Rh(CO)]BF$_4$ | | | | | [84] |

Scheme 18. Selected structures of transition metal complexes with the carbones 9a and 9b. a) [Rh(cod)Cl]$_2$/NaOMe, b) 9a-RhCl/styrene/NaBF$_4$.

The neutral complexes 9a-RhCl and 9b-RhCl where prepared upon reacting the cations 9aH$^+$ or 9bH$^+$, respectively with [Rh(cod)Cl]$_2$/NaOMe; if treated with AgBF$_4$/MeCN the cationic spezies [9a-Rh(MeCN)]BF$_4$ and [9b-Rh(MeCN)]BF$_4$, respectively, were isolated. The related carbonyl complexes [9a-Rh(CO)]BF$_4$ and [9b-Rh(CO)]BF formed similarly upon reaction with [Rh(CO)$_2$Cl]$_2$/NaOMe [84]. The styrene complex [9a-Rh(styrene)]$^+$ was obtained upon treating the related chloro complex with styrene/NaBAr$_4$; the styrene complex catalyzes
the hydroarylation of dienes. Protonation of [9a-Rh(CO)]+ with HBF$_4$ OEt$_2$ generates [9aH-Rh(CO)]$^{2+}$ in which the carbone acts as four electron donor [85].

2.10. Tetraaminoallene (TAA) transition metal complexes

![Tetraaminoallene (TAA) transition metal complexes](image)

**Figure 13.** Linear tetraaminoallene (TAA) and the extreme formulation as a carbodicarbene with a bent array. TAA’s has hidden or masked pairs of electrons.

The $^{13}$C NMR shift of the central carbon atom amounts to 142.8 ppm. The first and second PAs of 10 are 282.5 and 151.6 kcal/mol, respectively [16,74].

![Scheme 19: Structure of [10-AuPPh$_3$]SbF$_6$; a) AuClPPh$_3$/NaSbF$_6)](image)

**Scheme 19:** Structure of [10-AuPPh$_3$]SbF$_6$; a) AuClPPh$_3$/NaSbF$_6$

The salt [10-AuPPh$_3$]SbF$_6$ is the only transition metal complex of TAA, which has been reported so far. Both carbene moieties are planar, but are tilted relative each other, to relieve allylic strain [86]. The Au-C bond lengths amounts to 2.072(3) Å and the slightly different C-C dative bonds has interatomic distances of 1.406(5) and 1.424(5) Å. The central C-C-C bond angle is reported with 118.5(3)$^\circ$. 

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2.11. Transition metal complexes of carbones with the P-C-C skeleton

Mixed carbene-phosphine stabilized carbones from the working group of Bestmann (1974) and Alkarazo (2009).

\[ \text{Ph}_3\text{P} \quad \begin{array}{c} \text{C} \end{array} \quad \begin{array}{c} \text{C} \text{OEt} \end{array} \quad \text{OEt} \]

\[ \text{Ph}_3\text{P} \quad \begin{array}{c} \text{C} \end{array} \quad \begin{array}{c} \text{C} \text{NMe}_2 \end{array} \quad \text{OEt} \]

Figure 14. In compounds 11 the C(0) is stabilized by a phophine and a carbene ligand.

The crystal structure of 11a reveals a planar configuration of the carbene ligand C(OEt)\(_2\). Short P-C and C-C distances indicate some p back donation; P-C = 1.682(4) Å, C-C = 1.316(10) Å, C-C-C 125.6° [87].

Table 11. Transition metal complexes with the mixed carbones 11a and 11b. \(^{31}\)P NMR shifts in ppm.

| Nr    | \(^{31}\)P NMR | M-C     | P-C     | P-C-C   | Ref.   |
|-------|----------------|---------|---------|---------|--------|
|       |                | C-C     |         |         |        |
|       | Transition metal complexes with the carbone 11a       |         |         |         |        |
| 11a-RhCl(CO)\(_2\) | 25.1           | nr      | nr-     | nr      | [88]   |
| 11a-AuCl     | 26.7           | 2.014916| 1.7449(16)| 114.30(12) | [88]   |
|              |                |         | 1.362(2) |         |        |
| 11a-(AuCl)\(_2\) | 28.1           | 2.081(4)| 2.103(4)| 1.785(4)| 114.2(3) | [88]   |
|              |                |         |         | 1.425(6)|        |
| Transition metal complexes with the carbone 11b       |         |         |         |         |        |
| 11b-AuCl     | 22.2           | nr      | nr      | nr      | [88]   |
Scheme 20. Selected structural representation of transition metal complexes of 11a. a) one equiv. of AuCl(SMe₂), b) two equiv. of AuCl(SMe₂).

The neutral Rh complex 11a-RhCl(CO)₂ was obtained from reacting the carbone 11a with [Rh(CO)₂Cl]₂. Similarly, the complex 11b-AuCl results from reaction of 11b with AuCl(SMe₂) [88].

2.12. Transition metal complexes of carbones with the P-C-Si skeleton

The neutral compound 12 is a carbone in which the C(0) atom is stabilized by a donor stabilized silylene and a phosphine ligand.

Figure 15. Carbone complex reported by Kato et al [89].

The crystal structure of a related compound to 12 (a cyclopentene instead of a cyclohexene ring) shows a P-C distance of 1.6226(4) Å and Si-C distance of 1.6844(4) Å; the Si-C-P angle amounts to 140.03(3)°. Addition of CuCl generates the complex 12-CuCl. No spectroscopic or structural details are available [89].
2.13. Transition metal complexes of carbones with the P-C-S skeleton

A series of carbones (13a to 13c) based on a P-C-S core containing the neutral S(IV) ligands SPh₂=NMe (Figure 16) were reported by Fujii [90].

