Carbocyclic Carbene Metal Complexes

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Contents

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Karl Öfele was born in 1932 in Munich (Germany). He studied at the Technische Hochschule München and received his Ph.D. degree under supervision of Ernst Otto Fischer in 1959. He was research associate with E. O. Fischer at both universities in Munich and was appointed to Akademischer Director in 1972 at the Technische Universität München. In 1975/76 he spent seven months in the research group of Reuben D. Rieke at the University of North Carolina in Chapel Hill. He has been a member of the group of Wolfgang A. Herrmann at the Technische Universität München since 1984, where he is still engaged after his retirement in 1997 with investigations on metal complexes with heterocyclic and carbocyclic carbene ligands.

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Christian Taubmann was born in Altötting, Germany, in 1977. He studied chemistry at the Technische Universität München and at the National University of Singapore. He graduated from Technische Universität München and joined the research group of W. A. Herrmann as a Ph.D. student in 2005. His current work comprises synthesis, structural elucidation, and catalytic applications of carbocyclic carbene complexes.

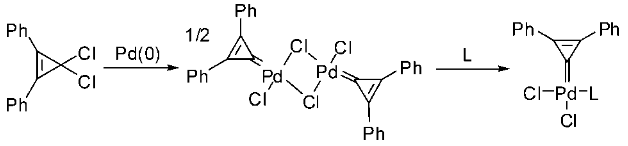
Wolfgang A. Herrmann was born in 1948 in Kelheim/Donau (Germany) and received his organometallic academic education with E. O. Fischer (Munich), H. Brunner (Regensburg), and P. S. Skell (Pennsylvania State University) before he became a professor of chemistry at the University of Regensburg (1979) and then Frankfurt (1982). In 1985 he was appointed the professor of inorganic chemistry at Technische Universität München to succeed E. O. Fischer. His research is focused on homogeneous catalysis, with a strong synthetic, spectroscopic, and structural background. He has authored approximately 750 scientific publications, numerous patents, and a number of review articles. He holds 10 honorary doctorates as well as numerous scientific awards, such as the Leibniz Award of the DFG, the Wilhelm Klemm Award of the German Chemical society, the Alexander von Humboldt Award, the Max Plank Research Award, the Bundesverdienstkreuz, the Ordre d'Honeur of the French President, the ACS Award in Organometallic Chemistry, and the Bavarian State Medal. Professor Herrmann has been the President of the Technische Universität München since 1995 and a member of the editorial board of Angewandte Chemie.

1. Introduction

In 1968, the first metal complexes with N-heterocyclic carbene (NHC) ligands were reported.[1,2] From this time, many complexes of transition metals both in low and high oxidation states as well as main group metals bearing such ligands were synthesized and characterized.[3,4] These singlet carbenes gain stability from electron donation by adjacent heteroatoms into the vacant p-orbital of the carbene carbon atoms. This electron donation causes the nucleophilic character of N-heterocyclic carbenes, which act as typical σ-donor ligands comparable to phosphanes or amines in metal coordination chemistry.[5]

The exploration of carbocyclic carbenes began with the early work of Jones and co-workers, who in 1967 could show for the first time that carbocyclic carbenes cyclopropenylidene and cycloheptatrienylidene can be stabilized by integration of the vacant p-orbital of the carbene into the π-electron system of an aromatic carbocycle and exist in a singlet configuration with nucleophilic behavior of the carbene.[6] This fundamental work inspired our efforts to use such carbenes without stabilizing heteroatoms as ligands in metal complexes comparable to N-heterocyclic carbene ligands. The first transition metal complexes with a carbocyclic 2-π-electron carbene could be synthesized in 1968 and 1970.[7,8] Since then, numerous articles have been published reporting complexation of this ligand system to different metals, with variation of substituents at the cyclopropene ring and alternative preparation methods of cyclopropenylidene complexes. Though relatively unexplored as a ligand class, work by Bertrand and co-workers, in which they succeeded

Scheme 1



in synthesizing a stable free cyclopropenylidene and the corresponding lithium adduct, has stimulated research in this area.[9,10]

In 1978, the first transition metal complexes with the homologeous carbocyclic 6-π-electron carbene cycloheptatrienylidene (CHT) were described by Jones.[11] During the following 20 years, the exploration was pushed forward exclusively by the group of Jones, including the discovery that the ligand C_7H_6 may exist in two different bonding modes, a carbene (cycloheptatrienylidene) or an allene (cycloheptatetraene) structure, depending on the electron configuration of the transition metal. Later on, other groups got involved in this work, primarily focusing on heterobimetallic complexes, in which the cycloheptatrienylidene simultaneously serves as an η-ligand such as Cp.

During the last two years, carbocyclic carbenes have gained importance as ancillary ligands in palladium precatalysts for coupling reactions. Apart from these cyclopropenylidene and cycloheptatrienylidene complexes, several reports concerning metal complexes bearing four- or five-membered carbocyclic carbene ligands have been published. These ligands obviously lack the special feature of nucleophilic carbenes based on an aromatic ring system; however, some of their metal complexes, especially ruthenium indenylidene complexes, have been applied to metathesis reactions as active carbenes in the last ten years.

Although several review articles have been published covering transition metal complexes of acyclic and heterocyclic carbenes, there is as of yet no summarizing description of analogous complexes bearing carbocyclic carbene ligands. In the present review, our aim has been to provide a systematic overview of carbocyclic carbene complexes from the synthetic methods employed for preparation, unique structure, and bonding features as well as reactivity and catalytic behavior from initial discovery in the late 1960s to present.

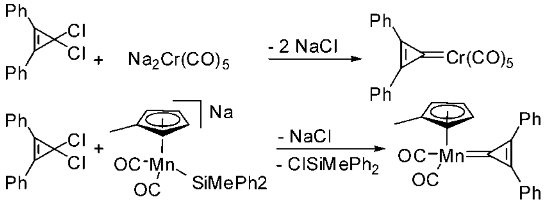
2. Synthesis of Complexes

2.1. Synthesis of Cyclopropenylidene Metal Compounds

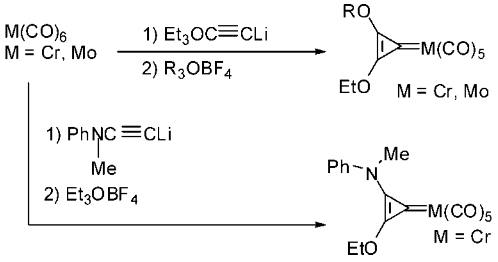
2.1.1. Synthesis via Oxidative Addition of Dihalogenocyclopropenylidenes

Dimeric cyclopropenylidene complexes of metals are readily accessible through the oxidative addition of geminal dihalocyclopropenes to metals such as palladium (Scheme 1) and platinum.[12−14,122] The halogen bridge of the dinuclear complex can easily be cleaved with neutral donor ligands (L) such as pyridine, dimethyl sulfoxide (DMSO), or phosphanes, affording the monomeric complex.[7] The in situ formation of such complexes with labile ligands turned out to be useful in the preparation of catalysts bearing the cyclopropenylidene (C3) moiety and was employed in the screening of catalytic precursors that may be difficult to isolate.[15]

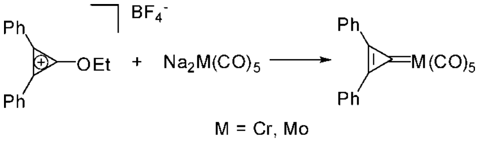
Scheme 2



Scheme 3



Scheme 4



In addition, metal compounds of transition metals in low oxidation states such as carbonylmetallates of Cr, Mo, W, and Mn have been shown to readily react with geminal dichlorocyclopropenes to form the carbene complexes according to Scheme 2.[8,14,16−19] Anionic iron(0) silyl complexes also react in this manner.[19]

2.1.2. Synthesis via Reaction of Hexacarbonyl Metal Complexes with 1-Ethoxy-2-lithioethyne Followed By Alkylation with Meerwein's Reagent

An alternative route is synthesis by reaction of hexacarbonyl metal complexes with 1-ethoxy-2-lithioethyne followed by alkylation with Et_3OBF_4, which was discovered by Hegedus and co-workers. They were able to produce a variety of group 6 alkoxycyclopropenylidene complexes in good-to-excellent yields. In addition, when the lithium salt of an ynamine was used instead of the ethoxyacetylene anion, the corresponding aminoalkoxycyclopropenylidene complex was obtained (Scheme 3).[20]

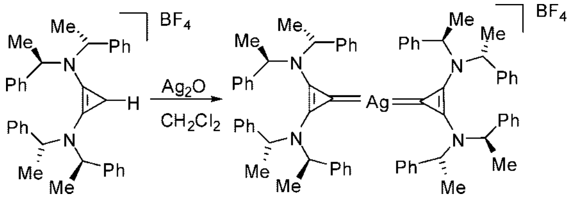
2.1.3. Synthesis via Reaction of Cyclopropenium Salts

Rees and co-workers were able to prepare molybdenum and chromium diphenylcyclopropenylidenepentacarbonyl complexes by reaction of 3-ethoxy-1,2-diphenylcyclopropenylium tetrafluoroborate instead of 1,1′-dichlorocyclopropenes with sodium pentacarbonyl complexes (Scheme 4).[21]

Deprotonation of bis[di(*R*-1-phenylethyl)amino]cyclopropenylium tetrafluoroborate in the presence of a strong base with Ag_2O gives the corresponding chiral dicarbene silver(I) tetrafluoroborate complex in moderate yields (67%) (Scheme 5).[22] Silver carbene complexes have been shown to be very useful carbene transfer agents, and this route may be of use in preparation of complexes bearing highly reactive carbocyclic carbenes, which are inaccessible by other synthetic routes.

Yoshida and co-workers have described the reaction of diaminocyclopropenium perchlorates with mercury acetate,

Scheme 5



which yields the corresponding diaminocyclopropenylidene mercury complexes shown in Scheme 6.[23]

Cyclopropenylidene complexes of germanium, tin, and lead could be prepared by reaction of a 1-chlorocyclopropenium salt with *n*-BuLi in situ, leading to lithiocyclopropenium salts and subsequent reaction with group 14 bisamides (Scheme 7a).[24] Palladium, platinum, and rhodium complexes have been prepared in a similar manner as shown below (Scheme 7b).

2.1.4. Synthesis via Reaction of Metal Complexes with a Stable Free Carbocyclic Carbene

After their breakthrough isolation of the free bis(diisopropylamino)cyclopropenylidene,[10] Bertrand and co-workers expanded their investigations into the utility of the free carbene for synthetic strategies based on ligand association/displacement reactions with metal complexes bearing labile ligands to yield novel cyclopropenylidene complexes (Scheme 8). They have shown that the isolated carbene is not only able to cleave halogen bridged complexes as other donor ligands (see section 2.1.1) but also able to displace phosphanes, yielding carbocyclic carbene complexes. In addition, reaction of the free carbene with Pd(TMEDA)Me_2, Ni$(COD)_2$, or bridged $[Rh(COD)Cl_2]_2$ results in the formation of monometallic biscarbene complexes due to the restricted steric bulk of the cyclopropenylidene carbene moiety.[25] Although these synthetic strategies are limited to relatively stable diaminocarbenes, this diverse route should spark renewed interest in these ligand systems.

2.1.5. Synthesis from Ruthenium Vinylidene Complexes

Lin and co-workers were able to prepare ruthenium cyclopropenylidene complexes in good yields via cyclization of vinylidene ligands. Methanolysis in acetone of half-sandwich ruthenium complexes bearing TCNQ-substituted vinylidene moieties induces ring closure of the latter, forming neutral methoxycyclopropenyl complexes. Removal of the methoxy group by acid gives cationic cyclopropenylidene complexes (Scheme 9).[26−28]

2.1.6. Synthesis via Deoxygenation, Desulfurization, and Deselenization

Cyclopropenethiones and cyclopropeneselones have been shown to provide access to cyclopropenylidene complexes via desulfurization and deselenization by reflux in toluene with group 6 metal hexacarbonyl complexes (Scheme 10). Through this method, Yoshida and co-workers were able to prepare metal complexes with a range of carbocyclic carbenes bearing nitrogen and sulfur substituents.[14]

Deoxygenation via oxygen transfer from cyclopropenone into an iron−zirconium bond to yield a bimetallic oxygen-bridged cyclopropenylidene complex (Scheme 11) was reported by Gade and co-workers. The reaction was shown to be a cooperative reaction of two complementary metals as attempts to deoxygenate cyclopropenones by monometallic iron half-sandwich complexes did not yield carbene complexes but instead gave metallacyclopenta-2,5-diones.[29] Therefore, this exceptionally attractive synthetic route based on readily available precursors is limited to bimetallic systems of this type.

2.1.7. Synthesis via Reaction of Terminal Carbido Complexes with Dimethyl Acetylenedicarboxylate

Johnson and co-workers found that the surprisingly stable ruthenium carbido complexes react with dimethyl acetylenedicarboxylate to form the cyclopropenylidene complex, $Ru(C(CO_2Me_2)_2))(PCy_3)_2Cl_2$ (Scheme 12).[30]

2.2. Synthesis of Cycloheptatrienylidene and Cycloheptatetraene Complexes

As explained in section 3.2 the C_7H_6 ligand may be bound in metal complexes either in a carbene (CHT) or an allene (CHTE) form. The synthesis of CHTE complexes will be described in sections 2.2.7 and 2.2.8.

2.2.1. Preparation via Cycloheptatrienyl−Metal Compounds

Since the reactions of 7,7′-dihalogen or 7,7′-dimethoxycycloheptatrienes with anionic metal carbonyl compounds (similar to the analogous and versatile method for preparing transition metal complexes with cyclopropenylidene ligands, see section 2.1.1) failed due to easy reduction of the tropyl ring, Jones developed a synthetic approach in which the cycloheptatrienyl metal bond is formed before the final conversion to a carbene ligand.[11] As outlined in Scheme 13, cycloheptatrienyl metal complexes are prepared by reaction of cycloheptatrienyl lithium with suitable transition metal halides and transformed to carbene complexes by subsequent hydride abstraction.

Additionally, CHT complexes of W(0), Fe(II),[11,31] Ru(II),[32] and Pt(II)[33] could be prepared in good yields by this method as well as complexes of Fe(II)[31,34] and Ru(II)[32] with dibenzannelated CHT ligands **A** and **B** in Figure 1.

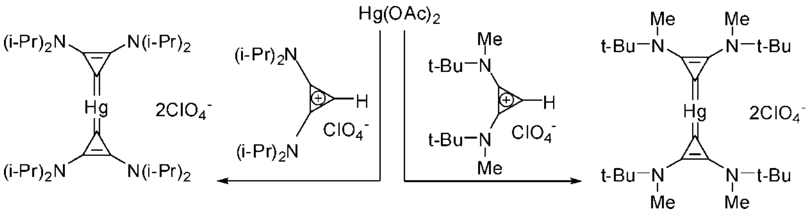
2.2.1.1. Variation 1. Starting with 2-trimethylstannylcycloheptatriene, instead of a mixture of isomeric bromocycloheptatrienes, much better yields (72% vs 29%) of isomerically pure 2-cyclohepatrienyl $Fe(CO)_2Cp$ could be achieved. This method was used to synthesize a heterobimetallic CHT complex bearing an η^7-coordinated $Cr(CO)_3$ moiety at the cycloheptatrienylidene ligand (Scheme 14).[35,36]

2.2.1.2. Variation 2. The synthesis of a pincer-CHT iridium complex was reported by Mayer and Kaska.[37,38] Metalation of a 1,6-bis(phosphinomethyl)-1,3,5-cycloheptatriene with iridium carbonyl chloride provides a pincer-7-cycloheptatrienyl iridium complex, which may be converted into the CHT complex by subsequent hydride abstraction with trimethylsilyl triflate (Scheme 15).

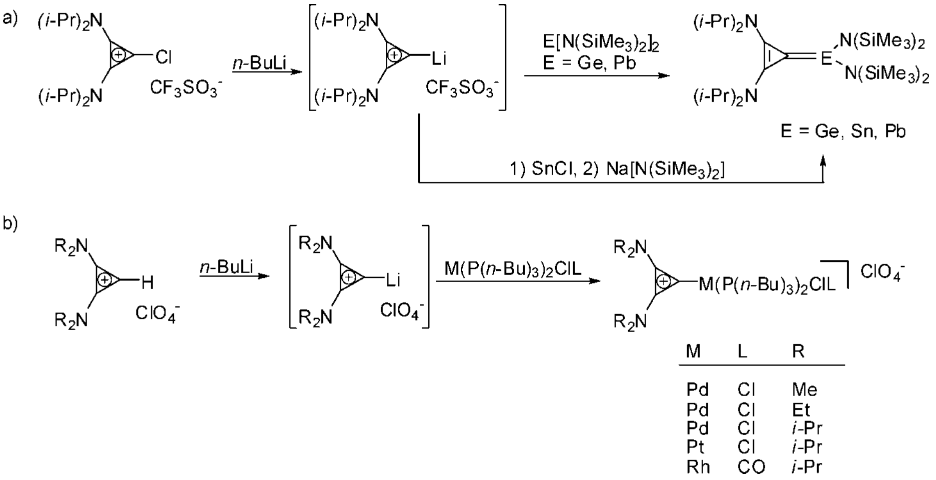
2.2.2. Preparation via a Cycloheptadienyne Complex

A rather special method for the synthesis of CHT−Pt(II) complexes was reported by Jones.[39] By abstraction of HBr from a mixture of isomeric bromocycloheptatrienes in the presence of a Pt(0) compound, two isomeric Pt(0) cycloheptadienyne complexes are formed that can be converted into an air-stable Pt(0) cycloheptadiynylium complex by hydride abstraction. The latter readily reacts with HCl or

Scheme 6

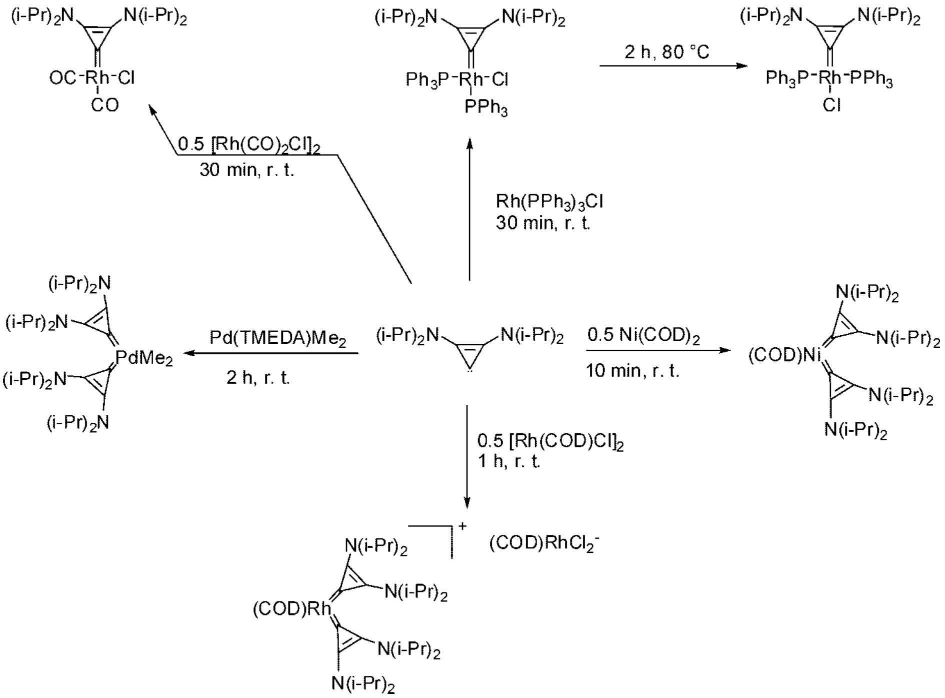


Scheme 7



M	L	R
Pd	Cl	Me
Pd	Cl	Et
Pd	Cl	*i*-Pr
Pt	Cl	*i*-Pr
Rh	CO	*i*-Pr

Scheme 8



HBr and results in the formation of CHT−Pt(II) complexes (Scheme 16).[33]

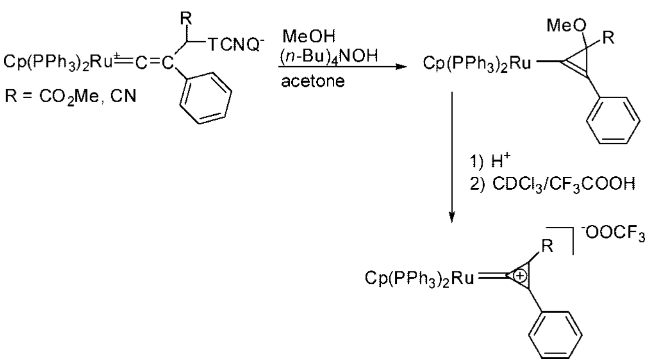
2.2.3. Synthesis via Diazo Precursors

Early investigations by Jones into the utility of diazo precursors showed only decomposition of troponetosylhydrazone in the presence of suitable transition metal precursors and no signs of the formation of carbene complexes. Later, Herrmann and Dötz succeeded in the preparation of dibenzannelated cycloheptatrienylidene complexes by reaction of 5-diazo-5*H*-dibenzo[a,d]cycloheptene with manganese[40] and chromium precursors[41,42] bearing weakly bonded ligands (Scheme 17).

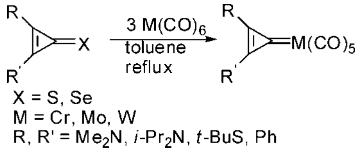
2.2.4. Synthesis via Oxidative Addition of Dihalogenocycloheptatrienes to Metals

As reported by Jones, reductive decomposition occurs when dihalogenocycloheptatrienes react with carbonyl metallates or other low-valent metal precursors.[11] In contrast to this behavior, the straightforward oxidative addition of 7,7′-dichloro- or dibromocycloheptatriene to highly dispersed palladium metal leads to the formation of dimeric dihalo-

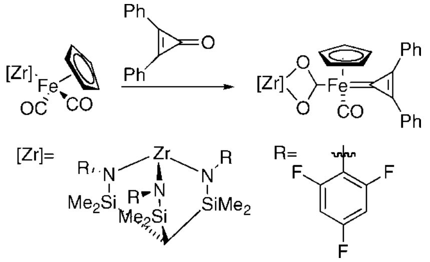
Scheme 9



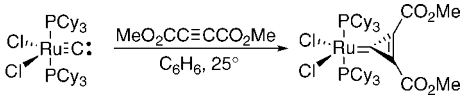
Scheme 10



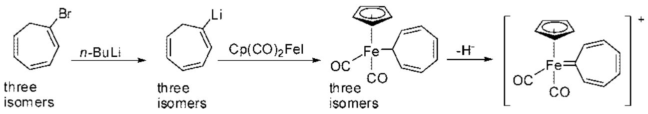
Scheme 11



Scheme 12



Scheme 13



geno−CHT−palladium(II) complexes at room temperature in very good yields. In the first reaction step, an η^3-allyl palladium complex is formed, which in a second step yields the carbene complex (Scheme 18). The η^3-allyl intermediate could be isolated and characterized during the reaction of dichlorocycloheptatriene with palladium.[43] As dihalogenocycloheptatrienes dissociate in polar solvents, the initial absorption of halogenide anions on the surface of the metal particles is assumed.[44−46]

The reaction sequence is in agreement with Jones's suggestion that the cycloheptatriene must be fixed to the metal before its conversion into a carbene ligand. In addition to soluble Pd black, Pd(0) sources such as $Pd(dba)_2$ have also been used successfully as metal precursors in the preparation of CHT−Pd complexes by oxidative addition of 7,7′-dihalogenocycloheptatrienes.[15]

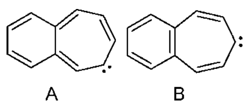


Figure 1.