![Figure 16](https://example.com/figure16.png)

**Figure 16.** Carbone complexes reported by Fujii et al [90].

Crystal structures and ³¹P NMR shifts of the following basic carbones are available:

13a, $\delta = -2.64$ ppm; 13b $\delta = -1.39$ ppm, P-C = 1.663(2) Å, S-C 1.602(2) Å, P-C-S = 125.59(15)°. The authors revealed a high electron density at the central carbon atom.

Table 12. Collection of transition metal complexes with the carbones 13a to 13c. ³¹P NMR signals (in ppm) are given.

| Nr  | ³¹P NMR | M-C | P-C   | S-C   | P-C-S  | Ref  |
|-----|---------|-----|-------|-------|--------|------|
|     |         |     |       |       |        |      |
| 13a-AgCl          | 10.8  | 2.131| 1.711 | 1.648 | 121.9  | [90] |
| [13a-AuPPh₃]OTf   | 15.2  | nr  | nr    | nr    | nr     | [90] |
| [13a-(AuPPh₃)₂]OTf₂| 29.7  | nr  | nr    | nr    | nr     | [90] |
| 13b-AgCl          | 9.13  | 2.098| 1.728 | 1.636 | 119.1  | [90] |
| [13b-AuPh₃]OTf    | 12.88 | nr  | nr    | nr    | nr     | [90] |
| [13b-(AuPPh₃)₂]OTf₂| 27.45 | 2.127| 2.118 | 1.788 | 1.737  | 115.6 | [90] |
| 13b-Ag-13b         | 8.43  | 2.160| 1.707 | 1.635 | 121.8  | 127.0 | [90] |
| 13b-HAuPPh₃       | 17.1  | 2.106| 1.817 | 1.782 | 116.3  | [90] |

Transition metal complexes with the carbone 13c based on a P-C-S core

13c-CuN(SiMe₃)₂ [90]
Scheme 21. Selected structures with the carbones 13a and 13b: a) 0.5 eq. of AgOTf, b) 2 eq. of AuCl(PPh₃)/2 eq. of AgSbF₆, c) 1 eq. of AuCl(PPh₃)/1 eq. of AgSbF₆, d) ion exchange (OH⁻ form), 1 eq. of AuClPPh₃/1 eq. of AgOTf [90].

The addition products 13a-AgCl and 13b-AgCl were obtained from reacting [13aH]⁺ or [13bH]⁺, respectively with ion exchange resin (Cl⁻ form) and Ag₂O/CH₂Cl₂. For the other products, see Scheme 21 [90].

Addition of TM fragments to 13a or 13b elongates P-C and S-C bond length as reported for 1a. That of [13bH-AuPPh₃](OTf)₂ in which 13b acts as four electron donor are elongated to normal single bonds [90].
2.14. Transition metal complex with a P-C-S core possessing a neutral S(II) ligand

The carbene 14 contains a phosphine and a S(II) ligand with a free pair of electrons to stabilize the C(0) atom. However, the bare 14 could not be isolated, but only the protonated cation [14H]+ and used as starting material [91].

![Figure 17](image_url)

**Figure 17.** Mixed P and S stabilized carbene 14.

The transition metal complex [14-CuN(SiMe3)2]OTf was prepared upon reacting [14H]+ with KHMDS/CuCl. X-ray analysis reveals a Cu-C distance of 1.903(4) Å and the P-C and S-C distances amount to 1.709(5) and 1.677(5) Å, respectively. As found in carbene addition compounds of 13a and 13b the P-C distance is longer than the S-C distance. An acute P-C-S angle of 115.3(2)° was recorded. The 31P NMR signal is shifted to lower fields at 66.5 ppm [91].

2.15. Transition metal complexes of carbones with the S-C-S skeleton

In the carbones 15 (carbodisulfanes, CDS) the central carbon atom is stabilized by two neutral S(II) ligands (15a), or S(II), S(IV) groups (15b) or two S(IV) (15c) ligands.

![Figure 18](image_url)

**Figure 18.** Sulfur based carbones 15 as ligands for transition metal complexes.

The molecular structure of 15a was investigated computationally [92]. For the carbones the following parameters were recorded: 15b, C-SII 1.707(2), S-SIV 1.648(2), S-C-S 106.67(14). 13C NMR, d = 35.4 ppm [93]. 15c: S-C 1.635(4), 1.636(2); S-C-S 116.8(2) [94].
Similar to CDCs the first and second PAs of 15b amount to 288.0 and 184.4 kcal/mol, respectively.

Table 13. Transition metal complexes with selected bond length (Å) and angles (deg) of the carbone ligands 15a to 15c. $^{13}$C NMR signal (in ppm) of the central carbon atom.

| Transition metal complexes with the CDS 15a | $^{13}$C NMR | C-M | S^I-C | S^II-C | S^III-M-S^IV | Ref. |
|------------------------------------------|-------------|-----|-------|--------|-------------|------|
| 15a-AgCl                                 | not obs     | 2.058(8) | 1.707(8) | 1.698(8) | 107.3(5) | [92] |
| [15a-AuPPh$_3$]OTf                       | 65.4        | -   | -     | -      | -          | [92] |
| [15a-(AuPPh$_3$)$_2$]$_2^+$               | not obs     | 2.116(6) | 2.084(5) | 1.782(6) | 1.767(6) | 115.4(3) | [92] |
| [15aH-AuPPh$_3$]$_2^+$                   | 66.0        | 2.090(7) | 1.837(7) | 1.805(7) | 104.4     | [92] |

| Transition metal complexes with the CDS 15b | $^{13}$C NMR | C-M | S^I-C | S^IV-C | S^III-M-S^IV | Ref. |
|-------------------------------------------|-------------|-----|-------|--------|-------------|------|
| 15b-AuPPh$_3$]OTf                         | 67.4        | -   | -     | -      | -          | [92] |
| [15b-Ag-15b]OTf                           | not obs     | 2.111(7) | 2.097(7) | 1.718(6) | 1.664(7) | 106.3(6) | [92,95] |
| [15b-(AuPPh$_3$)$_2$](OTf)$_2$             | not obs     | 2.130(3) | 2.103(3) | 1.792(3) | 1.746(3) | 106.27(18) | [92] |
| [15b-Ag$_2$-15b](OTf)$_2$                 | not obs     | -   | -     | -      | -          | [95] |
| [15b-Ag$_4$-15b](OTf)$_4$                 | not obs     | 2.192 2.187 |       |         |           | [95] |
| [15bH-AuPPh$_3$](OTf)$_2$                | 72.1        | 2.098(3) | 1.796(3) | 1.789(3) | 106.83(17) | [92] |

| Transition metal complexes with the CDS 15c | C-M | S^IV-C | S^III-M-S^IV |
|-------------------------------------------|-----|--------|--------------|
| [15c-AuPPh$_3$]OTf                        | 65.1| -      | -            | [92] |
| 15c-AgCl                                  | not obs     | 2.134(3) | 1.690(3) | 1.678(3) | 112.16(14) | [92] |
| [15c-(AuPPh$_3$)$_2$](OTf)$_2$             | not obs     | 2.126(4) | 2.125(4) | 1.789(4) | 1.735(5) | 112.5(2) | [92] |
| [15c-Ag$_2$-15c](OTf)$_2$                 | 40.0        | 2.116 2.127 | 1.671-1.696 | 114.6 115.6 | [95] |
| [15c-Ag$_4$-15c](OTf)$_4$                 | 43.1        | 2.147 | 1.666 | 1.696 | 114.7 | [95] |
| [15c-Ag$_4$-15c](OTf)$_4$                 | nr          | 2.228 2.193 | nr         | nr | [95] |
| {[15c(AuPPh$_3$)$_2$AgOTf](OTf)$_4$}$_2$  | nr          | 2.139 2.108 | 1.757 | 1.747 | 116.8 | [92] |
Scheme 22. Selected of complexes with the carbone 15a. a) 2 eq AuCl(PPh$_3$)$_2$, b) AuCl(PPh$_3$)$_2$.

Scheme 23. Selected of complexes with the carbone 15b. a) 0.5 eq AgOTf, b) 1.0 eq AgOTf, c) 2.0 eq AgOTf, d) 2 eq AuCl(PPh$_3$)$_2$, e) AuCl(PPh$_3$)$_2$. 
Scheme 24. Selected complexes with the carbone ligand 15c; a) AgOTf, b) 0.5 eq AgOTf, c) 1.0 eq AgOTf, d) 2.0 eq AgOTf. \(\{15c-(\text{AuPPh}_3)_2\text{AgOTf}\}^2\text{(OTf)}_2\) is dimeric linked by two OTf anions.

15a-AgCl was obtained from \(15a\text{H}^+\) upon treating with Ag₂O/CH₂Cl₂. The salt \(15a\text{AuPPh}_3\text{OTf}\) formed reacting the bare 15a with AuCl(PPh₃) followed by addition of NaTfO in THF. \(15a-(\text{AuPPh}_3)_2\text{AgOTf}\text{(OTf)}_2\) and \(15a\text{H}-\text{AuPPh}_3\text{(SbF}_6\text{)}\) are sketched in Scheme 22 [92].

\[15b\text{-AuPPh}_3\text{OTf}\] was obtained analogously formed from reacting 15b with AuCl(PPh₃) followed by addition of NaTfO in THF. For the other compounds, see Scheme 23 [92].
The preparation of $[15c$-$\text{AuPPh}_3]\text{OTf}$ and $15c$-$\text{AgCl}$ follows the procedure outlined for the related $15b$ compounds [92]. For the other compounds, see Scheme 24 [92,95]. The heterohexametallic cluster $\{[15c$-(\text{AuPPh}_3)\text{AgOTf})(\text{OTf})_4\}_2$ is supported by two carbone ligands that adopt a $\kappa^4C,C',N,N'$ coordination mode. The Au---Ag separation amounts to 3.003 Å [92].

$^{13}$C NMR signals of the donating C(0) atoms (if available) of all addition compounds of $15a$ to $15c$ are less shielded than that of the basic carbones [92].

2.16. Transition metal complexes of carbones with the S-C-Se skeleton (16)

Compound 16 is the first carbone containing a Se(II) compound together with a S(IV) one as ligand for stabilization of a C(0) atom.