2.2.5. Synthesis by Insertion of Pt(0) into C_7H_6−Si and C_7H_6−Ge Bonds

Starting with silicon- or germanium-bridged *ansa*-cycloheptatrienyl−cyclopentadienyl complexes of titanium, vanadium, and chromium, Tamm[47] and Braunschweig[48] generated μ-(η^1:η^7-CHT)platinum complexes by regioselective insertion of a $Pt(PEt_3)_2$ moiety into the C_7H_6−Si and C_7H_6−Ge bond, respectively of the η^7-coordinated cycloheptatrienylium ligand (Scheme 19).

2.2.6. Synthesis from Aromatic Nitrone Precursors

The phenylide anion resonance forms representing an anionic carbene are proposed as a possible six-membered congener of cycloheptatrienylidene by Yao. He realized the concept of a carbocyclic carbene ligand based on a benzene skeleton by appending a stable cationic substituent, in this case an iminium group, to the anionic carbene carbocycle providing the required charge balance. As a result, the coordinating carbon atom can serve as a neutral donor (Scheme 20).[49]

By reaction of the nitrone with $Pd(OAc)_2$ in acetic acid, dimeric acetate-bridged chelating Pd(II) complexes could be isolated in excellent yields (Scheme 21).

2.2.7. Synthesis of Cycloheptatetraene Pt(0) Complexes via in situ Generated C_7H_6

Metal complexes of the C_7H_6 allene species have been prepared by dehydrobromination of bromocycloheptatriene and trapping the in situ generated ligand with $Pt(PPh_3)_3$ (Scheme 22).[50,51]

The corresponding Pt(0) complexes **A** and **B** with mono- and dibenzannelated cycloheptatetraenes are accessible by the same method.

2.2.8. Synthesis of a Tungsten−Dibenzocycloheptatetraene Complex by Rearrangement of a Dibenzonorcaradiene Complex

Reaction of $CpW(CO)_3I$ with lithiated 7,7-dichlorodibenzonorcaradiene yields 7-chloro-7-tricarbonylcyclopentadienyltungstenio dibenzonorcaradiene **A** in moderate yield (Scheme 23). Photolysis of **A** affords the metastable dibenzonorcaradine complex **B**. Upon warming of **B** to 25 °C, the thermally stable dibenzocycloheptatetraene tungsten complex **109** is formed in 67% by intramolecular rearrangement.[52]

2.3. Synthesis of Other Carbocyclic Carbene Complexes

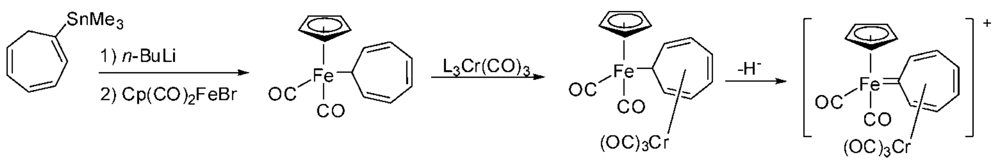
2.3.1. Preparation by Hydride Abstraction from Cycloalkenyl Compounds

One of the first metal complexes of a carbocyclic carbene not stabilized by an aromatic π-electron system was prepared by reaction of an η^1-benzocyclobutenyl−iron complex with trityl hexafluorophosphate by Giering (Scheme 24).[53]

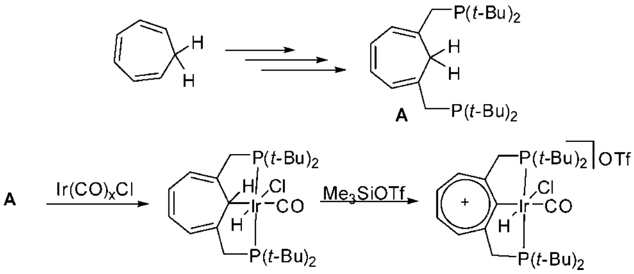
2.3.2. Synthesis by Carbene Transfer from a Diazo Compound upon Coordinatively Unsaturated Metal Centers

The reaction of diazoalkanes with appropriate metal precursors such as $Cr(CO)_5(COE)$, $(Cp)Mn(CO)_2THF$,

Scheme 14



Scheme 15



$RuCl_2(PPh_3)_3$ $RhCl_2(C_2H_4)(Sb$*i*$-Pr_3)_2$, and $Pd(PPh_3)_2(C_2H_4)$ according to Scheme 25 proved to be a versatile method for the preparation of metal complexes with cyclopentadienylidene,[54] fluorenylidene,[41,42,55−57] and dibenzocycloheptenylidene.[40−42,58]

2.3.3. Synthesis of Indenylidene Complexes using Propargylalcohol as a Carbene Precursor

A highly efficient and large-scale adaptable synthesis for phenylindenylidene complexes of ruthenium was found in the reaction of $RuCl(PPh_3)_n$ ($n = 3, 4$) with 3,3-diphenylpropyn-3-ol (Scheme 26).[59,60]

It is open, whether the indenylidene complex is formed directly or via a transient allenylidene species in this reaction.[61,62] However, the rearrangement of allenylidene to indenylidene complexes could be studied extensively with η^6-arene−ruthenium allenylidene complexes by Dixneuf and co-workers (Scheme 27). Treatment of the isolated allenylidene complex **A** with excess HOTf yields the temperature-sensitive indenylidene complex **B** via a dicationic alkenylcarbyne intermediate $[(\eta^6\text{-}p\text{-cymene})RuClCC^+HCPh_2(PR_3)](OTf)_2$.[63,64]

2.3.4. Synthesis of Cyclobutenylidene Complexes by Cycloaddition of Alkynes to Vinylidene Complexes

As shown by Härter, iron(II) vinylidene complexes in a [2 + 2]-cycloaddition react with phenylpropyne, forming cyclobutenylidene complexes in good yields (Scheme 28).[65]

In a similar reaction, Fischer and co-workers succeeded in the preparation of pentacarbonyl cyclobutenylidene complexes of chromium and tungsten by regiospecific addition of electron-rich alkynes to the $C_\alpha{=}C_\beta$ bond in pentacarbonyl vinylidene complexes (Scheme 29).[66]

Cycloaddition to vinylidene complexes was performed by Fischer's group also with alkynyl metal compounds instead of alkynes, yielding heterobinuclear cyclobutenylidene complexes (Scheme 30).[67]

2.3.5. Synthesis of Binuclear Cyclobutenylidene Complexes by Dimerization of Acetylide Metal Complexes

Protonation of an σ-phenylacetylide complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}CPh$ with strong Brønsted acids gives a cationic vinyl complex that, in the absence of a competing nucleophile, reacts with a second molecule of acetylide, yielding a 1,3-*homo*binuclear complex with a bridging cyclobutenylidene ligand (Scheme 31). This synthesis was independently published by Davison and Solar[68] and Kolobova.[69]

A comparable synthesis of a cyclobutenylidene-bridged binuclear rhenium complex was reported by Gladysz and co-workers by $ZnCl_2$ induced dimerization of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re(C{\equiv}CH)$ (Scheme 32). Initial generation of a cationic vinylidene complex **B** by attack of an electrophile ($ZnCl_2$) upon C_β of **A** is supposed to effect the cyclization.[70]

3. Structure and Bonding

In the following section, we would like to give an overview of general trends of metal complexes bearing carbocyclic carbenes and the effects of metals and substitution patterns of these ligands. Moreover, particularly interesting systems will be included and discussed, though deeper insights into these systems are often restricted because of limited data. For structural information on complexes not mentioned in this section, please refer to section 7, which includes selected structural details and relevant references for carbocyclic carbene complexes.

3.1. Cyclopropenylidene Complexes

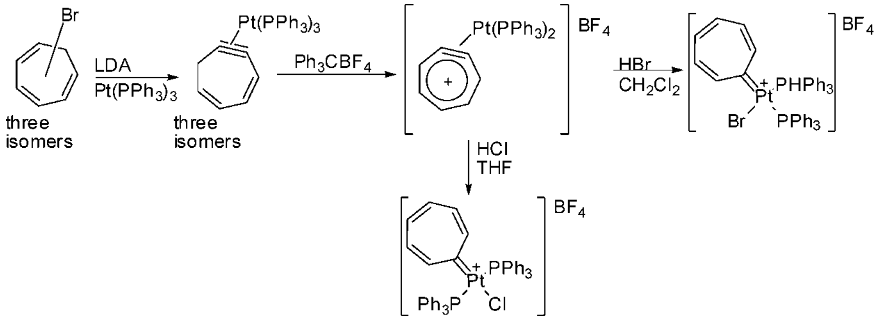
With transition metal complexes from group 6 to group 12, the cyclopropenylidene carbene is the most versatile of this ligand class. The structure and bonding of this ligand system with a very malleable design motif has been represented in many structural forms, shown below in Scheme 33. Donation from an electron-rich substituent R can result in the shortening of the $R{-}C_3$ bond, as shown in resonance structure **D**, and contributes to the kinetic stability.[14]

3.1.1. Cyclopropenylidene Complexes of Group 6 Metals

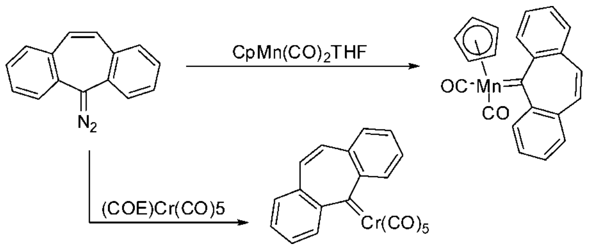
Though general trends are observed when moving down a period, or across a row, the most variance in complex behavior is caused by different substituents at the carbocyclic carbene.

The first major evaluation of this class of complexes was undertaken by Yoshida, who reported several metal complexes bearing the cyclopropenylidene moiety and provided a thorough discussion outlining the role and effects of substituents attached to the three-membered ring. In these studies, Yoshida used in situ IR techniques to observe group 6 carbonyl complexes. Complexes bearing cyclopropenylidene ligands with two amino substituents show the highest σ-donor/least π-acceptor ability, and those containing two phenyl groups show the least σ-donor/most π-acceptor ability for chromium and molybdenum pentacarbonyl complexes. Relative strengths are shown in Scheme 34 based on the frequencies of CO stretching A_{1a} bands. They state that the extended Hückel HOMO−LUMO (highest occupied molecular orbital−lowest unoccupied molecular orbital) gap

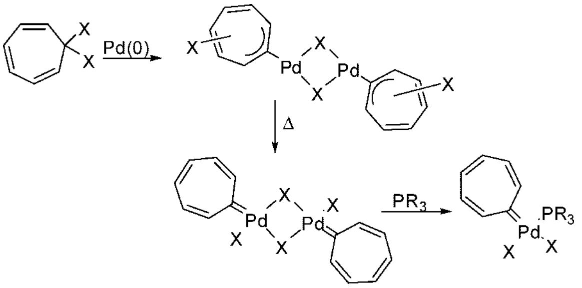
Scheme 16



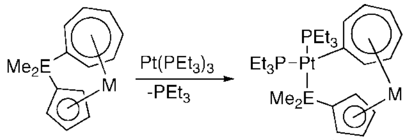
Scheme 17



Scheme 18



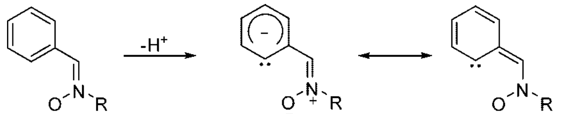
Scheme 19



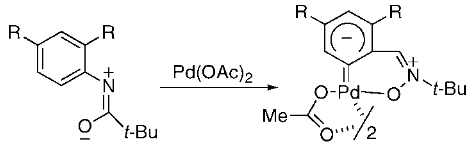
A a (E = Si, M = Ti)
b (E = Si, M = V)
c (E = Si, M = Cr)
d E = Ge, M = Ti)

B a-d

Scheme 20



Scheme 21

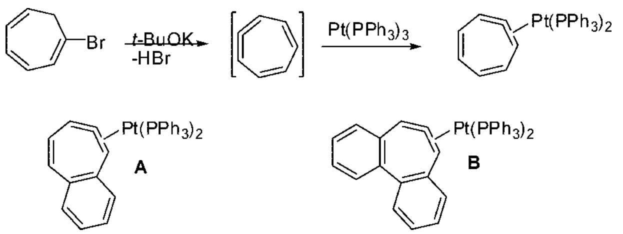


R = H, OMe

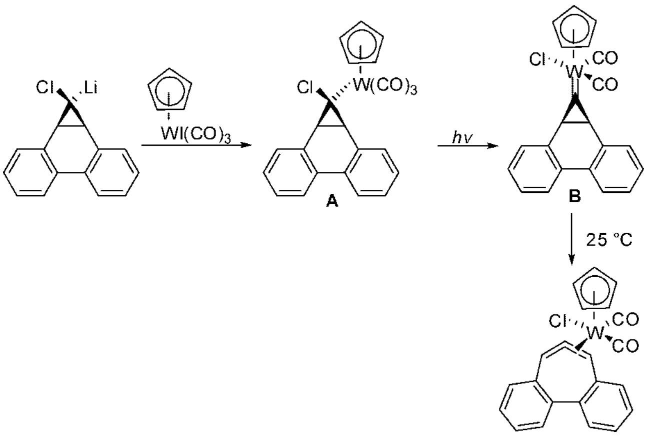
for the free carbene is the largest for ring systems substituted with electron-donating substituents that act to shift the structure from **A**, **B**, and **C** to **D** (Scheme 33).[14] Confirming this work, Scherer and co-workers recently evaluated cyclopropenylidene ligands using an experimental charge density approach including analysis of the topology of the Laplacian of the electron-density distribution and the out-of-plane atomic quadrupole moments. They classify the alkyl and amino substituents as σ-donors, with the latter showing greater stabilization of the cyclopropenium system through electron donation from the amino substituents.[71]

The first mononuclear cyclopropenylidene metal complex that could be structurally characterized by X-ray crystallography was $(CO)_5Cr(C(CPh)_2)$ (**2**). This complex exhibits

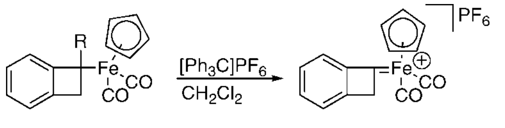
Scheme 22



Scheme 23

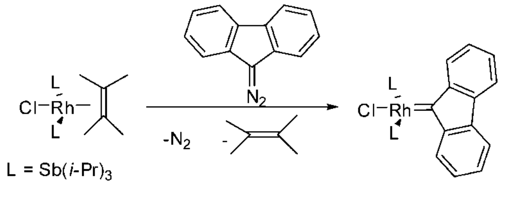


Scheme 24



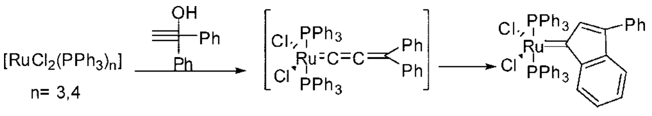
R = H, D, OMe, OH

Scheme 25

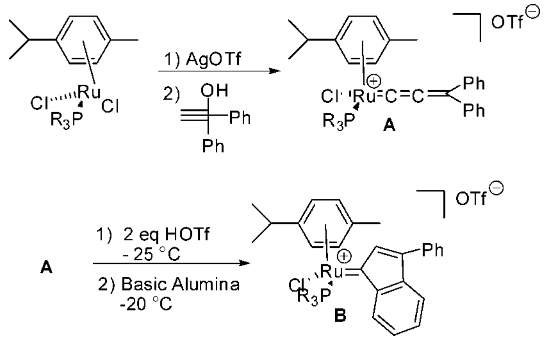


L = Sb(*i*-Pr)$_3$

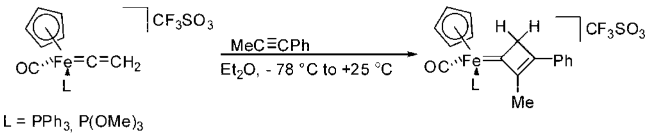
Scheme 26



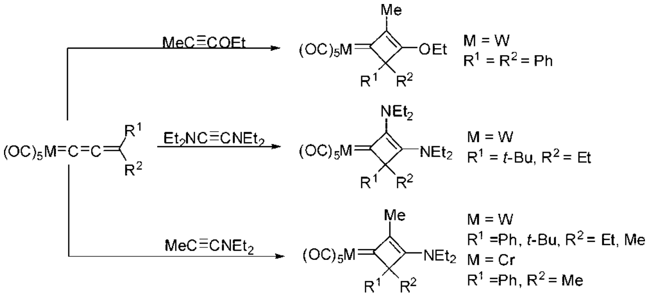
Scheme 27



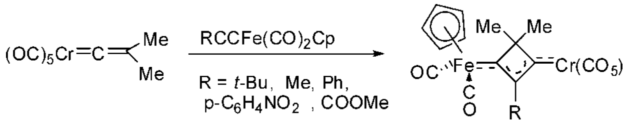
Scheme 28



Scheme 29



Scheme 30



a typical octahedral geometry of a substituted group 6 pentacarbonyl complex with the plane of the C3 ring at a 45° degree angle to the equatorial complex plane and the C_2 and C_3 carbons of the ring staggered between the carbonyl ligands in the equatorial position. One of the phenyl ring substituents is in-plane with the three-membered ring and the other is twisted out of plane by 7.5°. The authors suggest that the twisting is due to repulsions by phenyl *ortho*-hydrogens and the C_1-Cr bond distance of 2.0437 ± 0.0004 Å. The C_2-C_3 bond (1.3577(5) Å) is shorter than the C_1-C_2 (1.4076(5) Å) and the C_1-C_3 (1.4085(5) Å) bonds.[71,72]

Substitution of Ph for an electron-rich substituent in the design motif results in stabilization of the group 6 pentacarbonyl complexes. The bisethoxy-substituted Cr compound **6** has been prepared and structurally characterized. The C_2-O and C_3-O bond lengths displayed are shorter compared to the C(Et)$-$O bond lengths (1.300(5) Å vs 1.472(5) Å), suggesting electron donation form the oxygen atoms that act to stabilize the ring system. The C_1-C_2 and C_1-C_3 bond lengths are longer than the C_2-C_3 bond length (1.4010(8) Å vs 1.337(7) Å).[20]

Similarly, this trend of stabilization is observed for amino substituents. In the tungsten pentacarbonyl bis(diisopropylamino)cyclopropenylidene complex **30**, the nucleophilic carbene is a strong σ-donor and the W$-$C distance of 2.238(5) Å is very close in length to that of the analogous unsaturated NHC complex, indicating similar σ-donor/π-acceptor ratios. The C_1-C_2 and C_1-C_3 bond lengths are 1.376(7) Å and 1.373(7) Å, whereas the bond length for the C_2-C_3 bond is shorter 1.360(7) Å.[73] The difference in bond lengths C_1-C_2/C_1-C_3 versus C_2-C_3 is appreciably smaller than in the diphenylcyclopropenylidene ligand because of the contribution of resonance structures **C** and **D**. Reported M$-$C bond lengths for group 6 metal$-$carbonyl complexes are listed in Table 1.

In addition to IR and crystallographic studies, ^{17}O NMR work by Kawada and co-workers has also been shown to be an effective probe for the study of metal$-$carbonyl bonds in pentacarbonyl$-$carbene complexes including the cyclopropenylidene moiety. However, the amount of sample required (200$-$300 mg) is prohibitive for routine analysis.[74]

3.1.2. Cyclopropenylidene Complexes of Group 7 and 9 Metals

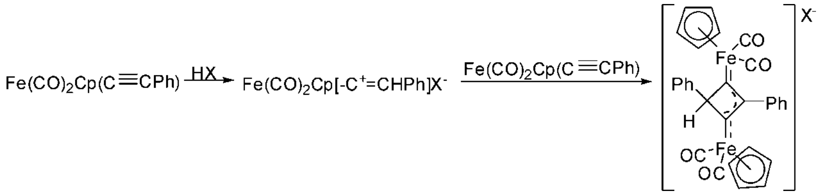
The **manganese** complex **34** $(MeCp)Mn(CO)_2(C(CPh)_2)$ has been structurally characterized by X-ray crystallography. While one phenyl substituent is coplanar with the C3 ring, the other is twisted by 11°, the angle between the plane of the C3 ring and the mirror plane of the Cp complex is 14°. The $Mn-C_1$ bond length is 1.896(4) Å, and the C_1-C_2, C_1-C_3, and C_2-C_3 distances are 1.424(6), 1.424(6), and 1.349(6) Å, respectively.[19]

Both mono- and biscarbene complexes of **rhodium** have been prepared by Bertrand and co-workers. The mononuclear **47**, *trans*-$RhCl(PPh_3)_2(C(CN(i\text{-}Pr)_2)_2)$, is of distorted square planar geometry with the plane of the C3 ring perpendicular to the coordination plane of the complex. The $Rh-C_1$ bond length observed is 2.411(3) Å, and C_1-C_2, C_1-C_3, and C_2-C_3 bond lengths are 1.352(16), 1.390(16), and 1.378(17) Å, respectively. This deviation from expected bond lengths where C_2-C_3 would be expected to be the shortest bond distance is most likely due to steric conditions enforced by the phosphane ligands. The Rh(0) biscarbene complex **48**, $[(C(CN(iPr)_2)_2)_2Rh(COD)][(COD)RhCl_2]$, displays $Rh-C_1$ bond lengths of 2.028(6) Å, and the expected C_1-C_2, C_1-C_3, and C_2-C_3 bond lengths of 1.380(9), 1.389(9), and 1.368(9) Å, respectively.[25]

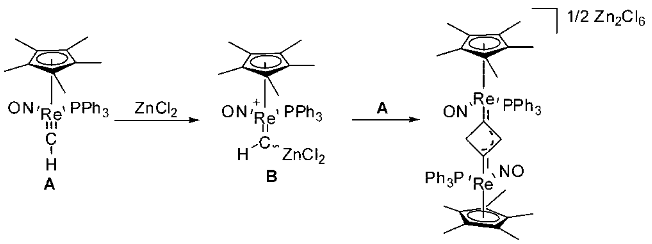
3.1.3. Cyclopropenylidene Complexes of Group 10 Metals

Mononuclear carbene complexes of palladium of the type $(Carbene)MX_2PR_3$ adopt square planar geometry with the plane of the carbene ligand ring perpendicular to the coordination plane of the complex. This was established by early work in the group of Yoshida, who used IR and ^{13}C NMR as previously discussed in this section.[13,14,75,76] The structure has been confirmed by X-ray crystallography. Shown below in Table 2 are the lengths of C$-$C bonds in the diphenylcyclopropenylidene ligands of palladium complexes, which suggest a high degree of π delocalization about the ring though the C_2-C_3 bond is typically shorter. Similar geometry is observed for the diaminocyclopropenylidene complex **78**, $PdCl_2P(n\text{-}Bu)_3[C(C(NMe_2)_2)_2]$, reported by