![Figure 19. Carbone with Se and S based ligands L.](image)

Table 14. Transition metal complexes with selected bond length (Å) and angles (deg) of the carbene 16 $^{13}$C NMR signal (in ppm) of the central carbon atom.

|             | $^{13}$C NMR | C-M   | C-S   | S-C-Se | Ref. |
|-------------|--------------|-------|-------|--------|------|
| $[16$-Ag-16$]$OTf | not obs.     | nr    | nr    | nr     | [95] |
| $[16$-Ag$_2$-16$]$(OTf)$_2$ | 52.7         | nr    | nr    | nr     | [95] |
| $[16$-Ag$_4$-16$]$(OTf)$_4$ | not obs      | 2.174(5) | 1.714(5) | 106.4(3) | [95] |
| $[16$H-Ag-16H$]$(BF$_4$)$_3$ | not obs      | 2.164(4) 2.177(4) | 1.772(5) 1.771(5) | 103.8(2) | [93] |
Scheme 25. Transition metal complexes with the carbone 16 as two and four electron donor. a) 0.5 eq AgOTf, b) 1 eq AgOTf, c) 2.0 eq AgOTf, d) AgBF₄/CH₂Cl₂.

The tetranuclear complex [16-Ag₁-16]⁴⁺ contains a rhomboidal [Ag₄]⁴⁺ core surrounded by two carbones 16. In this and in [16H-Ag₁-16H]³⁺ the donating C(0) acts as a four electron donor [95].

3. Transition metal carbido complexes [M]-C

The second part of this review summarizes the research of transition metal complexes with a naked carbon atom as ligand [M]-C. They are often termed as carbides but the bonding situation is clearly different from well-known carbides of the alkaline and alkaline earth elements E, which are salt compounds of acetylene E₆C₂. The electron configuration of carbon atom in the ¹D state (2s²2p2²) is perfectly suited for dative bonding with a transition metal following the DCD model [7] in terms of σ donation and π backdonation [M]-E[C]. Carbon complexes [M]-C may thus be considered as carbone complexes [M]-CL₂ without the ligands L at the carbon atoms. A theoretical study showed in 2000 that the 18 valence electron (VE) complex [(CO)₄Fe(C)] is an energy minimum structure with a rather strong Fe-C bond [96]. However, such 18 VE systems could not be synthesized as isolated species but were only found as ligands where the lone-pair electron at the carbon atom serves as donor (see below).
seems that the electron lone-pair at carbon in the 18 VE complexes [M]-C makes the adducts too reactive to become isolated.

It came as a surprise when Heppert and co-workers reported in 2002 the first neutral adducts with a naked carbon atom as a ligand, which are the formally 16 VE diamagnetic ruthenium complexes [(PCy$_3$)LCl$_2$Ru(C)] (L= PCy and 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; Cy = Cyclohexyl) [22]. A subsequent bonding analysis of the model compound [(Me$_3$P)$_2$Cl$_2$Ru-C] considered five different models A – E for the Ru-C bonds that are shown in Figure 20 [23]. It turned out that the best description for the bonding interactions is a combination of electron-sharing and dative bonds. An energy decomposition analysis [97] suggested that the model B provides the most faithful account of the bond, where the $\sigma$ bond and the $\pi$ bond in the Cl$_2$M plane come from electron-sharing interactions Cl$_2$M=C whereas the $\pi$ bond in the P$_2$M plane is due to backdonation (Me$_3$P)$_2$Ru$\rightarrow$C. The compounds [(PCy$_3$)LCl$_2$Ru(C)] should therefore be considered as 18 VE Ru(IV) adducts. The following section summarizes the research of transition metal complexes with a naked carbon atom as ligand [M]-C that has been accomplished since 2002.

![Bonding models A – E for the bonding between a transition metal (TM) and a naked carbon atom in the compound [(R$_3$P)$_2$Cl$_2$Ru-C].](image)

Figure 20.
3.1. The system RuCl₂(PCy₃)₂C ([Ru]C)

By far the most known complexes with carbido ligands that have been synthesized and structurally characterized are ruthenium adducts. The progress in the chemistry of ruthenium carbido complexes was reviewed in 2012 by Takemoto and Matsuzaka [121]. In the following we summarize the present knowledge on ruthenium carbido complexes, which was reported in the literature.

The X-ray analysis of [Ru]C exhibits a Ru-C distance of 1.632(6) Å. A signal at 471.8 ppm was attributed to the ligand carbon atom [98]. A general route to carbon complexes is described in [99].

![Figure 21. The [Ru]C core](image)

Addition of PdCl₂(SMe₂)₂ gives the complex [Ru]C→PdCl₂(SMe₂), while with Mo(CO)₅(NMe₃) the carbonyl complex [Ru]C→Mo(CO)₅ is generated [24,98]. A series of [Ru]C→PtCl₂L complexes were obtained by Bendix from reacting the dimeric complex {[Ru]C→PtCl₂}₂ with various ligands L (L = PPh₃, PCy₃, P(OPh)₃, AsPh₃, CN'Bu, CNCy). Complexes with bridging Ligands L such as {[Ru]C→PtCl₂}₂bipy, {[Ru]C→PtCl₂}₂pyz, and {[Ru]C→PtCl₂}₂pym formed upon displacing ethylene from the related (C₂H₄)PtCl₂-L-PtCl₂(C₂H₄) by [Ru]C. {[Ru]C→PtCl₂}₂(μ-Cl)pz results from an ethylene complex and [Ru]C as depicted in Scheme 26 [100]. A series of Pt, Pd, Rh, Ir, Ag, Ru complexes were presented by Bendix with X-ray data and ¹³C NMR shifts of the ligand carbon atom ranging between 340 and 412 ppm [101]. Sulfur containing TM complexes with the metals Pd, Pt, Au, and Cu stem from the same laboratory. The sulfur ligands are tcn = 1,4,7-trithiacyclononane and S₄(MCp*)₃ (see Fig. 22) [102].
Table 15. Selected structural (in Å and deg) and spectroscopic ($^{13}$C NMR in ppm) details of [Ru]C addition compounds