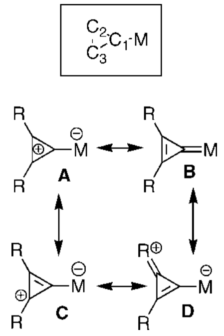
Scheme 31



Scheme 32



Scheme 33



Scheme 34

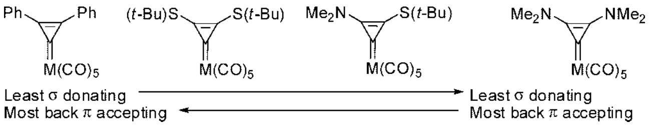
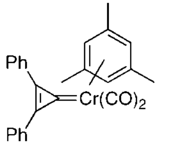
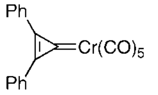
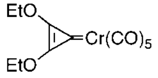
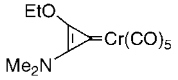
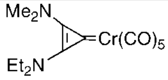
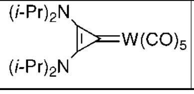


Table 1

Number	Structure	M-C bond length / Å
3		1.956(4)
2		2.0437(4)
6		2.010(7)
11		2.068(2)
10		2.086(1)
30		2.238(5)

Ibers. For this complex, sp^2 hybridization of the N atoms is observed, resulting in a position coplanar to the C3 ring. In addition, a relatively short C−N bond length of 1.320(4) Å is observed, giving further evidence of isomerization to maximize stability through charge separation for complexes bearing the amino substituted ring systems.[77] It is noteworthy that, for the $C(C(NR_2)_2)_2$ complex, the C−C bond lengths about the C3 ring are almost equivalent and Pd−Cl$_{trans}$ bond length is longer, suggesting the carbene in this system is not as strong a π-acceptor as $C(CPh_2)_2$; this is in agreement with observations in the chromium carbonyl systems discussed earlier.[15,77]

The only example of a structurally (by X-ray analysis) characterized dimeric chloro-bridged cyclopropenylidene palladium complex **54** $[PdCl_2(C(CMes)_2)]_2$ has been reported by Herrmann and co-workers. Mesitylene substituents bonded to the carbocyclic carbene ring are not in the plane with the C3 ring. This disruption in conjugation results in the remarkable solubility of this complex, in contrast to **53** $[PdCl_2(C(CPh)_2)]_2$ and **55** $[PdCl_2(C(CNap)_2)]_2$. Palladium carbon bond lengths are slightly shorter than those found in the corresponding mononuclear phosphane-substituted carbene complex **77** (0.01−0.05 Å shorter).[78]

Bertrand and co-workers were able to synthesize a biscarbene palladium complex **89** $Pd(C(C(NMe_2)_2)_2Me_2$, via the free carbene route. The carbene complex geometry is distorted square planar with the carbene rings twisted and not perpendicular to the coordination plane of the molecule, presumably due to steric hindrance of substituents at the C3 ring. The palladium carbene bond lengths are 2.0242(13) and 2.0306(12) Å. Bond lengths for C_1−C_2 and C_1−C_3 are 1.3903(19) and 1.3923(18) Å, respectively; as expected, the C_2−C_3 bond length with 1.3708(19) Å is slightly shorter.[25] *Cis*-dichloro- and *trans*-diiodo**platinum**−biscarbene complexes **91** and **96** have been prepared by Yoshida and co-workers via 2-fold oxidative addition of the dihalogenocyclopropenes to platinum metal, leading first to Pt(IV)−biscarbene complexes, isolated in the form of the chlorocomplex **92**. The Pt(IV) complexes are reduced to the corresponding Pt(II)−biscarbene complexes either by reaction with $SnCl_2$ or by reductive elimination of I_2. *Trans*-diiodo- and *cis*-chloro-Pt(II)−biscarbene complexes **94** and **95** could be prepared by reaction of lithiocyclopropenium perchlorates with $PtI_2(COD)$ and $PtCl_2$, respectively.[122]

3.1.4. Cyclopropenylidene Complexes of Group 11 and Group 14 Elements

A chiral bis(diamino)cyclopropenylidene complex of silver has been reported by Tamm. It crystallizes with two crystallographically independent dicarbene−silver cations **101** of almost linear shape (C−Ag−C angles 172.1(2)° and 175.3(2)°). The planes of the two cyclopropenylidene moieties in each cation are twisted from coplanarity (62.6° and 37.3°). In comparison to the free carbene, also isolated and characterized by this group, the coordinated carbene exhibits shorter N−C ring bonds and longer C−C bonds.

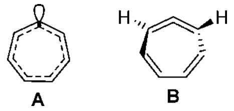


Figure 2.

Whether or not the stereochemistry of the cyclopropenylidene moiety is conserved upon further transmetalation, for which this complex would be well-suited, remains to be seen.[22]

Not limited to transition metal complexes, the cyclopropenylidene moiety has also been observed and characterized as a ligand in a series of group 14 complexes of the type substituted ((*i*-Pr$_2$NC)$_2$C)M(N(SiMe$_3$)$_2$)$_2$ **104**, **105**, and **106**, where M = Ge, Sn, Pb, respectively. A lengthening of the carbon metalloid/metal bond from 2.085(3) Å, 2.303(9) Å, to 2.423(8) Å is observed as one moves down the period, changing the metal from Ge to Sn and Pb, respectively.[24]

3.2. CHT and CHTE Complexes

The monocyclic C$_7$H$_6$ intermediate can exist in two valence isomeric structures: a carbene form **A** (cycloheptatrienylidene, CHT) and a twisted allene form **B** (cycloheptatetraene, CHTE), shown below in Figure 2. The latter appears to be the ground state.[79,80]

3.2.1. Allene Complexes

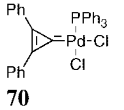
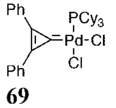
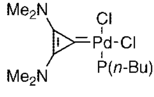
The CHTE ligand structure so far has been observed in some Pt(0) complexes (**134**, **135**, **136**, **141**) due to a d^{10} configuration lacking a low-energy LUMO with a$_1$ symmetry that could be used to form the important σ-bond to a carbene carbon.[51] An X-ray crystal structure analysis of **134** has been reported: the Pt atom is asymmetrically bonded with C and P atoms.[81] Distance Pt–C$_1$ is shorter than Pt–C$_2$, with C$_1$ exerting a slightly stronger *trans*-influence than C$_2$ due to higher electronegativity owing to an extra π-bond around it. The Pt atom lies in the plane of coordination that forms an angle of 131.5° with the planes of the allene moiety C$_1$–C$_2$–C$_3$–C$_7$.[82] The molecule shows no fluxionality at room temperature. As determined by spin saturation transfer experiments, an activation enthalpy of 26.8 kcal/mol is required for the platinum to move between the double bonds (C$_1$–C$_2$/C$_2$–C$_3$) following an intermolecular mechanism superimposed on a lower-energy intramolecular process. It is also the minimum enthalpy for the conversion of **134** into its valence isomeric carbene form.[33] An acceleration of the fluxional process was observed after addition of a η^6-bonded Mo(CO)$_3$ moiety to the heptatriene array as in **141** with simultaneous movement of Pt and Mo(CO)$_3$ along the allene double bonds and the heptatriene system, respectively, at 20 °C.[83] Mono- and dibenzanellated cycloheptatetraenes do not differ from the parent ring in forming the allene complexes **135** and **136** with Pt(0); their structure has not been resolved by X-ray analysis but has been sufficiently elucidated by spectroscopic methods.[50] Due to MO calculations, benzannelation at the C$_7$H$_6$ ring should increase the separation between the allene and the carbene form.[32] Correspondingly, by rearrangement of a metastable dibenzonorcaradiene complex of tungsten, the tungsten–dibenzocycloheptatetraene complex **109** is formed and not the alternative cycloheptatrienylidene complex (Scheme 23, section 2.2.8).[52] The allene complex structure of **109** was confirmed by single-crystal X-ray analysis. The molecule appears in a pseudotetragonal pyramidal configuration. Its metal–allene array is quite similar to that of the **platinum** cycloheptatetraene complex **134** and to that of an cycloheptatrienylidene **iron** complex.[34]

3.2.2. Carbene Complexes

Among all other complexes of W, Fe, Ru, Pd, Pt(II), and Ir with C$_7$H$_6$ ligands and their benzannelated analogues hitherto described, the carbene structure (CHT) of the carbocyclic ligand is preferred. This has been confirmed by X-ray crystal structure analysis for several typical examples of such complexes (**112**, **114**, **123**, **130**, **133**, and **134**). In no case have examples been observed of conversions from an allene-type C$_7$H$_6$ complex to the isomeric carbene complex and reverse. Aromaticity of the tropylium resonance form in the seven-membered ring and low-lying vacant orbitals on the metal atoms are important features that enable the formation of a σ-bond to the carbene carbon in these complexes.[33] In this aspect, CHT complexes may be described also as substituted tropylium salts as elucidated in the following passages.

3.2.2.1. CHT Complexes of Group 6 and Group 7 Metals. The **tungsten** complex (C$_7$H$_6$)W(CO)$_5$ **108** is one of the first described CHT complexes. It could not be characterized by X-ray crystal analysis. The high dipole moment of 7.7 ± 0.2 D is conclusive evidence for a dipolar character due to substantial contribution from a resonance form with positive charge at the carbene ring, shown in Figure 3.

Table 2

Structure/ Number	Pd-C$_1$	C$_1$-C$_2$	C$_1$-C$_3$	C$_2$-C$_3$	Pd-Cl$_{trans}$	Pd-Cl$_{cis}$
 **70**	1.945(2)	1.377(4)	1.381(3)	1.363(3)	2.3444(8)	2.3620(8)
 **69**	1.931(4)	1.380(5)	1.366(5)	1.333(6)	2.3439(10)	2.3615(10)
 **78**	1.961(3)	1.385(5)	1.380(4)	1.384(5)	2.361(1)	2.385(1)

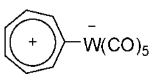


Figure 3.

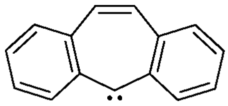


Figure 4.

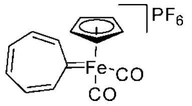


Figure 5.

Less metal−$C_{carbene}$ backbonding than in other pentacarbonyl tungsten carbene complexes is deduced by comparison of CO-stretching force constants.[11,16]

The pentacarbonyl−**chromium** complex **107**[41,42] and the cyclopentadienyl−dicarbonyl−**manganese** complexes **110** and **111**[40] with the dibenzannelated carbene, the complexed dibenzannelated carbene, shown below in Figure 4, may be formally considered as a CHT complex. The free carbene shows a triplet ground state[31] and reacts as an electrophilic carbene, in contrast to CHT. Correspondingly, this carbene with a nonplanar seven-membered central carbocycle[84,86] behaves as a diphenylcarbene ligand. The $C_{carbene}$ in complexes **107** and **110** exhibits an unprecedented downfield shift in ^{13}C NMR, which together with very high CO-stretching frequencies suggests strong metal−carbene back-bonding as in analogous diphenylcarbene complexes. The analogous metal complexes **289** and **290** with a $-CH_2-CH_2-$ backbone in the seven-membered ring of the tricyclic ligand show spectroscopic data (^{13}C NMR and IR) very similar to that of **107** and **110**, respectively, which is a hint that the ligand properties of the above-depicted dibenzannelated carbocyclic carbene do not primarily depend on the cycloheptatriene system.

3.2.2.2. CHT Complexes of Group 8 Metals. The structures of the cationic CHT−iron complexes **112** and **114**[34,87] have been resolved by X-ray analysis. In both pseudotetrahedral molecules, the CHT rings are planar—including the annelated benzene ring in **114**. The C−C distances in the C_7 rings do not differ significantly with mean values of 1.49 ± 0.03 Å (**112**) and 1.39 ± 0.02 Å (**114**). They are in agreement with the average C−C distances in the phenyltropylium ion (1.39 ± 0.08 Å). Moreover, the mean values for the internal angles of the seven-membered rings in **112** and **114** with 129 ± 3° and 129 ± 4°, respectively, are consistent with the idealized value 128.6° for a regular heptagon. These structural features indicate that aromaticity of the CHT rings in these complexes has been maintained and the carbene ligands principally act as σ-donors (Figure 5).

This structure is confirmed also by an appreciably highfield shift of the $C_{carbene}$ resonance in CHT complexes compared to most transition metal−carbene complexes: the incorporation of the carbene carbon into a tropylium ring should increase the separation of the σ-bond HOMO and the LUMO and delocalize the latter into the ring, which reduces the paramagnetic contribution to the chemical shift.[32] Nevertheless there is sufficient evidence from crystallographic (p-π-acceptor orbitals of CHT suitably oriented to backbond with filled 1a′d-π orbitals of Fe) and spectroscopic data that d π−p-π backbonding is not completely absent.[87] It is suggested as significant in the parent CHT complex **112** and less in the benzannelated analogue **114**.

Ruthenium complexes **118**, **119**, and **120** of the type $[(\eta^1\text{-CHT})(\eta^5\text{-}C_5H_5)Ru(CO)_2]^+$ have not been characterized by X-ray analysis.[32] But comparable ^1H and ^{13}C NMR data unequivocally confirm their nature as carbene σ-complexes, analogous to the above-mentioned **iron** complexes **112**, **113**, and **114**. The barrier of rotation about the metal−CHT bond in the phosphane-substituted ruthenium complex **121** was found to be less than that in the corresponding iron complex **115**, which is a hint that going from iron to ruthenium reduced steric constraint must be more important than increased backbonding.[32]

3.2.2.3. CHT Complexes of Group 9 Metals. A bis(phosphinomethyl) substituted CHT-pincer ligand is coordinated to **iridium** in complex **123**, and the solid-state structure has been deduced by X-ray analysis.[38] The geometry about the iridium center is best described as a distorted octahedron, with phosphane groups bent away from the chlorine ligand. As in all other hitherto known CHT complexes, the seven-membered ring is almost planar due to an aromatic 6π-electron arrangement delocalized over all seven ring carbon atoms. This delocalization is reflected by the C−C bond lengths in the cycle (mean value 1.40 ± 0.02 Å), whose distribution is in accordance with values obtained by density functional theory (DFT) calculations of a CHT fragment in the closed-shell singlet state.[79] The crystal structure data reveal a good match with those obtained by DFT quantum chemical calculations (B3LYP). Differences in the coordination geometry around the iridium center are attributed to packing effects in the crystalline state.[79]

3.2.2.4. CHT Complexes of Group 10 Metals. Structural data in the solid state are available for **palladium**−CHT complexes **127** and **130**.[15,43] Both compounds exhibit a square planar geometry in *cis*-configuration with nearly identical C−C bond lengths in the seven-membered ring (mean values 1.39 ± 0.01 Å), suggesting extensive 6π delocalization as observed in all CHT complexes mentioned in this article. The Pd−$C_{carbene}$ distances are in the range typical for analogous Pd−NHC complexes. A substantially lower π-acceptor character of the CHT ligand compared to cyclopropenylidene ligands, even to the strong donating 2,3-diaminocyclopropenylidene, is demonstrated by a considerably strengthened Pd−Cl_{trans} bond in **127** relative to the corresponding palladium−cyclopropenylidene complexes. Accordingly, as compared to the latter, **127** exhibits a slightly longer Pd−$C_{carbene}$ distance (1.986 vs 1.945 Å).[78]

Arguments for the preferred carbene structure of the cationic **platinum**−CHT complex **133** in solution are based on the absence of evidence of fluxionality at room temperature and the similarity of the ^1H and ^{13}C NMR spectra to those of the iron and ruthenium complexes **112** and **118**. Also notable is the significantly downfield-shifted $C_{carbene}$ resonance (δ 210.5 ppm) compared to that of the central carbon of an allene complex (e.g., δ 150.1 ppm for a 1,2-cycloheptadiene−iron complex). An orbital interaction diagram exhibits good overlap between the $2a_1$ LUMO of Pt(II) and the a_1 HOMO of the carbene. The coupling constant, $^1J_{Pt-C}$ of $C_{carbene}$ (969 Hz) is comparable with those of other Pt(II) carbene complexes.[33] In the solid state, the complex has square planar geometry with phosphanes *trans* to each other and a planar CHT ligand, almost perpendicular to the coordination plane. Dependent on the solvent, it crystallizes

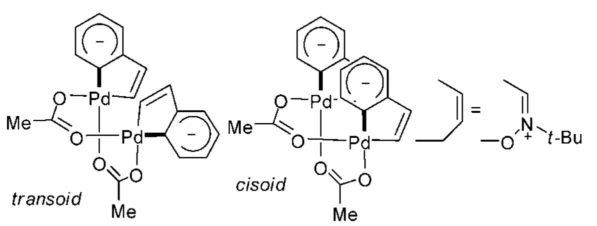


Figure 6.

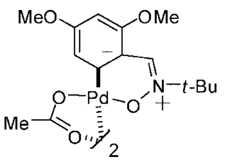


Figure 7.

either in the monoclinic or in the orthorhombic crystal system. While Pt−$C_{carbene}$ distances in both systems are in good agreement with each other, there are significant differences between the Br−Pt−$C_{carbene}$ angles and the position of the CHT plane relative to the coordination plane.[33]

The **palladium** complexes **131** and **132** with a six-membered congener of CHT as ligand exist in solution as a mixture of two diastereoisomers of the dinuclear molecule, with the C-2 symmetric *transoid* form as the major isomer shown below (Figure 6).

Complex **132** crystallizes as a single diastereoisomer in the *transoid* form. The nitrogen atom adopt a nearly planar geometry. Bond lengths at the benzylic carbon (C—C = 1.44 Å, C═N = 1.29 Å) and bond distances in the benzene ring are highly indicative of a zwitterionic iminium resonance form as depicted in Scheme 20, section 2.2.6 with a major contribution of structure shown in Figure 7.[49]

3.2.2.5. Heterobimetallic CHT Complexes. The heterobimetallic CHT−**iron** complex **117** with η^7-coordinated seven-membered ring to a $Cr(CO)_3$ unit exhibits in the crystalline state the same coordination geometry around Fe as the parent monometallic complex **112**. The CHT plane is almost perpendicular to the plane defined by $C_{carbene}$, Fe, and the centroid of the Cp ring. The $Cr(CO)_3$ fragment is located in "*trans*-position" relative to the Cp ligand. The Fe−$C_{carbene}$ bond and the C−C distances of the seven-membered ring are only slightly longer (mean values 1.42 ± 0.02 Å) than in the parent monometallic complex.[36] The ^1H NMR C_5H_5 resonance of **117** is observed at substancially higher field (δ 5.14 ppm) than that of **112** (δ 5.50 ppm), indicating that (η^7-CHT)$Cr(CO)_3$ is a weaker π-acceptor than cycloheptatrienylidene and that the canonical tropylium form of the CHT ligand contributes more strongly to the electronic structure of **117** compared to **112**.[35]

The structure of the heterobimetallic CHT-pincer complex of **iridium 124**, in which the seven-membered CHT system coordinates to a $Mo(CO)_3$ fragment, could be confirmed just spectroscopically due to ready decomposition. In comparison to the parent monometallic complex **123**, the number of resonances in the NMR spectra remains unchanged, but as observed at the above-mentioned iron complex **117**, the ^1H and the ^{13}C NMR resonances are significantly shifted to higher field—most dramatically for the metal-bonded ring carbon atom by 84 ppm—due to coordination of the $Mo(CO)_3$ moiety to the CHT ring. Structural data derived from DFT calculations indicate an absolutely planar seven-membered ring; almost equal C−C bonds (1.400−1.452 Å) reflect charge delocalization within the aromatic ring system. These bonds are elongated by the coordination of the $Mo(CO)_3$ fragment compared to those in the monometallic complex **123** (1.368−1.430 Å).[38]

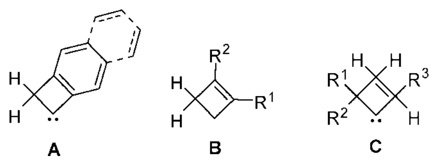


Figure 8.

The heterobimetallic C_7H_6−**platinum** complexes **137**, **138**, **139**, based on silicon-bridged *ansa*-cycloheptatrienyl−cyclopentadienyl complexes of titanium, vanadium, and **chromium**,[47,48] are all isotypic, crystallizing in an orthorhombic system. The platinum centers are in a slightly distorted planar environment with a significant longer Pt−P distance *trans* to silicium than that of Pt−P *trans* to C_7H_6 (e.g., in **137**, 2.3874 vs 2.2962 Å), resulting from the strong *trans*-influence of the silyl groups compared to the η^1-C_7H_6 ligand.

The Pt−C distances of all three complexes are distinctly longer (2.096(3) to 2.087(4) Å) than the Pt−$C_{carbene}$ distance in the monometallic CHT−Pt(II) complex **133** (1.99(1) to 2.03(2) Å, respectively). The shapes of the seven-membered rings (C−C distances, angles) in the heterobimetallic complexes **137** and **138** and in the parent compound [$Me_2Si(\eta$-$C_7H_6)Ti(\eta$-$C_5H_4)$] are almost identical.

An X-ray analysis of the germanium-bridged heterobimetallic platinum complex **140** was not reported, but the similarity of its structure to that of the silicon-bridged congener **137** could be confirmed by multinuclear NMR spectroscopy and mass spectrometry.[89]

On the basis of theoretical calculations, the seven-membered ring in group 4 cycloheptatrienyl−cyclopentadienyl sandwich complexes has to be regarded as a $[\eta^7$-$C_7H_7]^{3-}$ trianion with a 10-electron π-system.[89] Therefore, it is uncertain if the Pt−C_7H_6 bond in platinasilatroticenophane **137** and its congeners is comparable to metal−CHT bonds in the above-mentioned heterobimetallic complexes with a neutral $M(CO)_3$ group attached to a η^1-metal coordinated cycloheptatrienylidene ligand. A satisfactory answer to this question presumalbly should be given by theoretical calculations.

3.3. Complexes with Nonaromatic Carbocyclic Carbenes

3.3.1. Four-Membered Ring Systems

Cationic iron complexes **142** and **143** with benzo and naphthocyclobutenylidene (**A**) reported by Giering et al. in 1973[90,91] and 1976[92] were the first isolated carbene complexes that lack stabilization by heteroatoms as well as by an aromatic π-electron system (Figure 8). The existence of a real carbene complex was proven by ^1H NMR experiments and reactivity studies. Later on, the potential of the nonbenzannelated cyclobutenylidene ligands (**B**) to form bridged dinuclear complexes ($R^2 = ML_n$), **144**, **145**, and **146**, was realized independently by Davison and Solar[68] and Kolobova et al.[69]

The first isolation of two stable mononuclear cyclobutenylidene complexes (**147**, **148**) with a nonbenzannelated cyclobutadienylidene ligand (**B**) achieved by Bauer and Härter in 1991[65] was of special interest because these species were and still are intensively discussed as [2 + 2]-cycloaddition intermediates (for example, see refs 94−96). In the solid state, the cyclic carbene ligand is coordinated to the Fe center with a distance of 1.85(3) Å, which is in the range of typical electrophilic carbenes of the type $[Cp(CO)LFe{=}CX_2]^+$ ($X = F, Cl$).[96] Moreover, the downfield shift of the carbene carbon signal (δ 322.1 ppm) underlines the Schrock character of this complex. Stabilization is achieved by π-donation of the almost coplanar (7.5°) phenyl substituent to the cyclobutenylidene moiety.