|                  | $^{13}$C NMR | Ru-C  | M-C   | Ru-C-M   | ref  |
|------------------|-------------|-------|-------|----------|------|
| [Ru]C→PdCl$_2$(SMe$_2$) | 381.23      | 1.662(2) | 1.946(2) | 175.1(1) | [98] |
| {[Ru]C→PdCl$_3$}^+ | 380.9       | nr     | nr    | nr       | [101]|
| [Ru]C→Mo(CO)$_5$  | 446.31      | nr     | nr    | nr       | [98] |
| [Ru]C→PtCl$_2$Py | 350.34      | nr     | nr    | nr       | [24] |
| [Ru]C→PtCl$_2$NCr(dbm)$_2$ | nr | 1.676(2) | 1.899(2) | 174.5(1) | [24] |
| {[Ru]C→PtCl$_3$}^+ | 344.7       | nr     | nr    | nr       | [24] |
| {[Ru]C→PtCl$_2$}$_2$ | 326.23      | 1.676(8) | 1.871(8) | 1796(4)  | [24] |
| [Ru]C→PtCl$_2$PPh$_3$ | 388.81      | 1.672(2) | 1.983(2) | 173.7(1) | [100]|
| [Ru]C→PtCl$_2$P(OPh)$_3$ | 387.54      | 1.659(2) | 2.001(2) | 179.3(2) | [100]|
| [Ru]C→PtCl$_2$AsPh$_3$ | 374.68      | 1.670(2) | 1.949(2) | 171.9(2) | [100]|
| [Ru]C→PtCl$_2$CN'Bu | 376.26      | 1.661(2) | 1.967(6) | 176.5(3) | [100]|
| [Ru]C→PtCl$_2$NCy | 376.04      | nr     | nr    | nr       | [100]|
| [Ru]C→PtCl$_2$PCy$_3$ | 396.77      | 1.666(3) | 1.971(2) | 174.5(2) | [100]|
| [Ru]C→PtCl$_2$(dmso) | 349.0       | nr     | nr    | nr       | [101]|
| {[Ru]C→PtCl$_2$}$_2$bipy | 348.27      | 1.679(3) | 1.891(4) | 171.4(2) | [100]|
| {[Ru]C→PtCl$_2$}$_2$pyz | 342.48      | 1.668(6) | 1.895(6) | 176.3(3) | [100]|
| {[Ru]C→PtCl$_2$}$_2$pym | 341.36      | 1.678(3) | 1.893(3) | 176.0(2) | [100]|
| {[Ru]C→PtCl$_2$}$_2$(μ-Cl)pz | 355.09      | 1.678(4) | 1.909(4) | 169.9(2) | [100]|
| [Ru]C→AuCl | 395.3       | nr     | nr    | nr       | [101]|
| {[Ru]C→Au←C[Ru]}^+ | 395.3       | nr     | nr    | nr       | [101]|
| {[Ru]C→IrCl(CO)←C[Ru]} | 397.4       | nr     | nr    | nr       | [101]|
| {[Ru]C→Rh(CO)$_2$(μ-Cl)$_2$ | 396.4      | nr     | nr    | nr       | [101]|
| [Ru]C→RhCl(cod) | 411.7       | nr     | nr    | nr       | [101]|
| [Ru]C→IrCl(cod) | 387.6       | nr     | nr    | nr       | [101]|
| [Ru]C→Ag(4'-H-terpy)} | 433.5       | nr     | nr    | nr       | [101]|
| {[Ru]C→Ag(4'-Ph-terpy)} | 433.1       | nr     | nr    | nr       | [101]|
| [Ru]C→Ag(ttcn) | nr          | 1.653(4) | 1.876(4) | 173.1(2) | [101]|
| [Ru]C→Cu(ttcn) | nr          | 1.622(7) | 2.098(7) | 176.9(5) | [101]|
| [Ru]C→Pd-S$_4$(MOCp*)$_3$ | nr | 1.672(3) | 1.971(3) | 178.3(2) | [101]|
| [Ru]C→Pt-S$_4$(MOCp*)$_3$ | nr | 1.689(7) | 1.896(7) | 178.2(5) | [101]|
| [Ru]C→Pd-S$_4$(WCP*)$_3$ | nr | 1.668(5) | 1.959(5) | 178.1(3) | [101]|
| [Ru]C→Pt-S$_4$(WCP*)$_3$ | nr | 1.699(9) | 1.874(9) | 178.8(6) | [101]|

Figure 22. Spezification of ligands of Table 15.
Scheme 26. Selected [Ru]C→M carbido complexes and synthesis of \{[Ru]C→PtCl\}_2(\mu-Cl)pz

3.2. The system RuCl_2(PCy_3)(NHC)C (NHC[Ru]C)

The X-ray analysis of NHC[Ru]C exhibits a Ru-C distance of 1.605(2) Å. A signal at 471.5 ppm was attributed to the ligand carbon atom. No addition compounds were described so far [22].