Ongoing accounts in the chemistry of substituted mono-, di-, tri-, and tetranuclear cyclobuocomplexes—almost exclusively achieved by the group of Fischer—resulted in an enormous structural variety as well as interesting structure−property relationships (nonlinear optical properties, push−pull systems) whose discussion is beyond the scope of this review (see Tables 3−5 for references and further details).

An exceptional example for a rhenium complex with a 1,3-dimetalated cyclic C_4H_3 species was reported by Gladysz et al.[70] The ^{13}C NMR Re−carbene resonance (δ 227.5 ppm) of the *meso* compound **240** was observed in between the chemical shift of well-known comparable alkenyl ($\delta < 150$ ppm) and alkylidene as well as vinylidene ($\delta > 280$ ppm) complexes. X-ray analysis revealed an essentially planar Re−cC_4H_3−Re unit with metal−carbene bond lengths of 2.00(1) and 2.03(1) Å. The rhenium−rhenium distance was 6.1025(6) Å. Protonation of complex **240** with $HBF_4\cdot Et_2O$ on NMR scale resulted in the formation of a novel dicationic, dinuclear C_4H_4 dicarbene complex **242** with a ligand formally derived from cyclobutane that could be unequivocally characterized by ^1H, ^{13}C, ^{31}P NMR and mass spectrometry. However, attempts at isolation failed. To the best of our knowledge, this is the only example for the existence of a cyclobuta-1,3-diylidene transition metal complex to date. Regarding mononuclear complexes, a formally unsaturated cyclobutylidene motif (**C**) could only be obtained for a few highly sophisticated ruthenium complexes **243**−**245**.[97−99]

3.3.2. Five-Membered Ring Systems

Complexes of five-membered carbocyclic carbenes could be isolated either for the mono- (indenylidene, **A**) and the dibenzannelated (fluorenylidene, **B**) congeners or for the tricyclic $C_{10}H_8$ dicarbene (**C**) (Figure 9).

The latter carbene (**C**) was observed as a ligand in dinuclear manganese complexes when Herrmann et al. attempted the preparation of a cyclopentadienylidene complex by metal-induced fragmentation of diazocyclopentadiene.[100] Surprisingly, because of [2 + 2]-cycloaddition, centrosymmetric dicarbene complexes were formed connected by a planar annelated four-membered ring. The remarkably high thermal stability of the complexes **283** and **284** was explained by conjugation of the Mn−C bonds (1.878(8) Å) with the vinylic double bonds of the bridging ligand system.

Only a few metal carbene complexes of the fluorenylidene ligand (**B**) have been reported to date. The first example was the rather stable Pd(0) complex **282** with a melting point at 135−140 °C. Unfortunately, besides IR data and elemental analysis, no further characterization was employed.[101] In contrast, the chromium pentacarbonyl congener reported by Dötz is thermally unstable (dec > −20 °C).[41,42] Its NMR resonance of the metal-bonded carbon atom appears in the region of other "Schrock-type" carbene complexes but is upfield-shifted (361.29 ppm vs 399.4 ppm) relative to that of the analogous diphenyl carbene complex $[(CO)_5(Ph_2C)Cr(0)]$. This was explained by an optimal overlap of the arene π-orbital and the p-orbital at the carbene carbon atom in the rigid, almost-planar fluorenylidene scaffold. Very recently Milstein and co-workers found that the neutral fluorenylidene ruthenium complex **278** stabilized by a *t*-Bu-PNP pincer ligand (Ru−$C_{carbene}$ 1.936(9) Å) could be easily converted into the cationic **16e** derivative via chloride dissociation either on heating or on treatment with HBF_4 or $AgBF_4$, respectively. With the change from a distorted octahedral to distorted square-pyramidal geometry came along a significant upfield shift of the carbene carbon signal ($\Delta \approx 17$ ppm) as well as shortening of the Ru−$C_{carbene}$ bond length (1.877(5) Å). This observation was explained by a larger *trans* effect of the carbene relative to chloride.[55]

The vast majority of the five-membered carbocyclic carbene complexes known to date bear a monobenzannelated 3-phenylindenylidene ligand (**A**) bound to ruthenium. This might be due to systematic structural variations in the course of their utilization as metathesis catalysts (see section 5.3). However, only a few of them are fully characterized, and the lack of analytical data still precludes the observation of general trends. Carbene carbon NMR shifts differ significantly depending on the other ligands attached to the ruthenium metal center and on the overall complex geometry. The lowest shift in this series was reported so far for the Schiff base derivative **268** (290.6 ppm)[144] in contrast to the highest known shift of an indenylidene carbon for the cationic *p*-cymene derivative **274** (336.1 ppm).[63] X-ray analysis could be performed for four examples. In indenylidene−bisphosphane complexes, *trans* conformation could be confirmed for the phobane congener **256**.[103] Unfortunately, detailed discussion was not possible because of a relatively high *R*-factor. A comparison of the carbene bond lengths in the indenylidene−NHC complex **261** revealed the imidazolylidene as clearly weaker π-acid. The NHC bond (2.113(4) Å) is by ca. 0.25 Å significantly longer than the Ru−C distance to the carbocyclic carbene (1.861(4) Å).[104] Similar effects occur in complex **264**.[106] Electronic features of the carbocyclic moiety, i.e., degree of delocalization, remain unclear. Although in the solid-state structure of **261** the indenylidene ring system appears in an almost ideal planar form, bond distances differ significantly but do not alter in the way it is suggested in the structural formula. However, complete π-delocalization can be precluded. Additionally, the phenyl substituent attached at 3-position is distorted out of the indenylidene plane by 145°, presumably not contributing to π-delocalization.

3.3.3. Six and Seven-Membered Ring Systems

Carbene complexes of six- and seven-membered nonaromatic carbocycles are rare. To our best knowledge, a cyclohexenylidene motif (**A**) (Figure 10) only occurs in the cationic ruthenium complex **285** and its alkoxy derivatives **286**, **287**, and **288** reported by Lin in 2007 (Figure 10).[107] The X-ray solid-state structure of complex **285** revealed a rather long Ru−$C_{carbene}$ bond distance of 1.957(4) Å. Additionally, a shortened $C_{carbene}$−C_α distance was observed, suggesting conjugation of the ruthenium−carbene bond with the vinylic double bond.

The 5(5*H*)-dibenzo[*a*,*d*]cycloheptylidene ligand (**B**) can be regarded as a diphenyl carbene analogue with a limited overlap of the arene π-orbital and the p-orbital at the carbene carbon atom due to nonplanarity. Early contributions of Herrmann[40,108] elucidate the properties of two stable man-

Table 3.

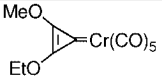
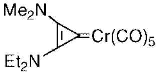
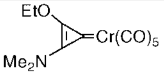
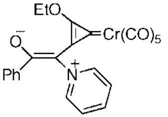
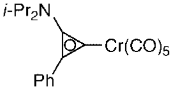
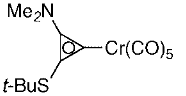
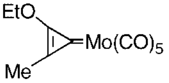
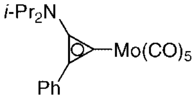
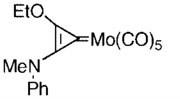
Compound	number	M-$C_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
$((i\text{-PrC})_2C)Cr(CO)_5$	**1**	-	2.1.1	plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
$((PhC)_2C)Cr(CO)_5$	**2**	2.05±0.01	2.1.1 (19)	plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands; mp (°C) 199-200; IR (C_6H_{12}) ν_{CO} 2061, 1938 cm^{-1}; UV/Vis; MS.	8,14,72
$((PhC)_2C)Cr(CO)_2(C_6H_6)$	**3**	-	2.1.1	IR (THF) ν_{CO} 1895, 1840 cm^{-1}.	120
$((PhC)_2C)Cr(CO)_2(Mes)$	**4**	1.956(4)	2.1.1 (44)	dark red crystals; mp (°C) 58 (dec.); IR (toluol) ν_{CO} 1887, 1836 cm^{-1}; ^1H, $^{13}C_{carbene}$ 252.0 ppm; MS; EA (CH).	120
$((PhC)_2C)Cr(CO)_2(C_6(CH_3)_6)$	**5**	-	2.1.1	IR ν_{CO} 1868, 1815 cm^{-1}, ^1H, $^{13}C_{carbene}$ 253.6 ppm.	120
$((EtOC)_2C)Cr(CO)_5$	**6**	2.010(7)	2.1.2 (84)	white solid; mp (°C) 62-64; IR ν_{CO} :2055, 1960, 1915, 1873 cm^{-1}; $^{13}C_{carbene}$ 191.74 ppm; EA (CH).	20
	**7**	-	2.1.2 (58)	cream solid; mp (°C) 51.5-52.5; IR (film) ν_{CO} 2045, 1972, 1960, 1925, 1867 cm^{-1}; $^{13}C_{carbene}$ 191.65 ppm; EA (CH).	20
$((Me_2NC)_2C)Cr(CO)_5$	**8**	-	4.1.2 (98)	pale yellow crystals; plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands; mp (°C) 128 (dec.); IR (KBr) ν_{CO} 2051, 1913 cm^{-1}; MS, EA(CHN).	14,110
$((i\text{-}Pr_2N)_2C)Cr(CO)_5$	**9**	-	2.1.3 (32)	air stable yellow solid; IR (KBr) 2052, 1930, 1907, 1874 cm^{-1}; $^{13}C_{carbene}$ 151.1 ppm; EA (CHN).	73
	**10**	2.086(1)	4.1.2 (99)	pale yellow crystals; mp (°C) 85; IR (KBr) ν_{CO} 2051, 1909 cm^{-1}; MS; EA (CHN).	110
	**11**	2.068(2)	2.1.2 (38)	pale yellow crystals; mp(°C) 38; IR (KBr) ν_{CO} 2056, 1917 cm^{-1}; MS; EA (CHN).	110
	**12**	-	4.1.2 (73)	bright yellow solid; mp (°C) 147 (dec.); IR (film) ν_{CO} 2052, 1912, 1898 cm^{-1}; EA (CHN).	20
	**13**	-	2.1.6	plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
$((t\text{-BuSC})_2C)Cr(CO)_5$	**14**	-	2.1.6	plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
	**15**	-	2.1.6	plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
$((MeC)_2C)Mo(CO)_5$	**16**	-	4.1.2 (36)	unstable white solid; IR (film) ν_{CO} 2049, 1911 cm^{-1}; $^{13}C_{carbene}$ 231.25 ppm.	20
$((i\text{-PrC})_2C)Mo(CO)_5$	**17**	-		plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
$((PhC)_2C)Mo(CO)_5$	**18**	-	(24)	yellow crystals; MS; EA (CH).	14,21,109
$((EtOC)_2C)Mo(CO)_5$	**19**	-	2.1.2 (86)	white solid; mp (°C) 53-54; IR(film) 2066, 1905, 1870 cm^{-1}; $^{13}C_{carbene}$ 183.12 ppm; EA (CH).	20
	**20**	-	4.1.2 (46)	unstable oily solid; IR(film) ν_{CO} 2050, 1913, 1860 cm^{-1}; $^{13}C_{carbene}$ 209.56 ppm.	20
$((Me_2NC)_2C)Mo(CO)_5$	**21**	-		plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
	**22**	-		plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
	**23**	-	2.1.2 (87)	pale cream crystals; mp (°C) 111.5-113; IR (film,) ν_{CO} 2054, 1966, 1904 cm^{-1}; $^{13}C_{carbene}$ 174.93 ppm; EA (CHN).	20

Table 3. (Continued)

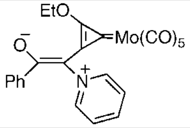
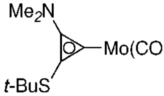
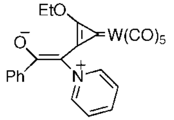
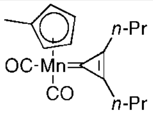
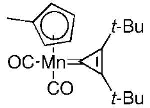
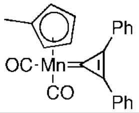
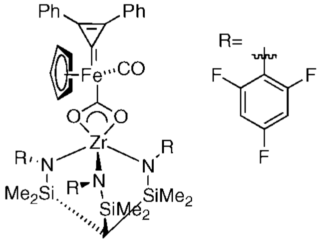
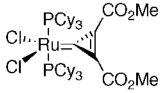
Compound	number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
	**24**	-	4.1.2 (63)	bright yellow solid; mp (°C) 144 (dec.); IR (nujol) ν_{CO} 2059, 1996, 1904, 1875 cm^{-1}; EA (CHN).	20
((*t*-BuSC)$_2$C)Mo(CO)$_5$	**25**	-		plot of frequencies of CO stretching E bands vs that of CO stretching A_{1a} bands	14
	**26**	-		plot of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands.	14
((*t*-BuC)$_2$C)W(CO)$_5$	**27**	-	2.1.1 (10)	pale yellow needles; mp (°C) 97.5-98.5; IR (C_6H_{12}) ν_{CO} 2066, 1969, 1932cm^{-1}; $^{13}C_{carbene}$ 211.3 ppm, $^{13}C_{COcis}$ 197.4 ppm, $^{13}C_{COtrans}$ 204.0 ppm; UV/Vis; dipole moment (C_6H_6): 7.71 D; EA (CH).	16,74
((PhC)$_2$C)W(CO)$_5$	**28**	-	2.1.1 (10)	bright yellow crystals; mp (°C) 215 (dec.); IR (KBr) ν_{CO} 2064, 1990, 1934 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 204 ppm, $^{13}C_{COcis}$ 197,2, $^{13}C_{COtrans}$ 206.1 ppm; dipole Moment (C_6H_6): 8.06 D; UV/Vis; EA (CH).	16
((EtOC)$_2$C)W(CO)$_5$	**29**	-	2.1.2 (93)	mp (°C) 58.5-59.5; IR (film) ν_{CO} 2063, 1897, 1868 cm^{-1}; $^{13}C_{carbene}$ 170.21; EA (CH).	20
((*i*-Pr$_2$NC)$_2$C)W(CO)$_5$	**30**	2.238(5)	2.1.3 (26)	yellow crystals; IR (KBr) ν_{CO} 2059, 1926, 1905, 1872 cm^{-1}; $^{13}C_{carbene}$ 136.7 ppm.	73
	**31**	-	4.1.2 (81)	bright yellow solid; mp (°C) 160-163; IR (film) ν_{CO} 2050, 1902 cm^{-1}; EA (CHN).	20
	**32**	-	2.1.1 (41)	orange red oil; EA (CH).	18
	**33**	-	2.1.1 (38)	yellow solid; ^{1}H; EA (CH).	18
	**34**	1.896(4)	2.1.1 (24)	red solid; mp (°C) 131; IR (toluene) ν_{CO} 1935, 1868 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 233.5ppm; EA (CH).	18,19
[((PhC)$_2$C)Mn(CO)$_5$]BF$_4$	**35**	-	2.1.3 (59)	mp (°C) 170; IR (CH_2Cl_2) ν_{CO} 2135, 2080, 2035, 1594, 1367, 1328, 1304, 1282 cm^{-1}; MS; EA (CH).	121
[((Et$_2$NC)$_2$C)Mn(CO)$_5$]ClO$_4$	**36**	-	2.1.3 (52)	mp (°C) 126-128 (dec.); IR (CH_2Cl_2) ν_{CO} 2130, 2075, 2025, 1885, 1540, 1294 cm^{-1}; MS; EA (CHN).	121
((PhC)$_2$C)Fe(CO)$_3$(PPh$_3$)	**37**	-	2.1.1 (22)	mp (°C) 85; IR (toluene) ν_{CO} 1888 cm^{-1}; $^{13}C_{carbene}$ 219.4 ppm; EA (CH).	19
((Et$_2$NC)$_2$C)Fe(CO)$_4$	**38**	-	2.1.3 (45)	mp (°C) 48; IR (CH_2Cl_2) ν_{CO} 2035, 1945, 1872, 1510, 1289 cm^{-1}; MS; EA (CHN).	121
	**39**	-	2.1.6 (45)	crystaline yellow solid; IR (benzene) ν_{CO} 1953 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 259.0 ppm, ^{17}O, ^{19}F, ^{29}Si; EA (CHN).	29
[((PhC)$_2$C)Fe(CO)$_2$(Cp)]BF$_4$	**40**	-	2.1.3(53)		121
	**41**	1.846(10)	2.1.7	blue-purple; ^{1}H, $^{13}C_{carbene}$ 195.7 ppm.	30

Table 3. (Continued)

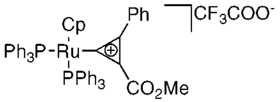
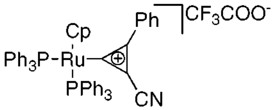
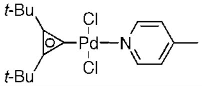
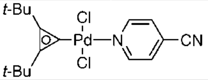
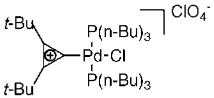
Compound	number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
	**42**	-	2.1.5 (92)	orange; ^1H, $^{13}C_{carbene}$ 213.6 ppm; MS-FAB; EA (CH).	28
	**43**	-	2.1.5 (78)	orange, sensitive to ether; ^1H, $^{13}C_{carbene}$ 213.0 ppm; MS-FAB; EA (CHN).	28
$[((i\text{-Pr}_2NC)_2C)Rh(CO)(Pn\text{-Bu}_3)_2]ClO_4$	**44**	-	2.1.3	yellow; mp (°C) 195; $^{13}C_{carbene}$ 147.0 ppm.	14
cis-$((i\text{-Pr}_2NC)_2C)RhCl(CO)_2$	**45**	-	2.1.4 (74)	mp (°C) 95; IR (CH_2Cl_2) ν_{CO} 2070, 1992 cm^{-1}; $^{13}C_{carbene}$ 141.2 ppm.	25
cis-$((i\text{-Pr}_2NC)_2C)RhCl(PPh_3)_2$	**46**	-	2.1.4	observed as an intermediate in the formation of the analogous trans complex; $^{13}C_{carbene}$ 138.2 ppm.	25
trans-$((i\text{-Pr}_2NC)_2C)RhCl(PPh_3)_2$	**47**	2.411(3)	2.1.4 (91)	orange; mp (°C) 218 (dec.); $^{13}C_{carbene}$ 139.8 ppm.	25
$[(i\text{-Pr}_2NC)_2C)_2Rh(COD)][(COD)RhCl_2]$	**48**	2.028(6)	2.1.4 (81)	blocky orange crystals; $^{13}C_{carbene}$ 149.8 ppm.	25
$[(i\text{-Pr}_2NC)_2C)_2Ni(COD)]$	**49**	-	2.1.4 (86)	orange; mp (°C) 121 (dec.); $^{13}C_{carbene}$ 176.8 ppm.	25
$[(i\text{-PrC})_2C)PdCl_2]_2$	**50**	-	2.1.1 (45)	orange; mp (°C) 164; $^{13}C_{carbene}$ 181.2 ppm; EA (CHN).	75
$[(i\text{-PrC})_2C)PdBr_2]_2$	**51**	-	4.1.3 (95)	orange; mp (°C) 172; EA (CH).	75
$[(t\text{-BuC})_2C)PdCl_2]_2$	**52**	-	2.1.1 (60)	orange; mp (°C) 233 (dec.); $^{13}C_{carbene}$ 183.1 ppm; EA (CH).	75,76
$[(PhC)_2C)PdCl_2]_2$	**53**	-	2.1.1 (51)	yellow powder; $^{13}C_{carbene}$ 174 ppm; EA (CHPd).	12,78
$[(MesC)_2C)PdCl_2]_2$	**54**	monoclinic (a)1.919(4) (b) 1.908(4) 1.921(4) triclinic 1.907 (7) 1.910(7)	2.1.1 (68)	yellow-orange powder; $^{13}C_{carbene}$ 182.9 ppm; EA (CHPd).	78
$[(NapC)_2C)PdCl_2]_2$	**55**	-	2.1.1 (34)	yellow powder; $^{13}C_{carbene}$ not observed; EA (CHPd).	78
$[(Me_2NC)_2C)PdCl_2]_2$	**56**	-	2.1.1 (44)	red/orange crystals; mp (°C) 210 (dec.); IR; UV/Vis; EA (CHN).	77
$[(i\text{-Pr}_2NC)_2C)PdCl_2]_2$	**57**	-	2.1.1 (44)	reddish brown; mp (°C) 240 (dec.); IR (KBr) 1856, 1500 cm^{-1}.	13,76
$[(i\text{-Pr}_2NC)_2C)PdI_2]_2$	**58**	-	2.1.1 (55)	reddish brown; mp (°C) 264 (dec.); IR (KBr) 1853, 1496 cm^{-1}; EA (CHN).	13
$((i\text{-PrC})_2C)PdCl_2(Pn\text{-Bu}_3)$	**59**	-	2.1.1 (69)	colorless; mp (°C) 153; $^{13}C_{carbene}$ 205.7 ppm; EA (CH).	14,75
$[$*trans*-$(i\text{-Pr}_2C)_2C)PdCl(Pn\text{-Bu}_3)_2]ClO_4$	**60**	-	2.1.1 in $HClO_{4\,(aq)}$	colorless; mp (°C) 151; $^{13}C_{carbene}$ 205.4 ppm.	14,75
$((t\text{-BuC})_2C)PdCl_2(Pn\text{-Bu}_3)$	**61**	-	2.1.1 (75)	colorless; mp (°C) 153 (dec.); $^{13}C_{carbene}$ 205.2 ppm; EA (CH).	14,75
$((t\text{-BuC})_2C)PdCl_2(NCCH_3)$	**62**	-	2.1.1 (75)	orange; mp (°C) 183 (dec.); EA (CHN).	75
$((t\text{-BuC})_2C)PdCl_2(Py)$	**63**	-	2.1.1 (82)	yellow; mp (°C) 82/150; IR (nujol) ν 1604, 1345, 346, 328 cm^{-1}; ^1H; EA(CHN)	75,76
	**64**	-	2.1.1	mp (°C) 147-148; IR (nujol) ν 1618, 1350 cm^{-1}; ^1H; EA (CHClN).	76
	**65**	-	2.1.1	mp (°C) 128-129; IR(nujol) ν 2230, 1612, 1344, 348, 330 cm^{-1}; ^1H; EA (CHClN).	76
$((t\text{-BuC})_2C)PdCl_2(OS(CH_3)_2)$	**66**	-	2.1.1 (67)	yellow; mp (°C) 202 (dec.); EA (CH).	75
	**67**	-	2.1.1 in $HClO_{4\,(aq)}$ (68)	colorless; mp (°C) 164; $^{13}C_{carbene}$ 205.8 ppm; EA (CH).	14,75
$((PhC)_2C)PdCl_2(Pn\text{-Bu}_3)$	**68**	-	2.2.1	$^{13}C_{carbene}$ 195.3 ppm.	14
cis-$((PhC)_2C)PdCl_2(PCy_3)$	**69**	1.931(4)	2.1.1 (93)	yellow powder; mp (°C) 205 (dec.); $^{13}C_{carbene}$ 197.7 ppm; ^{31}P; MS-FAB; EA (CHPd).	7,78