Figure 23. The NHC[Ru]C core
3.3. The system (NHC*)Cl₃RuC⁻ (NHC*[Ru]C)

![Figure 24. The NHC*[RuCl₃]⁻ C core](image)

Treating the carbene complex (NHC*)Cl₂(PCy₃)Ru=CH₂ at 55° in benzene generated the neutral complex depicted in Fig. 25. X-ray analysis revealed a Ru₁⁻C distance of 1.698(4) Å and the Ru₂⁻C distance of 1.875(4) Å with a Ru-C-Ru angle of 160.3(2)°. In the \(^{13}\)C NMR the bridging C atom resonates at the typical value of 414.0 ppm.[123]

![Figure 25. Structural representation of the Ru carbido complex Ru₂(NHC*)₂Cl₃H.](image)

3.4. The system RuClX(PCy₃)₂C ([Ru]XC)

Various carbido complexes were reported in which one or both chloride ions in [Ru]C are replaced by X (X = Br, I, CN, NCO, NCS). {[Ru](MeCN)C}OTf is the first cationic carbido complex which is also starting point for most of the substituted carbido complexes. X-ray data for {[Ru](MeCN)C}OTf, [Ru](CN)₂C, [Ru](Br)C, and [Ru](NCO)C are available [103].
Figure 26. Carbido compounds of [Ru]XC with various X.

Table 16. Carbido complexes with the [Ru]XC core.

|                   | $^{13}$C NMR | Ru-C | M-C | Ru-C-M | Ref  |
|-------------------|--------------|------|-----|--------|------|
| {[Ru(MeCN)C}OTf   | 464.75       | nr   | nr  | nr     | [103]|
| [Ru(CN)₂C        | 464.7        | nr   | nr  | nr     | [103]|
| [Ru](F)C         | 474.58       | nr   | nr  | nr     | [103]|
| [Ru](Br)C        | 471.38       | nr   | nr  | nr     | [103]|
| [Ru](I)C         | 469.74       | nr   | nr  | nr     | [103]|
| [Ru](CN)C        | 474.91       | nr   | nr  | nr     | [103]|
| [Ru](NCO)C       | 473.51       | nr   | nr  | nr     | [103]|
| [Ru](NCS)C       | 477.50       | nr   | nr  | nr     | [103]|

3.5. The systems OsCl₂(PCy₃)₂C, OsI₂(PCy₃)₂C and OsCl₂(PCy₃)₂C ([OsX]C)

The carbido complexes [OsX]C were studied by X-ray analysis. The most important structural parameter is the Os-C separation, which for X = Cl amounts to 1.689(5) Å [104]. Single-crystal X-ray diffraction reveals that molecular [OsX]C adopts an approximately square-pyramidal core geometry, with the carbido ligand occupying the apical position and a short Os-C bond. In the $^{13}$C NMR spectrum the signal at 471.8 ppm for X = Cl was attributed to the
ligand carbon atom. It was synthesized via S-atom abstraction from the thiocarbonyl complex Os(CS)(PCy$_3$)$_2$Cl$_2$ by Ta(Osi-t-Bu)$_3$. The diiodo derivative was synthesized from [OsCl]C upon reacting with 10 eq of Me$_3$SiI and exhibits a $^{13}$C NMR signal at 446.14 ppm.

![Figure 27. The [Os]C core](image)

3.6. The system [Tp*Mo(CO)$_3$≡C]$^+$ ([Mo]$^+$C)

![Figure 28. The [Mo]$^+$C core.](image)

The reaction between Tp*Mo(CO)$_2$CCl and KFeCp(CO)$_2$ generates the carbido complex [Mo]C→FeCp(CO)$_2$ [105]. When Tp*Mo(CO)$_2$CSe was allowed to react with [Ir(NCMe)(CO)(PPh$_3$)$_2$]BF$_4$ the tetrannuclear carbido complex (μ-Se)$_2$[Ir$_2$-{[Mo]C}$_2$(CO)$_2$(PPh$_3$)$_2$] was obtained, see Fig. 29 [106]. A solution of Tp*Mo(CO)$_2$CBr in THF was treated with BuLi followed by addition of HgCl$_2$ resulted in the formation of the carbido complex [Mo]C→Hg→C[Mo] [107].
Table 17. Compounds with [Mo]$^+$C core.

|                  | Mo-C   | M-C   | Mo-C-M       | $^{13}$C NMR | Ref  |
|------------------|--------|-------|--------------|--------------|------|
| [Mo]C→FeCp(CO)$_2$ | 1.819(6) | 1.911(8) | 172.2(5)     | 381          | [105]|
| (µ-Se)$_2$Ir$_2$-{[Mo]C$_2$(CO)$_2$(PPh$_3$)$_2$} | 1.843(5) | 1.974(5) | 171.3(3) 168.2(3) | 286.1        | [106]|
| [Mo]C→Hg←C[Mo]   | nr     | nr    | nr           | 373          | [107]|
| [Mo]C→AuPPh$_3$  | nr     | nr    | nr           | nr           | [108]|

Figure 29. Selected structures of compounds with the [Mo]$^+$C moiety.

3.7. Unique Mo carbido complex

A further unique carbido complex was described recently as shown in Fig. 28. A signal at 360.8 ppm in the $^{13}$C NMR spectrum was assigned to the ligand carbon atom [109].

Figure 30. The carbido complex with the P$_2$(CO)Mo≡C core.
3.8. The system \([Tp^*W(CO)_3≡C]^+(W^1C)\)

![Diagram](image.png)

**Figure 31.** The \([W]^1C\) core

Reaction of \([W]C Li(THF)\) with \(NiCl_2(PEt_3)_2\) produced the complex \([W]C\rightarrow NiCl(PEt_3)_2\) [110]. Similarly, with \([W]C Li(THF)\) and \(FeCl(CO)_2Cp\) or \(HgCl_2\) the compounds \([W]C\rightarrow Fe(CO)_2Cp\) and \([W]C\rightarrow Hg←C[W]\), respectively, were obtained. \([W]C\rightarrow AuPEt_3\) was prepared from reacting \([W]C\rightarrow SnMe_3\) with \(AuCl(SMe_2)\) followed by addition of \(PEt_3\). A similar reaction with \(AuCl(PPh_3)\) yielded \([W]C\rightarrow AuPPh_3\). \([W]C\rightarrow AuAsPh_3\) and \([W]C\rightarrow AuPPh_3\) form a tetrameric assembly as depicted in Fig. 32. The X-ray analysis of the tetrameric unit revealed \(Au-C\) distances of 1.995 and 2.078 Å and a \(W-C\) distances of 1.877 Å [108].

**Table 18.** Compounds with \([W]^1C\) core.

| W-C        | M-C | W-C-M | $^{13}$C NMR | Ref |
|------------|-----|-------|--------------|-----|
| \([W]C\rightarrow NiCl(PEt_3)_2\) | nr  | nr    | nr           | [110]|
| \([W]C\rightarrow Fe(CO)_2Cp\)   | nr  | nr    | nr           | [108]|
| \([W]C\rightarrow Hg←C[W]\)      | nr  | nr    | nr           | [108]|
| \([W]C\rightarrow AuAsPh_3\)     | nr  | nr    | nr           | [108]|
| \([W]C\rightarrow AuPPh_3\)      | nr  | nr    | nr           | [108]|
| \([W]C\rightarrow AuPEt_3\)      | nr  | nr    | 397.7        | [108]|
3.9. The systems N\textsubscript{3}MoC and O\textsubscript{3}MoC

The potassium salt of N\textsubscript{3}MoC\textsuperscript{−} is dimeric with two K\textsuperscript{+} ions bridging two anions and can be transformed with the crown ethers 2.0-benzo-15-crown-5 and 1.0 2,2,2-crypt into the related ion pairs. X-ray analysis of the crown ether salt revealed a Mo-C distance of 1.713(9) Å [21,111].

![Figure 32. Tetrameric unit from [W]C→AuAsPh\textsubscript{3} and [W]C→AuPPh\textsubscript{3} [108].](image)

Figure 32. Tetrameric unit from [W]C→AuAsPh\textsubscript{3} and [W]C→AuPPh\textsubscript{3} [108].

Figure 33. The [N\textsubscript{3}Mo]C and [O\textsubscript{3}W]C core.

The complex [O\textsubscript{3}W]C→Ru(CO)\textsubscript{2}Cp was prepared from reacting [O\textsubscript{3}W]C-Et with Ru(C≡CMe)(CO)\textsubscript{2}Cp under loss of MeCCEt. The ligand C atom resonates at 237.3 ppm (\textsuperscript{1}J\textsubscript{WC} = 290.1 Hz). Distances are W-C = 1.75(2) Å, Ru-C = 2.09(2) Å and the W-C-Ru angle amounts to 177(2) ° [112].
3.10. Symmetrically bridged carbido complexes M=C=M

3.10.1. The Fe=C=Fe core

[Fe(TPP)]_2C was obtained from Fe^{iii}(TPP)Cl in the presence of iron powder by reacting with Cl_4 (TPP = 5, 10, 15, 20-tetraphenylporphyrin; according to Fe^{ii} the complex is diamagnetic [113] X-ray analysis revealed an Fe-C bond length of 1.675 Å and a Fe-C-Fe angle of 180° [114].

[Fe(pc)(1-meim)]_2C was similarly obtained as the Tpp derivate; starting with pcFe and Cl_4 followed by addition of sodium dithionite gave the μ-carbido bridged dimer; the Fe-C bond distance amounts to 1.70(1) Å and the Fe-C-Fe angle is 178(1)° (1-meim = 1-methylimidazole, pc = phthalocyanine) [115].

3.10.2. The Rh=C=Rh core

[Rh(PEt_3)(SGePh_3)]_2C was obtained upon reacting Rh(PEt_3)_2(SGePh_3)CS with Rh(PEt_3)_3(Bpin) via the intermediate mixed carbido complex (SGePh_3)(PEt_3)_2Rh=C=Rh(PEt_3)_2(SBpin) which rearranges to this complex and [Rh(PEt_3)_2(SBpin)]_2. The X-ray analysis was performed (see Table 19) [116] [Rh(PEt_3)_2(SBpin)]_2C was prepared earlier by the same working group from Rh(PEt_3)_3(Bpin) and 0,5 eq of CS_2 (X-ray data see Table 19). Addition of MeOH generated the carbido complex [Rh(PEt_3)_2(SH)]_2C [117]. [Rh(Cl)(PPh_3)]_2C resulted from reacting the thiocarbonyl complex Rh(Cl)(PPh_3)_2CS with HBCat. The central C atom resonates at 424 ppm (t, ^1J_{RhC} = 47 Hz). In the chloro complex the chloride ion can be replaced with K[(H_2B(pz)_2), K[(H_2B(pzMMeZ)_2], or K[(HB(pz)]_3] to produce the carbido complexes [Rh(H_2B(pz)_2)(PPh_3)]_2C, [Rh(H_2B(pzMMeZ)_2)(PPh_3)]_2C, and [Rh(HB(pz)_3)(PPh_3)]_2C, respectively. The unusual asymmetric carbido complex [Rh_2H(μ-C)(μ-C_6H_4PPh_2-2){HB(pzMMeZ)_2}2] contains a Rh^{1} atom with a shorter Rh-C distance, while the Rh^{iii} –C distance is longer [118].
Table 19. Rh-C distances (in Å) and Rh-C-Rh angles (in deg). $^{13}$C NMR of the bridging carbon atom in ppm.