Table 3. (Continued)

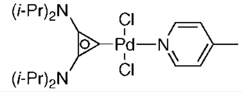
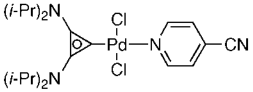
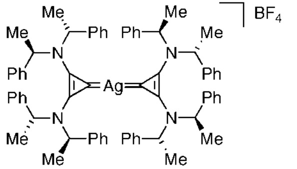
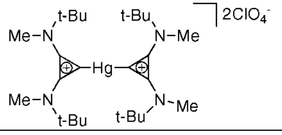
Compound	number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
cis-((PhC)$_2$C)PdCl$_2$(PPh$_3$)	**70**	1.945(2)	2.1.1 (91)	yellow powder; mp (°C) 185 (dec.); ^{13}C$_{carbene}$ 196.1 ppm, ^{31}P; MS-FAB; EA (CHPd).	7,78,117,118
((PhC)$_2$C)PdCl$_2$(OEt)	**71**	-	2.1.1	no details	7
((PhC)$_2$C)PdCl$_2$(OS(CH$_3$)$_2$)	**72**	-	2.1.1	no details	7
((PhC)$_2$C)PdCl$_2$(CNCH$_3$)	**73**	-	2.1.1	no details	7
((PhC)$_2$C)PdCl$_2$(Py)	**74**	-	2.1.1	no details	7
[*trans*-(Ph$_2$C)$_2$C)PdCl(P*n*-Bu$_3$)$_2$]ClO$_4$	**75**	-	2.1.1 in HClO$_{4(aq)}$	^{13}C$_{carbene}$ 195.2 ppm; EA (CH).	14,75
cis and *trans*–((MesC)$_2$C)PdCl$_2$(PCy$_3$)	**76**	-	2.1.1 (93)	yellowish powder, 2 isomers; mp (°C) 200 (dec.); ^{13}C$_{carbene}$ 209.2 ppm (trans), ^{13}C$_{carbene}$ 202.4 ppm (cis), ^{31}P; MS-FAB	14,75
cis-((NapC)$_2$C)PdCl$_2$(PCy$_3$)	**77**	-	2.1.1 (81)	yellow green microcrystaline powder; mp (°C) 205 (dec.); ^{13}C$_{carbene}$ 200.3 ppm, ^{31}P; MS-FAB	78
cis-((Me$_2$NC)$_2$C)PdCl$_2$(P*n*-Bu$_3$)	**78**	1.961(3)	2.1.1 (85)	white crystals; mp (°C) 172; IR (KBr) ν 2960, 2935, 2875, 1903, 1557, 1419, 1409, 1378, 1211 cm^{-1}; ^{13}C$_{carbene}$ 125 ppm; UV/Vis; EA (CHN).	14,77
[*trans*-(Me$_2$NC)$_2$C)PdCl(P*n*-Bu$_3$)$_2$]ClO$_4$	**79**	-	2.1.1 in HClO$_{4\,(aq)}$	^{13}C$_{carbene}$ 122.0 ppm; EA (CHN).	14,75
[*trans*-(Et$_2$NC)$_2$C)PdCl(P*n*-Bu$_3$)$_2$]ClO$_4$	**80**	-	2.1.1 in HClO$_{4\,(aq)}$	white; mp (°C) 78; ^{13}C$_{carbene}$ 122.0 ppm; EA (CHN).	14,75
cis-(*i*-Pr$_2$NC)$_2$C)PdCl$_2$(P*n*-Bu$_3$)	**81**	-	2.1.1 (78)	orange/white; mp (°C) 208; IR (KBr) ν 1858, 1487 cm^{-1}; ^{13}C$_{carbene}$ 128.4 ppm; EA (CHN).	13,14
cis-(*i*-Pr$_2$NC)$_2$C)PdI$_2$(P*n*-Bu$_3$)	**82**	-	2.1.1 (60)	orange; mp (°C) 145; IR (KBr) ν 1848, 1486 cm^{-1}; EA (CHN).	13
[*trans*-(*i*-Pr$_2$NC)$_2$C)PdCl(P*n*-Bu$_3$)$_2$]ClO$_4$	**83**	-	2.1.3 (67)	colorless/white; mp (°C) 120; IR (KBr) ν_{CO} 1855, 1492 cm^{-1}; ^{13}C$_{carbene}$ 125.6 ppm; EA (CHN).	13,14
[*trans*-(*i*-Pr$_2$NC)$_2$C)PdBr(P*n*-Bu$_3$)$_2$]ClO$_4$	**84**	-	2.1.3 (53)	colorless; mp (°C) 220 (dec.); IR (KBr) ν_{CO} 1855, 1495 cm^{-1}; EA (CHN).	13
[*trans*-(*i*-Pr$_2$NC)$_2$C)PdI(P*n*-Bu$_3$)$_2$]ClO$_4$	**85**	-	2.1.3 (49)	colorless; mp (°C) 210 (dec.); IR (KBr) ν 1850, 1492 cm^{-1}; EA (CHN).	13
trans-(*i*-Pr$_2$NC)$_2$C)PdCl$_2$Py	**86**	-	2.1.1	mp (°C) 276 (dec.); IR (KBr), FIR (nujol) ν 1851, 1500,1332, 337, cm^{-1}; ^{1}H; EA (CHClN).	76
	**87**	-	2.1.1	mp (°C) 276 (dec.); IR (KBr), FIR (nujol) ν 1853, 1498, 1328 cm^{-1}; ^{1}H; EA (CHClN).	76
	**88**	-	2.1.1	mp (°C) 274 (dec.); IR (KBr), FIR (nujol) ν 2225, 1848, 1498, 1322, 330, cm^{-1}, ^{1}H; EA (CHClN).	76
cis-[*i*-Pr$_2$NC)$_2$C]$_2$PdMe$_2$	**89**	-	2.1.4 (89)	mp(°C): 107 (dec), X-ray, colorless blocky crystals, ^{13}C$_{carbene}$:165.5 ppm, TOF HRMS	25
[(*i*-Pr$_2$NC)$_2$C)PtI$_2$]$_2$	**90**	-	2.1.1 (18)	reddish brown; mp (°C) 226 (dec); IR (KBr) ν_{CO} 1846, 1484 cm^{-1}; EA (CHN).	13
cis-[(*t*-BuC)$_2$C]$_2$PtCl$_2$	**91**	-	2.1.1 (33)	white crystals; mp (°C) 263 (dec.); IR (KBr) ν_{CO} 2950, 1474, 1370, 1330, 1230, 1176 cm^{-1}; ^{13}C$_{carbene}$ 178.8 ppm; EA (CHCl).	122
cis-[(*t*-BuC)$_2$C]$_2$PtCl$_4$	**92**	-	2.1.1 (19)	yellow crystals; mp (°C) 218 (dec.); IR(KBr)ν_{CO}:2950,1480, 1328,1226, 1220 cm^{-1}; ^{13}C$_{carbene}$ 166.6 ppm; EA (CHCl).	122
cis-(*t*-BuC)$_2$C)PtCl$_2$(PBu$_3$)	**93**	-	2.1.1 (22)	white crystals; mp (°C) 147; IR (KBr) ν_{CO}1960, 2925, 2875, 1485, 1466 cm^{-1}; ^{13}C$_{carbene}$ 192.5 ppm; EA (CHPCl).	122
trans-[*i*-Pr$_2$NC)$_2$C]$_2$PtCl$_2$	**94**	-	2.1.3 (4)	white crystals; mp (°C) >300 (dec.); IR(KBr)ν_{CO}:2975, 2935, 2880, 1854, 1490, 1467, 1378,1337 cm^{-1}; ^{13}C$_{carbene}$ 136.0; EA (CHNCl).	122
cis-[(*i*-Pr$_2$NC)$_2$C]$_2$PtI$_2$	**95**	-	2.1.3 (>20)	yellow crystals; mp (°C) >300 (dec.); IR (KBr) ν_{CO} 2950, 1840, 1328,1160 cm^{-1}; EA (CHNI).	122
trans-[(*i*-Pr$_2$NC)$_2$C]$_2$PtI$_2$	**96**	-	2.1.1 (>20)	yellow crystals; mp (°C) >300 (dec.); IR (KBr) ν_{CO} 2950, 1840, 1328,1160 cm^{-1}; ^{13}C$_{carbene}$ 131.8 ppm; EA (CHNI).	122

Table 3. (Continued)

Compound	number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
[*trans*-(*t*-BuC)$_2$C)PtCl(PBu$_3$)$_2$]ClO$_4$	**97**	-	2.1.1 + KClO$_4$ (66)	IR (KBr) ν_{CO} 2960, 2925, 2875, 1480, 1467 cm^{-1}; ^{13}C$_{carbene}$ 194.98 ppm; EA (CHNP).	122
[*trans*-(*i*-Pr$_2$NC)$_2$C)PtCl(P*n*-Bu$_3$)$_2$]ClO$_4$	**98**	-	2.1.3 (55)	colorless/ white; mp (°C) 225; IR (KBr) ν_{CO} 1862, 1494 cm^{-1}; EA (CHN).	13,14
[*trans*-(*i*-Pr$_2$NC)$_2$C)PtBr(P*n*-Bu$_3$)$_2$]ClO$_4$	**99**	-	2.1.3 (48)	colorless/ pale yellow; mp (°C) 247/154; IR (KBr) ν_{CO} 1856, 1490 cm^{-1}; EA (CHN).	13,14
[*trans*-(*i*-Pr$_2$NC)$_2$C)PtI(P*n*-Bu$_3$)$_2$]ClO$_4$	**100**	-	2.1.3 (46)	colorless; mp (°C) 255; IR (KBr) ν_{CO} 1855, 1490 cm^{-1}; EA (CHN).	13
	**101**	2.059(6)	2.1.3 (67)	^{13}C$_{carbene}$ 146.2 ppm.	22
	**102**	-	2.1.3 (60)	colorless crystals; mp (°C) 160 (dec.); ^{13}C$_{carbene}$ 137.3 ppm; EA (CHN).	23
[((*i*-Pr$_2$NC)$_2$C)$_2$Hg](ClO$_4$)$_2$	**103**	-	2.1.3 (75)	colorless crystals; mp (°C) 280; ^{13}C$_{carbene}$ 137.3 ppm; EA (CHN).	23
((*i*-Pr$_2$NC)$_2$C)Ge(N(SiMe$_3$)$_2$)$_2$	**104**	2.085(3)	2.1.3 (61)	yellow crystals; mp (°C) 125 (dec., 0.1 mbar); EA (CHN).	24
((*i*-Pr$_2$NC)$_2$C)Sn(N(SiMe$_3$)$_2$)$_2$	**105**	2.303(9)	2.1.3 (55)	yellow crystals; mp (°C) 137 (dec., 0.1 mbar); EA (CHN).	24
((*i*-Pr$_2$NC)$_2$C)Pb(N(SiMe$_3$)$_2$)$_2$	**106**	2.423(8)	2.1.3 (79)	yellow crystals; mp (°C) 135 (dec., 0.1 mbar); EA (CHN).	24

ganese complexes (**290**, **291**) bearing this ligand. X-ray analysis of compound **290** revealed a distortion angle of 54.5° for the two phenyl rings and a manganese−carbene bond length of 1.853(5) Å. Dötz observed for the highly sensitive chromium pentacarbonyl congener **289** with 419.14 ppm the so far largest downfield shift for metal-coordinated carbene carbon atoms.[42]

4. Properties and Reactions

4.1. Cyclopropenylidene Complexes

4.1.1. Ring Insertion to the Cyclopropenylidene Carbene Moiety

Rees and co-workers were the first to report ring-insertion reactions for cyclopropenylidene complexes.[21] By the addition of equimolar amounts of pyridinium ylides to diphenylcyclopropenylidene pentacarbonyl complexes, they were able to produce a series of chromium and molybdenum pyran-2-ylidene complexes (Scheme 35).[109]

A similar ring insertion was observed by Hegedus and co-workers with **6**, (diethoxycyclopropenylidene)Cr(CO)$_5$, which undergoes reaction with a pyridinium ylide, yielding a mixture of the corresponding pyran-2-ylidene complex as a minor product (23%) and a product resulting from displacement of an ethoxy group by the ylide moiety (Scheme 36).[20]

The different behavior of phenyl- and ethoxy-substituted cyclopropenylidene ligands in the reaction with pyridinium ylides is ascribed to the poor lability of a phenyl group relative to an ethoxy group.

4.1.2. Substitution of Ethoxy Groups Present in the Cyclopropenylidene Ligand

The substitution of functional groups bound to the carbene ring was explored by de Meijere and co-workers who showed that reaction of aminoalkoxycyclopropenylidene chromium complexes with dialkylamines gives dialkylamino-substituted cyclopropenylidene pentacarbonyl chromium complexes in excellent yields (Scheme 37).[110]

Divergent from Scheme 36, at the reaction of pentacarbonyl diethoxycyclopropenylidene complexes for all group 6 metals with pyridinium ylide at moderate conditions besides the ethoxy substitution, no formation of pyran-2-ylidene complexes is observed (Scheme 38).[20]

Substitution of one or both ethoxy groups for methyl groups in (diethoxycyclopropenylidene)Mo(CO)$_5$ by reaction with methyllithium (Scheme 39) was reportet by Hegedus and co-workers. The products were characterized by NMR and IR.[20]

4.1.3. Reactions at the Metal Center

Substitution of the halogen, after formation of the carbene complex, is possible. Chlorine could be replaced with bromine by the reaction of bimetallic chloro complexes with KBr in acetone (Scheme 40).[75]

4.1.4. Generation of Retrosynthetic Products in the Presence of an Electrophile

In the presence of an electrophile such as I$_2$, S$_8$, or H$^+$, cationic cyclopropenylidene mercury complexes, studied by

Table 4.

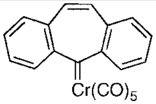
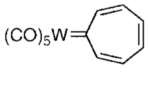
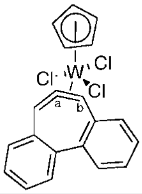
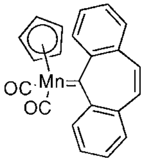
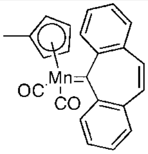
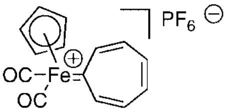
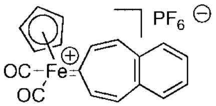
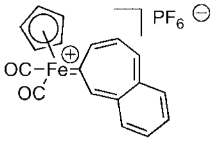
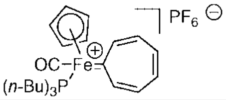
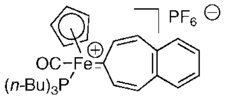
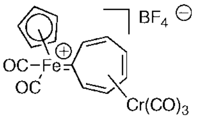
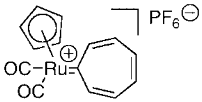
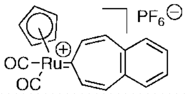
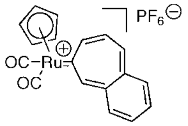
Compound	Number	M-$C_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
	**107**	-	2.2.3 (67)	black solid; dec. > -20 °C; IR (hexane) ν_{CO} 2068, 1987, 1958 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 404.24 ppm, $^{13}C_{COcis}$ 214.53 ppm, $^{13}C_{COtrans}$ 237.37 ppm; HR-MS.	41,42
	**108**	-	2.2.1 (15)	purple needles; mp (°C) 115-116 (dec.); IR (*n*-heptane) CO stretching force constant 15.72 (*trans*), 15.34 (*cis*) [mdyn/A], ^{1}H; UV/Vis; EA (CH); dipole moment (D) 7.7±0.2 (C_6H_6).	11,16
	**109**	a) 2.184(17) b) 2.265(20)	2.2.8 (59)	orange; mp (C°) 134-137(dec.); IR (CCl_4) ν_{CO} 2036, 1979 cm^{-1}; ^{1}H, $^{13}C_{sigma\ allene}$ 169.44 ppm; MS-CI; EA (CH).	52
	**110**	-	2.2.3 (82)	brown needles, air stable ; mp (°C) 134-135; IR (C_6H_{14}) ν_{CO} 1994, 1934 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 351.15 ppm; MS-EI; EA (CHMn).	40
	**111**	-	2.2.3 (84)	dark green oil, air sensitive; IR (C_6H_{14}) ν_{CO} 1991, 1932 cm^{-1}; ^{1}H; MS-EI; EA (CHMn).	40
	**112**	1.979(3)	2.2.1 (90)	yellow-orange solid, air stable; mp (°C) 180-180.5 (dec.), slow dec. in solution; IR (CH_2Cl_2) ν_{CO} 2045, 1996 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 242,3 ppm; UV/Vis; EA (CH).	11,31,34, 86
	**113**	-	2.2.1 (93)	red brown solid, air stable; mp (°C) 177-178 (dec.); IR (CH_2Cl_2) ν_{CO} 2045, 2000 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 265.9 ppm; UV/Vis; EA (CH).	31,34,86
	**114**	1.996(2)	2.2.1 (88)	violet solid, stable; mp (°C) 176-177 (dec.); IR (CH_2Cl_2) ν_{CO} 2037, 1992 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 201 ppm; UV/Vis; EA (CH).	34,86
	**115**	-	2.2.1 (54)	purple plates, stable in crystal form, slow dec. in solution; IR (neat) ν_{CO} 2995, 1920 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 278.8 ppm, $^{13}C_{CO}$ 217.5 ppm; EA (CH).	31
	**116**	-	2.2.1 (45)	blue purple solid, air sensitive; dec. at room temp.; IR (neat) ν_{CO} 3060, 2995 (sh), 1980 cm^{-1}, ^{1}H.	31
	**117**	1.993(5)	2.2.1.1 (89)	IR (CH_2Cl_2) ν_{CO} 2025, 1972, 1958, 1893, 1860 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 159.1 ppm, $^{13}C_{FeCO}$ 217.5, 216.7 ppm, $^{13}C_{CrCO}$ 235.1 ppm; EI-MS; EA (CH).	35,36
	**118**	-	2.2.1 (64)	brown solid, air stable; mp (°C) 180-181; IR ($CDCl_3$) ν_{CO} 2020, 1980 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 223.56 ppm, $^{13}C_{CO}$ 198.66 ppm; EA (CH).	32
	**119**	-	2.2.1	yellow-brown solid (impure); ^{1}H, $^{13}C_{carbene}$ 244.715 ppm.	32
	**120**	-	2.2.1	yellow brown solid (impure); ^{1}H, $^{13}C_{carbene}$ 186.63 ppm, $^{13}C_{CO}$ 200.27 ppm.	32

Table 4. (Continued)

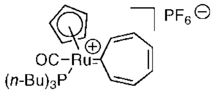
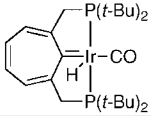
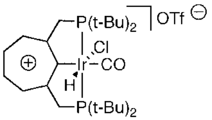
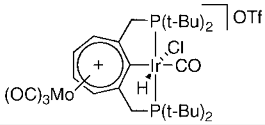
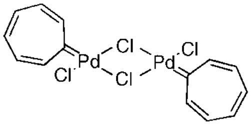
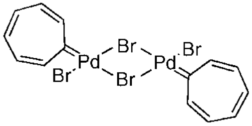
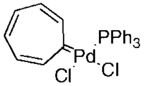
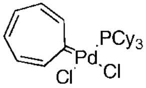
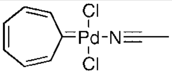
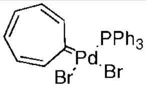
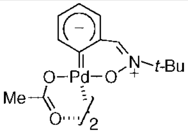
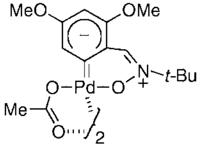
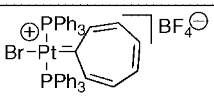
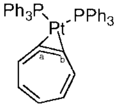
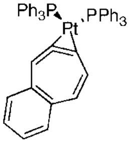
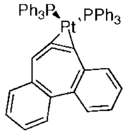
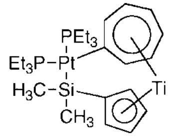
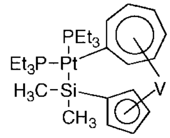
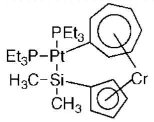
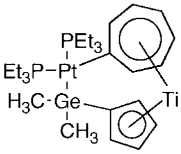
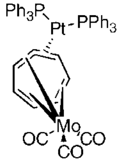
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
	**121**	-	2.2.1 (64)	red solid; mp (°C) 110-111; IR ν_{CO} 2020, 1980 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 256.2 ppm, ^{13}C$_{CO}$ 179.0 ppm; EA (CH).	32
	**122**	-	2.1.2	proposed intermediate, consistent with observed products, though not observed	123
	**123**	2.093(5)	2.2.1.2 (99.8)	yellow solid; IR (KBr) ν_{CO} 2030 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 213.3 ppm, ^{13}C$_{CO}$ 177.2 ppm, ^{31}P, ^{19}F; MS; EA (CHS).	37,38
	**124**	-	2.2.1.2 + L$_3$Mo(CO)$_3$ (84)	orange brown solid, dec. in solution; IR (KBr) ν_{CO} 2045, 2030, 1981, 1940 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 129.0 ppm, ^{13}C$_{IrCO}$ 175.3 ppm; MS-FAB.	38
	**125**	-	2.2.4 (64)	orange crystal, air stable; mp (°C) 150-160 (dec.); IR (nujol) ν_{Pd-Cl} 346, 313, 383 cm^{-1}; EA (CHPd).	43
	**126**	-	2.2.4 (97)	bright orange crystals, air stable; mp (°C) 179-184 (dec.); IR (nujol) ν_{Pd-Br} 250, 178, 161 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 217.5 ppm; EA (CHPd).	15,43,45
	**127**	1.968(2)	2.2.4 (93)	yellow crystals, air stable; ^{1}H, ^{31}P; MS-FAB; EA (CHPd).	15,45
	**128**	-	2.2.4	^{1}H, ^{31}P, MS-FAB; EA (CHPd).	15
	**129**	-	2.2.4 (51)	yellow crystals; ^{1}H, ^{13}C, ^{13}C$_{carbene}$ not detected; EA (CHNPd).	45
	**130**	1.983(3)	2.2.4	^{1}H, ^{31}P; MS-FAB; EA (CHPd).	15
	**131**	-	2.2.6 (82)	pale yellow solid, air stable, mixture of two diastereomers (trainsoid/cisoid 10:1); mp (°C) 213 (dec.); ^{1}H, ^{13}C (carbene not assigned); EA (CHN).	49
	**132**	1.948(3)	2.2.6 (66)	pale yellow solid, mixture of two diastereomers (transoid/cisoid 5:1); mp (°C) 222 (dec.); ^{1}H, ^{13}C (carbene not assigned); EA (CHN).	49
	**133**	1.99(1) (monoclinic) 2.03(2) (orthorombic)	2.2.1, 2.2.2 (87)	greenish-yellow crystals; ^{1}H, ^{13}C$_{carbene}$ 210.5; EA (CH).	33
	**134**	a)2.000(7) b)2.111(8)	2.2.7 (51)	light yellow powder; mp (°C) 140-144 (dec.); ^{1}H, ^{13}C, ^{31}P; EA (CH).	50,51
	**135**	-	2.2.7 (82)	mp (°C) 140-144 (dec.); ^{1}H, ^{13}C, ^{31}P; EA (CH).	50,51

Table 4. (Continued)

Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected data	Ref.
	**136**	-	2.2.7 (67)	mp (°C) 144-150 (dec.); ^{1}H, ^{13}C, ^{31}P; EA (CH).	50,51
	**137**	2.096(3)	2.2.5 (26)	green crystalline solid; ^{1}H, ^{13}C$_{carbene}$ 89.0 ppm, ^{31}P, ^{195}Pt; EA (CH).	47
	**138**	2.092(2)	2.2.5 (33)	blue grey crystals, paramagnetic; EPR; EA (CH).	47
	**139**	2.087(4)	2.2.5 (76)	green crystals; ^{1}H, ^{13}C$_{carbene}$ 94.7, ^{29}Si, ^{31}P; EA (CH).	48
	**140**	-	2.2.5 (76)	green crystalline solid; ^{1}H, ^{13}C, ^{29}Si, ^{31}P, MS-EI; EA (CH).	88
	**141**	-	2.2.5 followed by addition of $L_3Mo(CO)_3$	dark red-brown, stable in solution to 20 °C for a few hours; ^{1}H, ^{195}Pt, ^{31}P.	82

Yoshida, were found to decompose, giving the retrosynthetic cyclopropenium salts or cyclopropenethiones (Scheme 41).[23]

4.2. C_7H_6 Complexes

4.2.1. Allene Complexes

The platinum−allene complex **134**, prepared from Pt(PPh$_3$)$_3$ and in situ generated C_7H_6, reacts with excess ligand, forming the metallacyclophane **A** shown in Figure 11. The same reaction was observed with the benzannelated allene complex **135**, yielding the corresponding metallacyclophane **B**.[51]

Addition of (η^6-*p*-xylene)Mo(CO)$_3$ in THF to the allene complex **134** yields the heterobimetallic complex **141** (Figure 12), which in contrast to the thermally stable parent monometallic **platinum** complex decomposes slowly at room temperature.

4.2.2. Carbene Complexes

The pentacarbonyltungsten−CHT complex **108** is much more reactive than the analogous cyclopropenylidene complex **28**. In contrast to the latter, it rapidly undergoes decomposition by refluxing in heptane (under formation of heptafulvalene) and by reaction with dry HCl in CH_2Cl_2; its solutions are sensitive to air and light, and it reacts with DMSO under formation of tropone.[16] This greater reactivity of the CHT complex **108** has been ascribed to easier loss of CO from the W(CO)$_5$ moiety due to more W → carbene backbonding in the CHT complex than in the corresponding cyclopropenylidene complex.[16] However, this suggestion does not agree with later observations of palladium complexes, according to which the π-acceptor character of the CHT ligand is substantially lower compared than that of cyclopropenylidene ligands (see section 3.2.2.4).[78]

Differences in reactivity appear less pronounced between CHT and cyclopropenylidene complexes of palladium and platinum. The dimeric halogen-bridged CHT−Pd(II) complexes **125** and **126**, like their analogous cyclopropenylidene compounds, readily react with donor ligands such as phosphanes or acetonitrile to give the mononuclear donorsubstituted CHT complexes **127**−**130**. All these compounds are thermally stable and inert against air at room temperature.[15,43,45] However, their reaction with DMSO leads to substitution of the CHT ligand and its conversion to tropone.[78]

Reactions at the CHT ligand without breaking the metal−carbene bond have been reported with the CHT pincer complex of iridium **123**. As a consequence of the positively charged seven-membered ring, the hydrogen atoms on the methylene bridges to the phosphane groups become acidic and can be deprotonated, yielding a neutral cycloheptatrienyl pincer complex of Ir(III) with an extension of the π-system into one of the phosphane bridges (Scheme 42).

Treatment of the deprotonated product **A** with a second equivalent of base removes HCl from the iridium center, forming the Ir(I) complex **B** in a reversible reaction. Addition

Table 5. Nonaromatic Carbene Metal Complexes

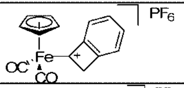
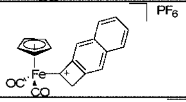
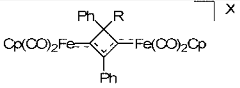
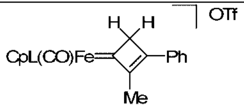
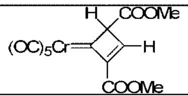
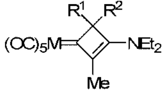
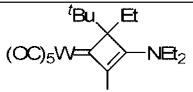
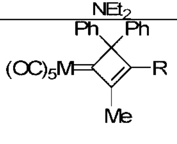
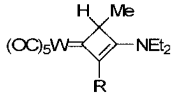
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
	**142**	-	2.3.1 (see C$_7$-complexes) (90)	deep orange-red crystals; ^{1}H; IR (neat) ν_{CO} 2003, 1942 cm^{-1}; EA (Fe).	90
	**143**	-	2.3.1 (see C$_7$-complexes) (33.5 %)	mp (°C) 161-163 (dec.); ^{1}H; IR (Nujol) ν_{CO} 2035, 2085 cm^{-1}; EA (Fe).	92
 R = H, X = ClO$_4^-$	**144**	-	2.3.5 (54)	orange crystalline compound, air-stable; mp (°C) 120 (dec.); ^{1}H; IR (CH$_2$Cl$_2$) ν_{CO} 2057, 2045, 2010 cm^{-1}; EA (CHFeCl).	124,69
R = H, X = BF$_4^-$	**145**	-	2.3.5 (61)	orange crystalline compound, air-stable; mp (°C) 149-150 / 160-161 (dec.); ^{1}H, ^{13}C$_{carbene}$ 261.03 ppm; IR (CH$_2$Cl$_2$) ν_{CO} 2052, 2041, 2010, 1997 cm^{-1}; EA (CHF).	68,124,69
R = Me, X = PF$_6^-$	**146**	-	2.3.5 (51)	orange crystalline compound; mp (°C) 167.5-170 (dec.) ^{1}H; IR (CH$_2$Cl$_2$) ν_{CO} 2055, 2044, 2008, 1999 cm^{-1}; EA (CHP).	68
 L = PPh$_3$	**147**	-	2.3.4 (45-60)	^{1}H, ^{13}C$_{carbene}$ 328.1 ppm.	65
L = P(OPh)$_3$	**148**	1.85(3)	2.3.4 (45-60)	^{1}H, ^{13}C$_{carbene}$ 322.1 ppm.	65
	**149**	-	2.3.4 (43)	dec. > 10°C; ^{1}H; IR (CCl$_4$) ν_{CO} 2080, 2030, 1995, 1980 cm^{-1}.	125
 M = W, R^1 = R^2 = Ph	**150**	-	2.3.4 (85)	yellow powder; mp (°C) 144; IR (*n*-pentane) ν_{CO} 2057, 1968, 1935, 1927 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 267.7 ppm; EA (CHN).	66
M = W, R^1 = ^{t}Bu, R^2 = Et	**151**	-	2.3.4 (19)	yellow crystals; mp (°C) 100; IR (*n*-pentane) ν_{CO} 2055, 1930, 1921 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 258.3 ppm; MS-FAB; EA (CHN).	66
M = W, R^1 = ^{t}Bu, R^2 = Me	**152**	2.259(6)	2.3.4 (58)	yellow crystals; mp (°C) 90; IR (*n*-pentane) ν_{CO} 2055, 1932, 1921, 1912 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 249.8 ppm; MS-FAB; EA (CHN).	66
M = Cr, R^1 = ^{t}Bu, R^2 = Me	**153**	-	2.3.4 (31)	yellow crystals; mp (°C) 73; IR (*n*-pentane) ν_{CO} 2044, 1958, 1930, 1925, 1914 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 268.3 ppm; MS-FAB; EA (CHN).	66
	**154**	-	2.3.4 (13)	yellow crystals; mp (°C) 131 (dec.); IR (*n*-pentane) ν_{CO} 2055, 1931, 1921, 1912 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 260.2 ppm; MS-FAB; EA (CHN).	66
 M = W, R = OEt	**155**	2.162(5)	2.3.4 (78)	ruby crystals; mp (°C) 84 (dec.); IR (*n*-pentane) ν_{CO} 2064, 1983, 1951, 1944, 1934 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 300.8 ppm; MS-FAB; EA (CH).	66
M = Cr, R = SMe	**156**	1.999(3)	2.3.4 (10)	black rhombi; mp (°C) 72-75; IR (pentane) ν_{CO} 2053, 1979, 1959, 1944 cm^{-1}; UV/Vis, MS-EI, EA (CHN).	146
 R = Ph	**157**	-	2.3.4 (32)	mp (°C) 76; IR (pentane) ν_{CO} 2056, 1930, 1927 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 262.3ppm; UV/Vis, MS-EI; EA(CHN).	127
R = *t*-Bu	**158**	-	2.3.4 (34)	mp (°C) 69; IR (pentane) ν_{CO} 2054, 1962, 1929, 1921 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 240.7; UV/Vis; MS-EI, EA (CHN).	127
R = *c*Hex	**159**	-	2.3.4 (37)	mp (°C) 103; IR(pentane) ν_{CO} 2054, 1962, 1924 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 257.5ppm; UV/Vis; MS-EI, EA (CH).	127

Table 5. (Continued)

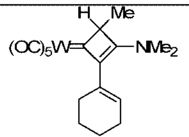
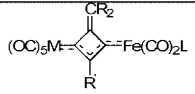
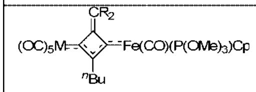
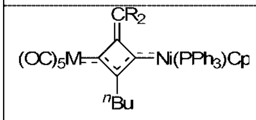
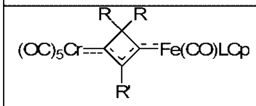
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
R = COOMe	**160**	-	2.3.4 (37)	mp (°C) 132; IR (pentane) ν_{CO} 2060, 1972, 1932, 1930 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 279.3ppm; UV/Vis; MS-EI; EA (CH).	127
R = C(=CH$_2$)Me	**161**	-	2.3.4 (26)	mp (°C) 95 (dec.), IR (pentane) ν_{CO} 2056, 1965, 1929, 1923 cm^{-1}, ^{1}H, ^{13}C$_{carbene}$ 261.7 ppm, UV/Vis, MS-EI, EA (CH).	127
R = CH=C(OMe)H	**162**	-	2.3.4 (21)	mp (°C) 70 (dec.); IR (pentane) ν_{CO} 2054, 1962, 1930, 1923 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 257.1 ppm; UV/Vis; MS-EI, EA (CHN).	127
	**163**	-	2.3.4 (28)	mp (°C) 101; IR(pentane) ν_{CO} 2054, 1932, 1927, 1920 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 261.7 ppm; MS-EI; EA (CHN).	127
 M = Cr, R = C$_6$H$_4$CH$_3$-*p*, R' = ^{n}Bu, L = Cp	**164**	Cr-C: 2.076(6) Fe-C: 1.959(6)	2.3.4	orange crystals; mp (°C) 128; IR (Et$_2$O) ν_{CO} 2052, 2032, 1991, 1973, 1933, 1921 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; MS-EI, EA (CH).	126
M = Cr, R = C$_6$H$_4$OCH$_3$-*p*, R' = ^{n}Bu, L = Cp	**165**	-	2.3.4	orange crystals; mp (°C) 129; IR (Et$_2$O) ν_{CO} 2051, 2032, 1991, 1973, 1932, 1918 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	126
M = W, R = C$_6$H$_4$CH$_3$-*p*, R' = ^{n}Bu, L = Cp	**166**	-	2.3.4	orange crystals; mp (°C) 135 (dec.); IR (Et$_2$O) ν_{CO} 2059, 2035, 1991, 1922, 1895 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	126
M = Cr, R = C$_6$H$_4$OCH$_3$-*p*, R' = Ph, L = Cp	**167**	-	2.3.4	orange crystals; mp (°C) 110 (dec.); IR (Et$_2$O) ν_{CO} 2054, 2035, 1995, 1973, 1931, 1915 cm^{-1}; ^{1}H, ^{13}C; MS-FAB, EA (CH).	126
M = Cr, R = C$_6$H$_4$CH$_3$-*p*, R' = ^{n}Bu, L = Cp*	**168**	-	2.3.4	orange microcrystals; mp (°C) 103; IR (Et$_2$O) ν_{CO} 2048, 2014, 1969, 1929, 1923, 1905 cm^{-1}; ^{1}H, ^{13}C; MS-FAB, EA.	126
 M = Cr, R = C$_6$H$_4$CH$_3$-*p*	**169**	Cr-C: 2.103(5) Fe-C: 1.907(4)	2.3.4	red crystals; mp (°C) 130; IR (Et$_2$O) ν_{CO} 2046, 1970, 1926, 1918, 1903 cm^{-1}; ^{1}H, ^{13}C; ^{31}P; UV/Vis; MS-EI.	126
M = Cr, R = C$_6$H$_4$OCH$_3$-*p*	**170**	-	2.3.4 (78)	red crystals; mp (°C) 135; , IR (Et$_2$O) ν_{CO} 2045, 1970, 1928, 1918, 1905 cm^{-1}; ^{1}H, ^{13}C, ^{31}P; UV/Vis; EA (CH).	126
M = W, R = C$_6$H$_4$CH$_3$-*p*	**171**	-	2.3.4	red crystals; mp (°C) 142; IR (Et$_2$O) ν_{CO} 2054, 1967, 1916, 1883 cm^{-1}; ^{1}H, ^{13}C, ^{31}P; UV/Vis; EA (CH).	126
 M = Cr, R = C$_6$H$_4$CH$_3$-*p*	**172**	-	2.3.4	red crystals; mp (°C) 108; IR (Et$_2$O) ν_{CO} 2046, 1973, 1929, 1910 cm^{-1}; ^{1}H, ^{13}C, ^{31}P; UV/Vis; MS-FAB.	126
M = Cr, R = C$_6$H$_4$OCH$_3$-*p*	**173**	-	2.3.4	red crystals; mp (°C) 127; IR (Et$_2$O) ν_{CO} 2046, 1971, 1929, 1913 cm^{-1}; ^{1}H, ^{13}C, ^{31}P; UV/Vis; MS-FAB.	126
M = W, R = C$_6$H$_4$CH$_3$-*p*	**174**	W-C: 2.210(10) Ni-C: 1.839(11)	2.3.4	dark red crystals; mp (°C) 110; IR (Et$_2$O) ν_{CO} 2055, 1975, 1918, 1875 cm^{-1}; ^{1}H, ^{13}C, ^{31}P, UV/Vis; EA (CH).	126
 R = Me, R' = ^{n}Bu, L = CO	**175**	-	2.3.4 (40)	yellow crystals; mp (°C) 64; IR (CH$_2$Cl$_2$) ν_{CO} 2049, 2028, 1982, 1923 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CHN).	67
R = Me, R' = Me, L = CO	**176**	-	2.3.4 (29)	red crystals; mp (°C) 88; IR (CH$_2$Cl$_2$) ν_{CO} 2049, 2029, 1984, 1923 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; MS-EI, EA (CH).	67
R = Me, R' = Ph, L = CO	**177**	-	2.3.4 (35)	dark red crystals; mp (°C) 82; IR (pentane) ν_{CO} 2051, 2028, 1988, 1948, 1933 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	67
R = Me, R' = C$_6$H$_4$NO$_2$-*p*, L = CO	**178**	-	2.3.4 (40)	dark red crystals; mp (°C) 85; IR (CH$_2$Cl$_2$) ν_{CO} 2051, 2030, 1988, 1936, 1925 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CHN).	67

Table 5. (Continued)

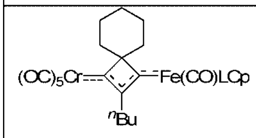
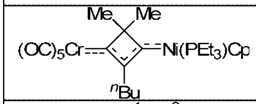
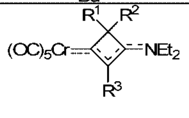
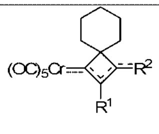
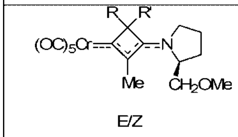
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
R = Me, R' = COOMe, L = CO	**179**	Cr-C: 2.010(3) Fe-C: 1.923(3)	2.3.4 (30)	brown crystals; mp (°C) 76; IR (CH$_2$Cl$_2$) ν_{CO} 2056, 2035, 1981, 1936, 1751 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	67
R = Me, R' = ^{n}Bu, L = P(OMe)$_3$	**180**	-	2.3.4 (46)	orange crystals; mp (°C) 83, IR (CH$_2$Cl$_2$) ν_{CO} 2041, 1952, 1916 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; UV/Vis; EA (CH).	67
R = Me, R' = ^{n}Bu, L = PPh$_3$	**181**	-	2.3.4 (20)	orange crystals; mp (°C) 148; IR (CH$_2$Cl$_2$) ν_{CO} 2042, 1948, 1919 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; UV/Vis; EA (CH).	67
R = Ph, R' = ^{n}Bu, L = CO	**182**	-	2.3.4 (15)	black crystals; mp (°C) 170; IR (pentane) ν_{CO} 2050, 2030, 1989, 1945, 1931 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	67
 L = CO	**183**	Cr-C: 2.093(4) Fe-C: 1.937(4)	2.3.4 (30)	orange crystals; mp (°C) 74; IR (pentane) ν_{CO} 2047, 1980, 1920 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	67
L = P(OMe)$_3$	**184**	Cr-C: 2.109(3) Fe-C: 1.944(3)	2.3.4 (37)	orange crystals; mp (°C) 140, IR (CH$_2$Cl$_2$) ν_{CO} 2042, 1947, 1916, 1889 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; UV/Vis, EA (CH).	67
	**185**	-	2.3.4 (27)	brown crystals; mp (°C) 65, IR (pentane) ν_{CO} 2044, 1923 cm^{-1}, ^{1}H, ^{13}C; MS-FAB, EA (CH).	67
 R^1 = R^2 = Ph, R^3 = Me	**186**	-	2.3.4 (34)	orange crystals; mp (°C) 134; IR (CH$_2$Cl$_2$) ν_{CO} 2044, 1964, 1928, 1914 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 282.6 ppm; MS-EI; UV/Vis; EA (CHN).	128
R^1, R^2 = (CH$_2$)$_5$, R^3 = Me	**187**	2.100(4)	2.3.4 (50)	lemon yellow crystals; mp (°C) 104; IR (CH$_2$Cl$_2$) ν_{CO} 2044, 1959, 1935, 1927, 1913 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 286.3 ppm; MS-FAB; UV/Vis; EA (CHN).	128
R^1 = R^2 = R^3 = Me	**188**	-	2.3.4 (47)	yellow crystals; mp (°C) 82; IR (pentane) ν_{CO} 2045, 1962, 1933, 1918 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 291.8 ppm; MS-FAB; UV/Vis; EA (CHN).	128
R^1 = H, R^2 = R^3 = Me	**189**	-	2.3.4 (12)	yellow-green needles; mp (°C) 99; IR (pentane) ν_{CO} 2046, 1962, 1931 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 285.2 ppm; MS-EI; UV/Vis; EA (CHN).	128
R^1 = H, R^2 = Me, R^3 = Ph	**190**	-	2.3.4 (34)	dark yellow crystals; mp (°C) 126; IR (pentane) ν_{CO} 2047, 1969, 1935, 1926 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 282.0 ppm; MS-EI; UV/Vis; EA (CHN).	128
 R^1 = R^2 = NMe$_2$	**191**	-	2.3.4 (19)	bright crystals; mp (°C) 126; IR (CH$_2$Cl$_2$) ν_{CO} 2040, 1954, 1922, 1904 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 285.3 ppm; MS-FAB; UV/Vis; EA (CHN).	128
R^1 = NMe$_2$, R^2 = OEt	**192**	-	2.3.4 (13)	orange-red amorphous solid; mp (°C) 73 (dec.); IR (CH$_2$Cl$_2$) ν_{CO} 2052, 1986, 1949, 1930 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 332.1 ppm; MS-FAB; UV/Vis; EA (CHN).	128
 R = R' = Ph	**193**	-	2.3.4 (36)	yellow, fluffy solid; *E*/*Z* mixture; mp (°C) 118; IR (pentane) ν_{CO} 2046, 1970, 1934, 1929 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 292.5 ppm; MS-EI; UV/Vis; EA (CHN).	128
R, R' = (CH$_2$)$_5$	**194**	-	2.3.4 (26)	yellow crystals; *E*/*Z* mixture; mp (°C) 66; IR (pentane) ν_{CO} 2044, 1959, 1932, 1914 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 286.4 ppm; MS-EI; UV/Vis; EA (CHN).	128
R = R' = Me	**195**	-	2.3.4 (16)	yellow oil; *E*/*Z* mixture; IR (pentane) ν_{CO} 2044, 1962, 1932, 1917 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 293.2 ppm; MS-EI; UV/Vis; EA (CHN).	128

Table 5. (Continued)