| Compound | $^{13}$C NMR | Rh-C | Rh-C | Rh-C-Rh | Ref |
|----------|--------------|------|------|---------|-----|
| [Rh(PEt$_3$)$_2$(SGePh$_3$)]$_2$C | 425.8 $^1J_{RhC} = 47$ | 1.788(4) | 1.798(4) | 175.6(2) | [116] |
| [Rh(PEt$_3$)$_2$(SBpin)]$_2$C | nr | 1.790(7) | 1.766(7) | 176.1(4) | [116,117] |
| [Rh(PEt$_3$)$_2$(SH)]$_2$C | nr | nr | nr | | [117] |
| [Rh(Cl)(PPh$_3$)$_2$]C | 424 t, $^1J_{RhC} = 47$ | 1.7828(19) | 1.7828(19) | | [118] |
| [Rh(H$_2$B(pz)$_2$)(PPh$_3$)]$_2$C | nr | 1.7644(11) | 1.7644(11) | 169.1(7) | [118] |
| [Rh(H$_2$B(pzMe$_2$)$_2$)(PPh$_3$)]$_2$C | nr | 1.7794(9) | 1.7794(9) | 168.8(6) | [118] |
| [Rh(HB(pz$_3$))(PPh$_3$)]$_2$C | nr | 1.7761(7) | 1.7761(7) | 163.7(4) | [118] |
| [Rh$_3$(μ-C)(μ-C$_6$H$_4$PPh$_2$-2)]{HB(pzMe$_2$)$_3$} | 447.2 $^1J_{RhC} = 40$, $^5J_{RhI} = 40$, $^5J_{RhIII} = 50$ | 1.740(6) | 1.818(6) | 165.9(3) | [118] |
| {HB(pzMe$_2$)$_3$}$_2$ | 50 | Rh$^1$ | Rh$^{III}$ |

Figure 34. Selected structures of Rh=C=Rh complexes.
3.10.3. The Ru=C=Ru core

The tetranuclear carbido complex [Ru(PEt$_3$)Cl(μ-Cl)$_3$RuAr]$_2$C was prepared from the reaction of [(p-cymene)Ru(μ-Cl)$_3$RuCl(C$_2$H$_4$)-(PCy$_3$)] with HCCH in THF. X-ray analysis adopts Ru-C distances of 1.877(9) Å and a Ru-C-Ru angle of 178.8(9)° [119].

\[
\text{Ar} = \text{phenyl group}
\]

**Figure 35.** Structural representation of the Ru carbido complex [Ru(PEt$_3$)Cl(μ-Cl)$_3$RuAr]$_2$C.

3.10.4. The Re=C=Re core

The unique carbido complex [Re(CO)$_2$Cp]$_2$C results from reaction of [Re(thf)(CO)$_2$($η$-C$_5$H$_5$)], CS$_2$, and PPh$_3$ (with the aim of the thiocarbonyl complex [Re(CS)(CO)($η$-C$_5$H$_5$)]) as by-product in small amounts. X-ray analysis revealed Re-C distances of 1.882(14) and 1.881(14) Å and a Re-C-Re angle of 173.3(7)°. A $^{13}$C NMR shift for the ligand carbon atom at δ$_C$ = 436.4 ppm was measured [120].

\[
\text{Cp}
\]

**Figure 36.** Structural representation of the Re carbido complex [Re(CO)$_2$Cp]$_2$C.
3.11. Asymmetrically bridged carbido complex M’=C=M

3.11.1. The Fe=C=Re core

The asymmetrical carbido complex (TPP)Fe=C=Re(CO)$_4$Re(CO)$_5$ was prepared upon reacting the dichlorocarbene complex (TPP)Fe=CCl with 2 eq of pentacarbonylrhenate, [Re(CO)$_5$]$^-$, under release of CO and 2 Cl$^-$; TPP is tetraphenylporphyrin. Crystals were analyzed by X-ray diffraction and revealed a Fe=C distance of 1.605(13) Å and a C=Re distance of 1.957(12) Å. The Fe-C-Re angle amounts to 173.3(9)°; the Fe-C distance is somewhat smaller than in [(TPP)Fe]$_2$C and the Re-C distance is appreciably longer than in [Re(CO)$_2$Cp]$_2$C. In the $^{13}$C NMR spectrum the central carbido C atom resonates at 211.7 ppm.

![Structural representation of the Fe=C=Re carbido complex (TPP)Fe=C=Re$_2$(CO)$_9$.](image)

Figure 37. Structural representation of the Fe=C=Re carbido complex (TPP)Fe=C=Re$_2$(CO)$_9$.

4. Conclusion

The experimental and theoretical research about transition metal complexes with carbone ligands [M]-CL$_2$ and carbido complexes [M]-C has blossomed in the recent past and it can be foreseen that it will remain a very active area of organometallic chemistry in the future. The well-known family of transition metal complexes with C1-bonded carbon ligands that comprise alkyl (CR$_3$), carbene (CR$_2$) and carbyne (CR) groups has been extended by carbones (CL$_2$) and carbido (C) ligands. The summary of recent work, which is described in this review, indicates that carbone and carbido complexes are still largely terra incognita and that many new discoveries can be expected.
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