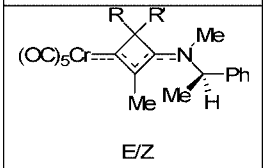
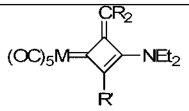
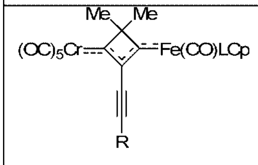
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
 E/Z R = R' = Ph	**196**	-	2.3.4 (22)	orange crystals; *E*/*Z* mixture; mp (°C) 135; IR (Et$_2$O) ν_{CO} 2044, 1967, 1930, 1922 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 293.3 ppm; MS-FAB; UV/Vis; EA (CHN).	128
R, R' = (CH$_2$)$_5$	**197**	2.073(5)	2.3.4 (37)	yellow crystals; *E*/*Z* mixture; mp (°C) 112; IR (pentane) ν_{CO} 2044, 1960, 1934, 1929, 1913 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 290.9 ppm; MS-MI; UV/Vis; EA (CHN).	128
R = R' = Me	**198**	-	2.3.4 (20)	yellow oil; *E*/*Z* mixture; IR (pentane) ν_{CO} 2044, 1962, 1932, 1918 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 295.1 / 294.5 ppm; MS-EI; UV/Vis; EA (CHN).	128
 M = Cr, R = Ph, R' = Me	**199**	-	2.3.4 (24)	yellow needles; mp (°C) 151; IR (Et$_2$O) ν_{CO} 2046, 1967, 1927, 1922, 1909 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 268.0 ppm; MS-FAB; EA (CHN).	129
M = Cr, R = C$_6$H$_4$Me-*p*, R' = Me	**200**	-	2.3.4 (11)	yellow needles; mp (°C) 135 (dec.); IR (Et$_2$O) ν_{CO} 2046, 1963, 1922, 1908 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 267.0 ppm; EA (CHN).	129
M = Cr, R = C$_6$H$_4$OMe-*p*, R' = Me	**201**	-	2.3.4 (8)	yellow needles, mp (°C) 126; IR (Et$_2$O) ν_{CO} 2046, 1967, 1912, 1909 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 268.1 ppm; EA (CHN).	129
M = Cr, R = C$_6$H$_4$NMe$_2$-*p*, R' = Me	**202**	-	2.3.4 (76)	brown yellow; mp (°C) 194; IR (Et$_2$O) ν_{CO} 2046, 1966, 1922, 1904 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 268.8 ppm; EA (CHN).	129
M = Cr, R = C$_6$H$_4$OMe-*p*, R' = Ph	**203**	-	2.3.4 (42)	yellow powder; mp (°C) 134; IR (Et$_2$O) ν_{CO} 2046, 1967, 1926, 1908 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 276.0 ppm; EA (CHN).	129
M = Cr, R = C$_6$H$_4$NMe$_2$-*p*, R' = Ph	**204**	-	2.3.4 (68)	brown yellow powder; mp (°C) 120 (dec.); IR (Et$_2$O) ν_{CO} 2045, 1968, 1924, 1904 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 274.5 ppm; EA (CHN).	129
M = W, R = Ph, R' = Me	**205**	-	2.3.4 (19)	yellow needles; mp (°C) 150 (dec.), IR (Et$_2$O) ν_{CO} 2055, 1965, 1919, 1907 cm^{-1}, ^{1}H, ^{13}C$_{carbene}$ 247.8 ppm; EA (CHN).	129
M = W, R = C$_6$H$_4$Me-*p*, R' = Me	**206**	-	2.3.4 (11)	yellow crystals; mp (°C) 135 (dec.); IR (Et$_2$O) ν_{CO} 2055, 1964, 1919, 1906 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 248.5 ppm; EA (CHN).	129
M = W, R = C$_6$H$_4$OMe-*p*, R' = Me	**207**	-	2.3.4 (7)	yellow crystals; mp (°C) 145 (dec.), IR (Et$_2$O) ν_{CO} 2045, 1963, 1921, 1917, 1905 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 248.4 ppm; EA (CHN).	129
M = W, R = C$_6$H$_4$NMe$_2$-*p*, R' = Me	**208**	-	2.3.4 (42)	brown yellow crystals; mp (°C) 211 (dec.); IR (Et$_2$O) ν_{CO} 2052, 1963, 1915, 1899 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 247.1 ppm; EA (CHN).	129
 R = SiMe$_3$, L = CO	**209**	-	2.3.4 (65)	red crystals; mp (°C) 84; IR (CH$_2$Cl$_2$) ν_{CO} 2053, 2034, 1990, 1939 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	130
R = ^{n}Bu, L = CO	**210**	-	2.3.4 (45)	red oil; IR (CH$_2$Cl$_2$) ν_{CO} 2051, 2031, 1981, 1935 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	130
R = Ph, L = CO	**211**	-	2.3.4 (60)	red crystals; mp (°C) 84; IR (CH$_2$Cl$_2$) ν_{CO} 2052, 2033, 1989, 1937 cm^{-1}; ^{1}H, ^{13}C; MS-FAB, EA (CH).	130
R = SiMe$_3$, L = PPh$_3$	**212**	Cr-C: 2.054(4) Fe-C: 1.910(4)	2.3.4 (65)	red crystals; mp (°C) 152; IR (CH$_2$Cl$_2$) ν_{CO} 2043, 1950, 1927 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	130
R = Ph, L = PPh$_3$	**213**	-	2.3.4 (76)	red crystals; mp (°C) 95 (dec.); IR(CH$_2$Cl$_2$) ν_{CO} 2043, 1950, 1925, 1901 cm^{-1}; ^{1}H, ^{31}P, ^{13}C. UV/Vis; MS-FAB; EA (CH).	130
R = H, L = CO	**214**	-	2.3.4 (67)	red crystals; mp (°C) 68; IR (CH$_2$Cl$_2$) ν_{CO} 2054, 2033, 1990, 1938 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	130

Table 5. (Continued)

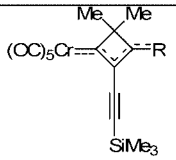
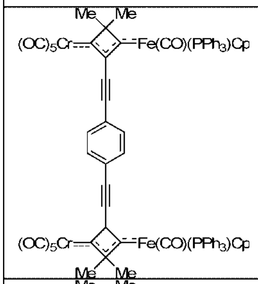
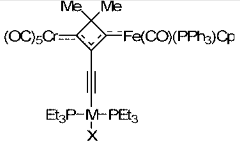
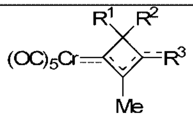
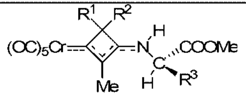
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
R = H, L = PPh$_3$	**215**	-	2.3.4 (57)	red crystals; mp (°C) 72; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2043, 1950, 1927, 1888 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; UV/Vis; MS-FAB; EA (CH).	130
R = Sn^{n}Bu$_3$, L = CO	**216**	-	2.3.4 (85)	red oil; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2054, 2033, 1990, 1951, 1938 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	130
R = C$_6$H$_4$I-*p*, L = CO	**217**	-	2.3.4 (20)	red crystals; mp (°C) 77; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2053, 2033, 1984, 1937 cm^{-1}; ^{1}H, ^{13}C; UV/Vis; EA (CH).	130
R = C$_6$H$_4$I-*p*, L = PPh$_3$	**218**	-	2.3.4 (38)	red crystals; mp (°C) 87; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2042, 1948, 1926, 1901 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; UV/Vis; MS-FAB; EA (CH).	130
 R = NMe$_2$	**219**	-	2.3.4 (83)	yellow crystals; mp (°C) 113; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2046, 1971, 1929, 1893 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 307.1 ppm; UV/Vis; EA (CH).	130
R = N(CH$_2$)$_5$	**220**	-	2.3.4 (40)	yellow crystals; mp (°C) 120; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2046, 1970, 1926, 1896 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 305.3ppm; MS-FAB, EA (CHN).	130
	**221**	-	2.3.4 (10)	red crystals; mp (°C) 72; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2043, 1947, 1925 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; UV/Vis; MS-FAB; EA (CH).	130
 M = Pd, X = I	**222**	-	2.3.4 (22)	orange powder; mp (°C) 82; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2042, 1965, 1942, 1919, 1888 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; MS-FAB; EA (CH).	130
M = Pt, X = Cl	**223**	-	2.3.4 (36)	orange powder; mp (°C) 78; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2041, 1963, 1940, 1918, 1889 cm^{-1}; ^{1}H, ^{31}P, ^{13}C; MS-FAB; EA (CH).	130
 R^1 = R^2 = Me, R^3 = OEt	**224**	-	2.3.4 (8)	slightly red needles; mp (°C) 28; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2054, 1976, 1950, 1933 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 335.9 ppm; UV/Vis; MS-EI; EA (CH).	131
R^1, R^2 = (CH$_2$)$_5$, R^3 = OEt	**225**	-	2.3.4	no details	131
R^1 = R^2 = Ph, R^3 = OEt	**226**	-	2.3.4 (16)	orange plates; mp (°C) 76; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2054, 1950, 1939 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 332.4 ppm; UV/Vis; MS EI; EA (CH).	131
 E/Z R^1, R^2 = (CH$_2$)$_5$, R^3 = CHMe$_2$	**227**	-	2.3.4 (94)	yellow crystals; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2044, 1960, 1923, 1917 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 304.9 ppm; UV/Vis; MS; EA (CHN).	131
R^1 = R^2 = Me, R^3 = CHMe$_2$	**228**	2.044(4)/ 2.050(4)	2.3.4 (92)	yellow crystals; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2044, 1961, 1923 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 308.6 ppm; UV/Vis; MS; EA (CHN).	131
R^1, R^2 = (CH$_2$)$_5$, R^3 = CH$_2$Ph	**229**	-	2.3.6 (90)	yellow powder; mp (°C) 61; IR (CH$_2$Cl$_2$) ν$_{CO}$ 2045, 1965 1921, 1917 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 306.0 ppm; UV/Vis; MS; EA (CHN).	131

Table 5. (Continued)

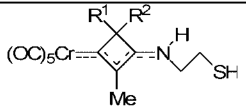
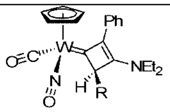
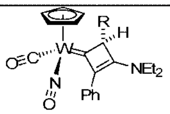
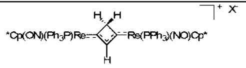
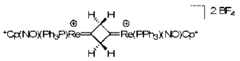
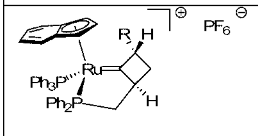
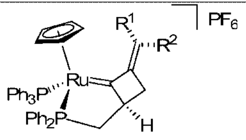
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
$R^1 = R^2 = Me$, $R^3 = CH_2Ph$ only *E*	**230**	-	2.3.4 (92)	orange-yellow sticky oil; IR (CH_2Cl_2) ν_{CO} 2045, 1965, 1921, 1917 cm^{-1}, ^1H, $^{13}C_{carbene}$ 308.8 ppm; UV/Vis; EA (CHN).	131
$R^1, R^2 = (CH_2)_5$, $R^3 = CH_2CH_2SMe$	**231**	-	2.3.4 (82)	red brown oil; IR (CH_2Cl_2) ν_{CO} 2044, 1960, 1923, 1917 cm^{-1}, ^1H, $^{13}C_{carbene}$ 305.6 ppm; UV/Vis; EA (CHN).	131
$R^1 = R^2 = Me$, $R^3 = CH_2CH_2SMe$	**232**	-	2.3.4 (92)	orange sticky oil; IR (CH_2Cl_2) ν_{CO} 2045, 1965, 1921, 1917 cm^{-1}, ^1H, $^{13}C_{carbene}$ 308.8 ppm; UV/Vis; EA (CHN).	131
 E/Z $R^1, R^2 = (CH_2)_5$ only *Z*	**233**	-	2.3.4 (70)	yellow powder; IR (CH_2Cl_2) ν_{CO} 2047, 1962, 1920 cm^{-1}; ^1H, $^{13}C_{carbene}$ 301.6 ppm; UV/Vis; MS-EI; EA (CHN).	131
$R^1 = R^2 = Me$	**234**	-	2.3.4 (86)	yellow viscous oil; IR (CH_2Cl_2) ν_{CO} 2048, 1938, 1923 cm^{-1}; ^1H, $^{13}C_{carbene}$ 301.1 ppm; UV/Vis; MS-EI; EA (CHN).	131
$R^1 = R^2 = Ph$	**235**	-	2.3.4 (73)	orange viscous oil; IR (CH_2Cl_2) ν_{CO} 2046, 1968, 1924 cm^{-1}; ^1H, $^{13}C_{carbene}$ 297.6 ppm; UV/Vis; MS-EI; EA (CHN).	131
 R = Me	**236**	2.045(4)	2.3.4 (34)	red crystals, IR (KBr) ν_{CO} 1905 cm^{-1}; ^1H, $^{13}C_{carbene}$ 270.8 ppm; MS; HR-MS; UV/vis; EA (CHN).	132
R = Et	**237**	-	2.3.4 (30)	red crystals, IR (KBr) ν_{CO} 1901 cm^{-1}; ^1H, $^{13}C_{carbene}$ 268.7 ppm; MS; HR-MS; UV/vis; EA (CHN).	132
 R = Me	**238**	-	2.3.4 (18)	red crystals, IR (KBr) ν_{CO} 1905 cm^{-1}; ^1H, $^{13}C_{carbene}$ 270.8 ppm; MS; HR-MS; EA (CHN).	132
R = Et	**239**	-	2.3.4 (17)	red crystals, IR (KBr) ν_{CO} 1901 cm^{-1}; ^1H, $^{13}C_{carbene}$ 270.1 ppm; MS; HR-MS; EA (CHN).	132
 $X^- = ½ [Zn_2Cl_6]^{2-}$	**240**	2.03(1)/ 2.00(1)	2.3.5 (94)	orange needles; mp (°C) >196 (slow dec.); IR (CH_2Cl_2/thin film) ν_{NO} 1655, 1642 cm^{-1}; ^1H, $^{13}C_{carbene}$ 227.5 ppm, ^{31}P; MS-FAB; EA (CH).	70
$X = BF_4$	**241**	-	2.3.5 (94)	orange needles; mp (°C) 173-176 (dec.); IR (CH_2Cl_2/thin film) ν_{NO} 1656, 1641 cm^{-1}; ^1H, $^{13}C_{carbene}$ 227.5 ppm, ^{31}P; UV/vis.	70
	**242**	-	2.3.5 (>95)	yellow solution; IR (CH_2Cl_2) ν_{NO} 1713 cm^{-1}; ^1H, $^{13}C_{carbene}$ 304.7 ppm, ^{31}P; MS-FAB.	70
 R = Ph	**243**	1.864(5)	2.3.4 (85)	yellow solid, air-stable; ^1H, $^{13}C_{carbene}$ 366.0 ppm, ^{31}P; EA (CH).	99
$R = C_6H_4Me$-*p*	**244**	-	2.3.4 (80)	yellow solid, air-stable; ^1H, $^{13}C_{carbene}$ 371.0 ppm, ^{31}P; EA (CH).	99
$R = SiMe_3$	**245**	-	2.3.4 (87)	yellow solid, air-stable; ^1H, $^{13}C_{carbene}$ 360.6 ppm, ^{31}P; EA (CH).	99
	**246**	-	2.3.4 (69)	brown solid; air-stable; ^1H, $^{13}C_{carbene}$ 320.6 ppm, ^{31}P; IR (KBr) ν_{PF6} 839 cm^{-1}; conductivity (acetone) 115 Ω^{-1} cm^2 mol^{-1}; MS-FAB.	97

Table 5. (Continued)

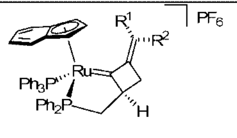
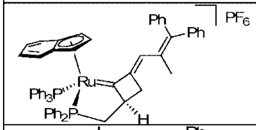
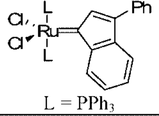
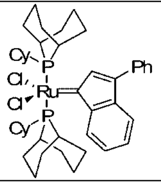
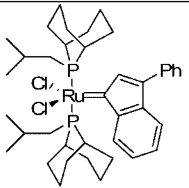
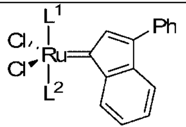
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
R^1, R^2 = $C_{12}H_8$ (fluoren)					
R^1 = R^2 = Ph	**247**	-	2.3.4 (68)	brown solid; air-stable; ^{1}H, ^{13}C$_{carbene}$ 328.1 ppm, ^{31}P; IR (KBr) ν_{PF6} 839 cm^{-1}; conductivity (acetone) 125 Ω^{-1} cm^2 mol^{-1}.	97
R^1 = Ph, R^2 = H	**248**	-	2.3.4 (68)	brown solid; air-stable; ^{1}H, ^{13}C$_{carbene}$ 333.1 ppm, ^{31}P; IR (KBr) ν_{PF6} 839 cm^{-1}; conductivity (acetone) 114 Ω^{-1} cm^2 mol^{-1}; MS-FAB.	97
 R^1, R^2 = $C_{12}H_8$ (fluoren)	**249**	1.914(3)	2.3.4 (70)	brown solid; air-stable; ^{1}H, ^{13}C$_{carbene}$ 318.6 ppm, ^{31}P; IR (KBr) ν_{PF6} 840 cm^{-1}; conductivity (acetone) 110 Ω^{-1} cm^2 mol^{-1}; EA (CH).	97
R^1 = R^2 = Ph	**250**	-	2.3.4 (68)	brown solid; air-stable; ^{1}H, ^{13}C $_{carbene}$ 325.2 ppm, ^{31}P; IR (KBr) ν_{PF6} 839 cm^{-1}; conductivity (acetone) 111 Ω^{-1} cm^2 mol^{-1}; MS-FAB.	97
R^1 = Ph, R^2 = H	**251**	-	2.3.4 (77)	brown solid; air-stable; ^{1}H, ^{13}C $_{carbene}$ 327.2 ppm, ^{31}P; IR (KBr) ν_{PF6} 838 cm^{-1}; conductivity (acetone) 132 Ω^{-1} cm^2 mol^{-1}; EA (CH).	97
R^1 = Ph, R^2 = Me	**252**	-	2.3.4 (68)	brown solid; air-stable; ^{1}H, ^{13}C $_{carbene}$ 326.4 ppm, ^{31}P; IR (KBr) ν_{PF6} 839 cm^{-1}; conductivity (acetone) 131 Ω^{-1} cm^2 mol^{-1}; MS-FAB; EA (CH).	97
	**253**	1.896(5)	2.3.4 (87)	brown solid; ^{1}H, ^{13}C$_{carbene}$ 328.3 ppm, ^{31}P; IR (KBr) ν_{PF6} 838 cm^{-1}; conductivity (acetone) 127 Ω^{-1} cm^2 mol^{-1}; MS-FAB; EA (CH).	133
 L = PPh$_3$	**254**	-	2.3.3 (100)	purple powder; ^{1}H, ^{31}P, ^{13}C$_{carbene}$ 301.0 ppm. Originally the species synthesized from [$RuCl_2(PPh_3)_3$] and HC≡CCPh$_2$OH was regarded as diphenylallenylidene complex.	60-62,134
L = PCy$_3$	**255**	-	2.3.3 (92)	Neolyst^{TM} M1; orange to brick-red solid; ^{1}H, ^{31}P, ^{13}C$_{carbene}$ 293.9 ppm.	61,135,136
	**256**	-	2.3.3 (72)	brown powder; ^{1}H, ^{31}P, ^{13}C$_{carbene}$ 294.5 ppm; EA (CHN); X-ray (high *R*-factor).	103
	**257**	-	2.3.3	Neolyst^{TM} M3; Sasol Technology UK and Umicore AG and Co KG, WO 2007/010453 A2.	137
 L^1 = SIMes, L^2 = PPh$_3$	**258**	-	2.3.3 (86-90)	deep red powder; ^{1}H, ^{31}P, ^{13}C$_{carbene}$ 300.3 ppm; EA (CHN).	105,138
L^1 = SIMes, L^2 = PCy$_3$	**259**	-	2.3.3 (82)	Neolyst^{TM} M2; red powder; ^{1}H, , ^{31}P; ^{13}C$_{carbene}$ 291.4 ppm; EA (CHN).	105,135,139,140
L^1 = IMes, L^2 = PPh$_3$	**260**	-	2.3.3 (83)	orange microcrystalline compound; ^{1}H, ^{31}P; EA (CHN).	104
L^1 = IMes, L^2 = PCy$_3$	**261**	1.861(4)	2.3.3 (79-86)	purple-brown precipitate; ^{1}H, ^{31}P; EA (CHN).	104
L^1 = IPr, L^2 = PPh$_3$	**262**	-	2.3.3 (70)	orange microcrystalline compound; ^{1}H, ^{31}P; EA (CHN).	104

Table 5. (Continued)

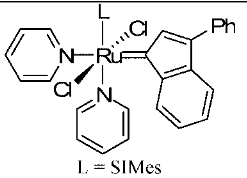
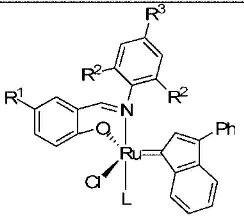
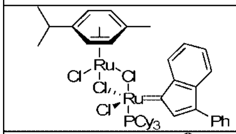
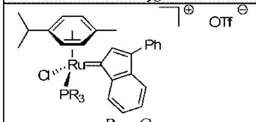
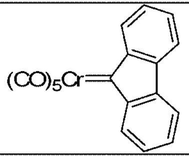
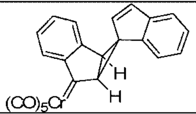
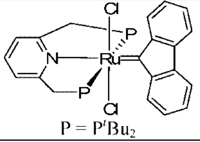
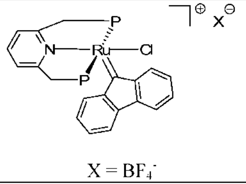
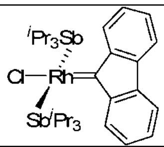
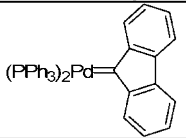
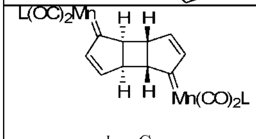
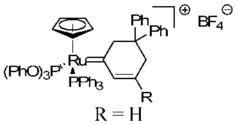
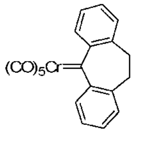
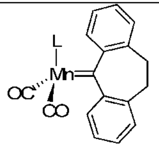
Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
L^1 = IPr, L^2 = PCy_3	**263**	-	2.3.3 (75)	orange microcrystalline compound; ^{1}H, ^{31}P; EA (CHN).	104
L^1 = SIMes, L^2 = py	**264**	1.91(2)	2.3.3 (95)	orange-brown to dark-brown microcrystalline compound; ^{1}H, $^{13}C_{carbene}$ 300.6 ppm; EA (CHN).	105,106
 L = SIMes	**265**	-	2.3.3 (89)	air-sensitive blackish red solid, ^{1}H, $^{13}C_{carbene}$ 301.3 ppm	141
L = IMes	**266**	-	2.3.3 (90)	air-sensitive blackish red solid, ^{1}H, $^{13}C_{carbene}$ 301.9 ppm	141
L = PCy_3	**267**	1.899(4)	2.3.3 (73)	brownish red solid; ^{1}H, ^{31}P, $^{13}C_{carbene}$ 309.3 ppm; EA (CHN).	142
 R^1 = H, R^2 = Me, R^3 = Br, L = PCy_3	**268**	-	2.3.3	dark red solid; ^{1}H, ^{31}P, $^{13}C_{carbene}$ 290.6 ppm; EA (CHN).	147
R^1 = R^3 = H, R^2 = ^{i}Pr, L = PCy_3	**269**	-	2.3.3	no details	140,143
R^1 = NO_2, R^2 = Me, R^3 = Br, L = PCy_3	**270**	-	2.3.3 [$RuCl_2$(Ind)(PCy_3)$_2$] + Tl-salt of salicylaldimin (80)	dark brown solid; ^{1}H, ^{31}P, $^{13}C_{carbene}$ 292.04 ppm; EA (CHN).	144
R^1 = NO_2, R^2 = Me, R^3 = Br, L = SIMes	**271**	-	2.3.3	no details	144
	**272**	-	**258** + [$RuCl_2$(*p*-cymene)]$_2$	Originally the species synthesized from (Ind)(PCy_3)$_2$$RuCl_2$ and [(*p*-cymene)$RuCl_2$]$_2$ was regarded as diphenylallenylidene complex.	61,134,145
 R = Cy	**273**	-	2.3.3 (83)	brown solid; decomposition at r.t.; IR; ^{1}H, ^{31}P, $^{13}C_{carbene}$ 334.1 ppm.	63,64
R = Ph	**274**	-	2.3.3 (90)	^{1}H, ^{31}P, $^{13}C_{carbene}$ 336.1 ppm.	63
R = ^{i}Pr	**275**	-	2.3.3 (83)	^{1}H, ^{31}P, $^{13}C_{carbene}$ 333.2 ppm.	63
	**276**	-	2.3.2 (67)	dark green solid; dec. > 20 °C; IR (hexane) ν_{CO} 2060, 1972, 1946 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 361.29 ppm; HR-MS.	41,42
	**277**	-	2.3.2 (47)	black solid; ^{1}H, $^{13}C_{carbene}$ 370.89 ppm; IR (hexane) ν_{CO} 2056, 1976, 1964 cm^{-1}; HR-MS.	42
 P = P^{t}Bu$_2$	**278**	1.936(9)	2.3.2 (83)	orange microcrystals; stable in solution at r.t.; ^{1}H, $^{13}C_{carbene}$ 316.8 ppm, ^{31}P; EA (CH).	55

Table 5. (Continued)

Compound	Number	M-C$_{carbene}$ [Å]	Method of Preparation (% yield)	Selected Data	Ref.
 X = BF$_4^-$	**279**	1.877(5)	**140** + AgBF$_4$ (90)	dark red solid; ^{1}H, ^{13}C$_{carbene}$ 299.9 ppm, ^{31}P, ^{19}F; EA (CH).	55
X = Cl$^-$	**280**	-	**140** at 110 °C in toluene (90)	dark red solid; ^{1}H, ^{13}C$_{carbene}$ 300.8 ppm, ^{31}P; EA (CH).	55
	**281**	-	2.3.2 (94)	brown crystals; mp (°C) 55 (dec.); ^{1}H, ^{13}C$_{carbene}$ 309.3 ppm; EA (CH).	55
	**282**	-	2.3.2	red purple powder; mp (°C) 135-140; IR; EA (CH).	101
 L = Cp	**283**	-	2.3.2 (21)	black crystals; air-stable; IR (CHCl$_3$) ν_{CO} 1963, 1900 cm^{-1}.	100
L = MeCp	**284**	1.878(8)	2.3.2 (20)	black crystals; air-stable; IR (CHCl$_3$) ν_{CO} 1965, 1897 cm^{-1}.	100
 R = H	**285**	1.957(4)	a) [Ru$^-$–C≡C–C(PPh$_3$)$_2$–CH$_2$-C=CH$_2$] + HBF$_4$ (92 %) b) [Ru$^+$=C=CH–C(PPh$_3$)$_2$–CH$_2$–C=CH$_2$] in MeOH (quantitative)	reddish orange solid; ^{1}H, ^{13}C$_{carbene}$ 321.4 ppm, ^{31}P; MS-FAB; EA (CH).	107
R = OH	**286**	-	[Ru$^+$=C=CH–C(PPh$_3$)$_2$–CH$_2$–C≡CH] + H$_2$O (91)	reddish orange solid; ^{1}H, ^{13}C$_{carbene}$ 300.5 ppm, ^{31}P; MS-FAB; EA (CH).	107
R = OMe	**287**	-	[Ru$^+$=C=CH–C(PPh$_3$)$_2$–CH$_2$–C≡CH] + MeOH (93)	reddish orange solid; ^{1}H, ^{13}C $_{carbene}$ 300.5 ppm, ^{31}P; MS-FAB; EA (CH).	107
R = OEt	**288**	-	[Ru$^+$=C=CH–C(PPh$_3$)$_2$–CH$_2$–C≡CH] + EtOH (89)	reddish orange solid; ^{1}H, ^{13}C$_{carbene}$ 300.7 ppm, ^{31}P; MS-FAB; EA (CH).	107
	**289**	-	2.3.2 (53)	black solid; IR (hexane) ν_{CO} 2066, 1981, 1960 cm^{-1}; ^{1}H, ^{13}C$_{carbene}$ 419.14 ppm; HR-MS.	42
 L = Cp	**290**	1.853(5)	2.3.2 (72)	deep green needles; air-stable; mp (°C) 108; ^{1}H, ^{13}C$_{carbene}$ 362.23 ppm; IR (CHCl$_3$) ν_{CO} 1991, 1933 cm^{-1}; MS-EI; EA (CHMn).	40,108
L = MeCp	**291**	-	2.3.2 (65)	deep green needles; mp (°C) 63-64; ^{1}H; IR (CHCl$_3$) ν_{CO} 1985, 1927 cm^{-1}; MS-EI; EA (CHMn).	40

of excess HCl to **A** restores the CHT complex **C**, differing from the initial complex **123** only by the counterion.[38] A further reaction at the CHT ligand of the iridium complex **123** occurs with (η^6-*p*-xylene)Mo(CO)$_3$, yielding the hetero-

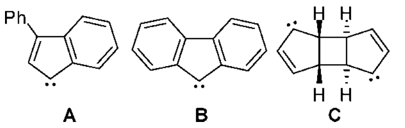


Figure 9.

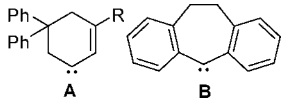
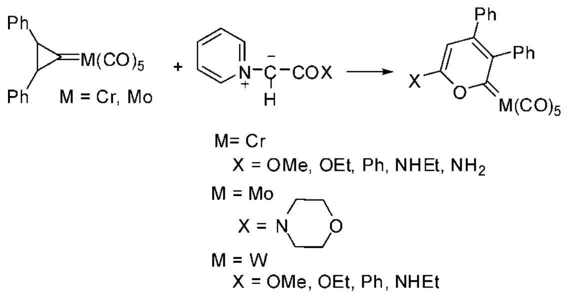
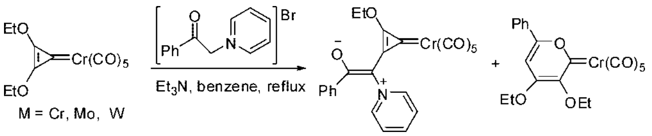


Figure 10.

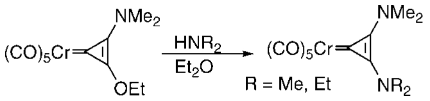
Scheme 35



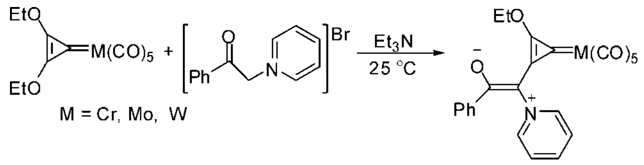
Scheme 36



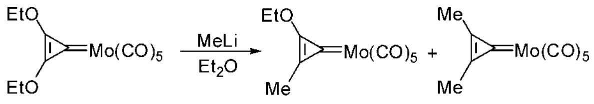
Scheme 37



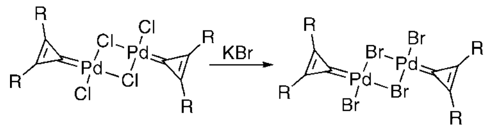
Scheme 38



Scheme 39



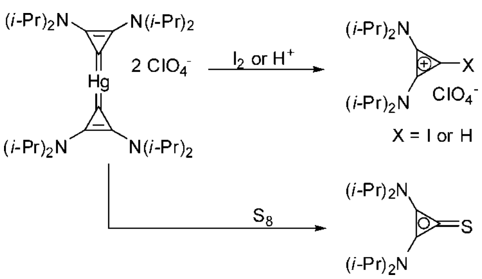
Scheme 40



bimetallic complex **124** with a Mo(CO)$_3$ moiety coordinated to the tropylium ring.[38]

With the exception of the above-mentioned iridium−pincer complex **123**, all hitherto in the literature reported CHT complexes are equipped with unsubstituted cycloheptatrienylidene ligands. However, several examples of metal complexes bearing the benzannelated CHT ligands **A**, **B**, and **C** (Figure 14) have been described.

Scheme 41



When comparing the iron complexes **113**, **114**, and **116** and the ruthenium complexes **119** and **120** bearing the benzannelated ligands **A** and **B** with their analogous nonannelated CHT complexes **112**, **115**, and **118**, there is found no significant difference in the chemical and spectroscopical properties. NMR shifts of the metal-bonded carbene carbon atoms and barriers of rotation about the metal−carbon bond in these complexes indicate slightly stronger metal−carbene backbonding to the benzannelated ligand **A** than to the monocyclic cycloheptatrienylidene; on the other hand, the latter is a better acceptor than the benzannelated carbene **B**.[31,32]

The reactions of all hitherto described metal complexes with the dibenzannelated cycloheptatrienylidene **C** reflect the electrophilic character of this carbene ligand, different from nonannelated CHT and its benzannelated congeners **A** and **B**. They undergo insertion reactions into the metal−carbene bond, similar to complexes with diphenylcarbene and other "Schrock-type" carbenes. The dicarbonyl (η^5-cyclopentadienyl)manganese complexes **110** and **111** are transferred into η^2-ketene complexes by high-pressure carbonylation (Scheme 43).[84]

The pentacarbonylchromium complex **107** reacts with nucleophilic alkynes such as ynamines under formation of unsaturated aminocarbene complexes (Scheme 44).[41,42]

Unfortunately, no metal complexes of the same type, both with the tricyclic carbene **C** and with the monobenzannelated CHTs **A** and **B** (Figure 14), are known for detailed comparative studies of their ligand properties.

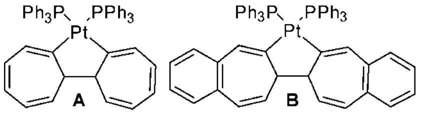


Figure 11.

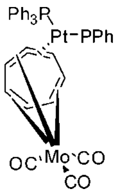
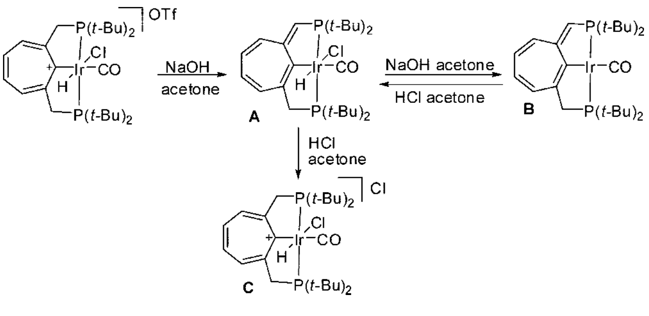


Figure 12.

Scheme 42



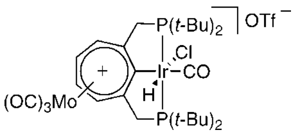
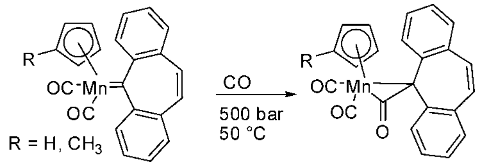
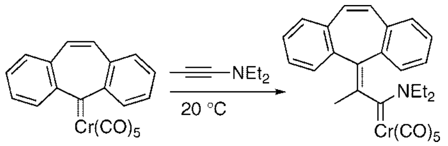


Figure 13.

Scheme 43



Scheme 44



5. Catalytic Applications

Early research concerning carbocyclic carbene complexes focused primarily on synthesis, structure, and reactivity. The application of these compounds in homogeneous catalysis was of minor interest and limited to a few highly sophisticated reactions or catalyst systems, respectively. However, this fact considerably changed during the last few years when, on the one hand, the ruthenium catalysts bearing the novel structural motif of a carbocyclic indenylidene ligand slowly emerged as an individual family of metathesis catalysts and, on the other hand, when palladium catalysts supported by carbocyclic carbene ligands entered the field of the intensively studied C−C and C−N coupling reactions.

5.1. Isomerization of Quadricyclane to Norbornadiene

In 1988, the first application of a carbocyclic carbene ligand in catalysis was reported by the group of Yoshida.[76] Interested in molecular energy storage processes, they found that cyclopropenylidene palladium complexes catalyze the exothermic valence isomerization of quadricyclane to norbornadiene (Scheme 45) and exhibit comparably high activities as di-μ-chloro-bis(norbornadiene)dirhodium(I), however, combined with the benefit of air stability.

A detailed mechanistic study revealed that the catalytic active species is formed by dissociation of the weakly coordinated pyridine derivative. Both the electronic nature of the carbene ligand (governed by the tertiary butyl or the diisopropylamino substituents) and the σ-donor strength of the leaving ligand were shown to affect the rate constant. It is noteworthy that a very similar concept was lately introduced as PEPPSI system by Organ and co-workers for NHC palladium catalysts (PEPPSI = pyridine-enhanced precatalyst preparation, stabilization, and initiation).[112−114]

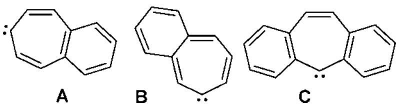
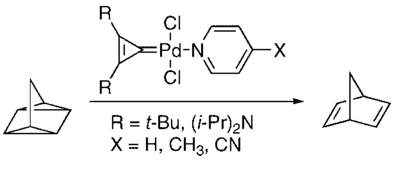
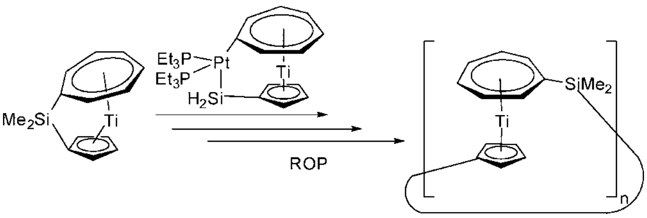


Figure 14.

Scheme 45



Scheme 46



5.2. Regioselective Si−C Activation

An exceptional catalyst system for regioselective Si−C activation in silicon-bridged *ansa*-cycloheptatrienyl−cyclopentadienyl complexes was discovered by Tamm et al. in 2005.[47] Platinasilatroticenophane, which is accessible by reaction of $Pt(PEt_3)_3$ with silatroticenophane, can be used as a single-source catalyst for the ring-opening polymerization of the original highly strained precursor (Scheme 46). Propagation is supposed to proceed via σ-bond metathesis of the Pt−Si and Si−C bonds and reductive elimination from intermediate platinacyclic oligomers, leading to cyclic oligotrotricenes.

The polymerization reaction was monitored by ^{1}H and ^{29}Si NMR spectroscopy, and the formation of a regioregular cyclic polymer was concluded. By MALDI-TOF mass spectrometry of the isolated polymeric material, molecular peaks for oligomers between $n = 5$ and $n = 23$ could be detected.[89] A similar reactivity is suggested for the vanadium analogue.[47]

5.3. Olefin Metathesis

The stable ruthenium−indenylidene complex **A**, originally regarded as allenylidene species, emerged to be the parent compound of a novel class of metathesis precatalysts shown in Figure 15. Offering several benefits like ease of access, improved activity and stability, and functional group tolerance, the congeners **B**−**F** can be regarded as valuable extensions of established alkylidene-based catalyst systems.

A wide application profile comprises polymerization reactions (ring-opening metathesis polymerization, ROMP; atom-transfer radical polymerization, ATRP), ring-closing reactions (RCM), and olefin cross-metathesis reactions. Additionally, Ru−indenylidene complexes exhibit catalytic

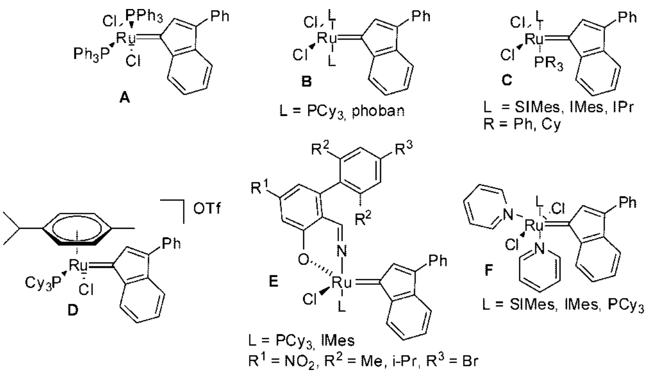


Figure 15.

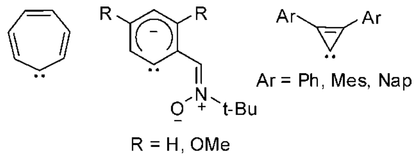


Figure 16.

activity in nonmetathesis chemistry such as nucleophilic additions and hydrosilylations of alkynes. As this specific topic was already reviewed once in 2005,[148,149] we would like to refer only to the latest literature here, i.e., two excellent articles by Monsaert et al.[105] and Nolan and coworkers[115] and a valuable, rather practical guideline given by Bieniek et al.[116]

5.4. Cross-Coupling Reactions

First application of the simple, carbocyclic carbene cycloheptatrienylidene (CHT) as a supporting ligand in palladium-catalyzed C−C coupling reactions in 2006 drew new attention to this ligand concept.[43] The activities found were comparable with or even superior to those of well-established NHCs. The complex *cis*-(CHT)(PPh$_3$)PdCl$_2$ gave good results in numerous variants of Heck and Suzuki coupling reactions. For instance, with only 10^{-4} mol % of this molecularly defined precatalyst, *p*-bromoacetophenone and *n*-butyl acrylate underwent C−C coupling at 145 °C, which corresponds to turn over numbers (TON) of the order of 10^6 at turn over frequencies (TOF) of $\gg 10^3$ h^{-1}. Biphenyl could be obtained quantitatively from bromobenzene and phenylboronic acid at 130 °C (10^{-3} mol % Pd), and the conversion rates (TON) were of the order of 10^4−10^6. With higher catalyst loadings, chloroarenes also could be coupled efficiently. In addition, the CHT-supported system did not suffer from an induction period.

It was a logical step to also include other carbocyclic ring systems into catalytic evaluation. Wass et al. found high activities in Heck and Suzuki reactions for the 2,3-diphenylcyclopropenylidene ligand.[117] However, only conversions were reported. A more detailed study for Suzuki coupling including a direct comparison of the CHT ligand and a series of 2,3-diarylcyclopropenylidene ligands in our group revealed the superior role of the seven-membered ring system. Faster initiation in line with generally higher yields was observed. A variation of the aryl substituents of the cyclopropenylidene system had only little influence on the catalytic activity.[78] The highest efficiencies so far involving a carbocyclic carbene complex were reported by Yao et al. for Heck reactions of aryl bromides; they used palladium precatalysts bearing their bidentate six-membered anionic carbene ligand (Figure 16). For example, with a very low catalyst loading of 8 × 10^{-5} mol % based on palladium, the deactivated substrate *p*-bromoanisole with styrene could be coupled with a TON > 900 000. However, high temperatures (140−160 °C) and long reaction times (20−169 h) are required. For chloroarenes, a significant loss in activity was observed.[49]

Recently, the application of carbocyclic carbene ligands was extended to palladium catalyzed C−N coupling reactions. Similar to the C−C coupling, the group around Wass and Green concentrated their efforts[118] on the smallest possible carbocyclic carbene, cyclopropenylidene, whereas in our laboratories the seven-membered ring system also was included into the studies.[15] With the CHT system, superior results could be realized in comparison to the 2,3-diphenylcyclopropenylidene system (Figure 17). The conditions for this yield versus time plot for the coupling of *p*-bromobenzotrifluoride (1.0 mmol) with morpholine (1.2 mmol) were room-temperature catalyzed by 0.5 equiv [LPdCl$_2$]$_2$ (**I**, −●−; **II**, --■--) in situ with 1.0 equiv of P*t*-Bu$_3$ (other conditions: 2.0 mol % Pd, 1.4 mmol of NaO*t*-Bu, 8 mL of toluene; GC yield with *n*-eicosane as the internal standard).[15] In addition, appreciable activity was only observed with a second strong donor ligand attached to the palladium metal center. The best results could be obtained with more basic alkyl phosphanes like P*t*-Bu$_3$. However, the crucial role of the carbocyclic carbene ligand was proven by comparison with a carbene-free palladium metal source. As already mentioned, carbocyclic carbene palladium precatalysts do not suffer from an induction period.

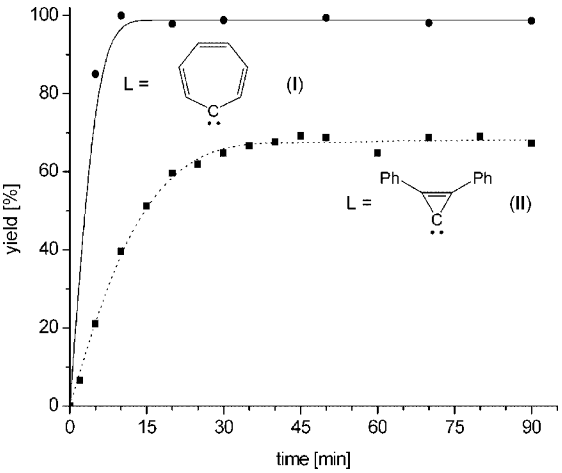


Figure 17.

6. Concluding Remarks

This review highlights the wide range of carbocyclic complexes, structure, reactivity, and catalytic applications studied to date. Although catalytic applications are primarily concerned with well-characterized complexes of palladium and ruthenium, the emergence of a free carbene route for the diaminosubstituted cyclopropenylidene ligand means this field is expected to blossom in coming years. Use of these carbenes as strong σ-donor ligands is expected to extend beyond simple phosphane substitutes as has been observed for N-heterocyclic carbene ligands. In the case of cyclopropenylidenes, a large variety of substituents at the carbocycle is available to influence the metal−ligand bond and the reactivity of the complexes. However, their ability to alter the steric environment around the metal center is limited because of the position of the substituents at the back of the cyclopropene ring pointing away from the metal center. The cycloheptatrienylidene motif would be better suited for tailored ligands because there is the possibility to control the coordination sphere of the metal. These alterations should expand the utility of such complexes for special applications, e.g., in homogeneous catalysis. The range of different CHT ligands is currently rather limited; attention should be focused on expanding cycloheptatriene derivatives to include systems substituted in the 2,7-position for the generation of new CHT ligands. In addition, new, generally more facile methods to prepare CHT metal complexes are necessary, though the free carbene route could be challenging to apply to CHT systems because of the high dimerization tendency of free cycloheptatriene. Furthermore, modern computational studies investigating the influence of substituents and benzannelation at the cycloheptatriene moiety, on the carbene−metal bond, and on the properties of resulting CHT metal complexes could be helpful. Recent computational studies[119] on the feasibility of silicon and germanium analogues of cyclopropenylidene suggest that these species could be viable targets to expand the class of carbocyclic carbene complexes.

7. Abbreviations

n-Bu	*n*-butyl
t-Bu	*tert*-butyl
C3	cyclopropenylidene
CHT	cycloheptatrienylidene
CHTE	cycloheptatetraene
CI	chemical ionization
COD	cyclooctadiene
COE	cyclooctene
Cp	cyclopentadienyl
Cy	cyclohexyl
dec.	decomposition
DFT	density functional theory
DMF	dimethylformamide
DMSO	dimethylsulfoxide
EA	elemental analysis
EI	electron impact
equiv	equivalent
Et	ethyl
FAB	fast atom bombardment
GC	gas chromatography
HOMO	highest occupied molecular orbital
IMes	1,3-dimesitylimidazolin-2-ylidene
IPr	1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
IR	infrared spectroscopy
LUMO	lowest unoccupied molecular orbital
MALDI	matrix-assisted laser desorption ionization
Me	methyl
Mes	mesityl
MO	molecular orbital
MS	mass spectrometry
Nap	naphthyl
NHC	N-heterocyclic carbene
OAc	acetoxy
OTf	triflate
Ph	phenyl
i-Prop	isopropyl
SIMes	1,3-dimesitylimidazolidin-2-ylidene
TCNQ	7,7,8,8-tetracyano-1,4-quinodimethane
THF	tetrahydrofuran
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TOF	turnover frequency
TON	turnover number
UV	ultraviolet spectroscopy

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