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STRUCTURAL CONSEQUENCES OF BONDING IN TRANSITION METAL CARBENE COMPLEXES

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CONTENTS

A. INTRODUCTION

In 1964 the first transition metal carbene complexes [1] were prepared and characterized by Fischer and Maasböl [2]. Today we know that carbene complexes are a principal class of compounds in organometallic chemistry and that they play an important role in metal-catalyzed reactions, particularly in olefin metathesis [3]. A prerequisite for understanding carbene complex reactions, both stoichiometric and catalytic, is to understand the nature of the metal carbon bond in these complexes and how this bond is influenced by the remainder of the molecule. The aim of this review is to derive this information from the available crystal structures of carbene complexes (about 160 in August 1983) [4–21]. Results of other physical chemical investigations will only be mentioned although their importance is not underestimated.

Each crystal structure contains information about the electronic structure of a particular compound. This information may be obscured by the limitations of the method of structure determination and by superimposed crystal packing effects. However, by comparison of a number of structures of

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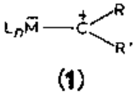
chemically related compounds, systematic trends for relevant structural parameters can be worked out, which, for statistical reasons, are more probably void of such restrictions. Bürgi, Dunitz and others have shown that such systematic analyses of crystal data are a powerful research technique for all kinds of stereochemical and structural problems [22].

Throughout this article the term "carbene complex", coined by Fischer [2], is exclusively used and is regarded as synonymous with the term "alkylidene complex". Only complexes in which a terminal ligand CRR′ or CR_2 (R,R′ = organic substituents) acts as a two-electron donor ligand, according to formal electron counting rules, are considered as carbene complexes. Complexes with "carbene bridges" ($L_nM{-}CR_2{-}ML_n$, L_nM = transition metal complex fragment) or with "carbyne bridges" ($L_nM\overset{\cdots}{-}CR\overset{\cdots}{-}ML_n$) between metal atoms will not be discussed here, though in the latter complexes bonding is closely related to carbene complexes. Also vinylidene and allenylidene complexes ($L_nM{=}C{=}CR_2$ and $L_nM{=}C{=}C{=}CR_2$) will not be taken into account. However, the bonding phenomena discussed for carbene complexes can also be applied to these complexes.

B. BONDING IN TRANSITION METAL CARBENE COMPLEXES

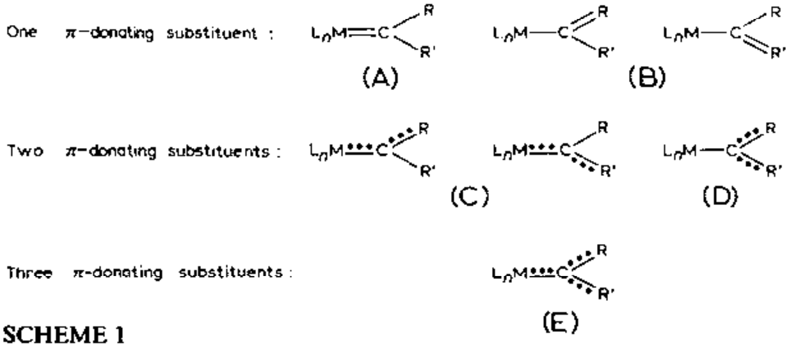
Bonding between a transition metal and a carbene ligand may be regarded as interaction between the orbitals of a singlet carbene CR_2 (a bent molecule having an sp^2-type electron lone pair within the CR_2 plane and an empty *p* orbital perpendicular to this plane) and the orbitals of a suitable metal complex fragment [23]. The carbene unit donates electrons from its lone pair to an empty metal orbital, thus forming the metal–carbon σ-bond. The bonding interaction between both atoms is usually stabilized by backbonding, i.e. by transfer of electron density from a filled *d*-like metal orbital into the empty carbene *p* orbital. The degree of electron transfer via bonding and backbonding is determined by the separation of the energy levels of the orbitals involved. The energy levels of the carbene (CR_2) orbitals depend on the electronic nature of the substituents R, while the metal orbitals are influenced by the kind of metal, its coordination geometry and the co-ligands.

In a more graphic approach carbene complexes may be viewed as metallated carbenium ions (**1**), i.e. carbenium ion, in which one of the substituents



(**1**)

is a metal complex moiety (L_nM) [24]. The empty *p* orbital at the carbene carbon atom is perpendicular to the plane of the three σ bonds of the carbene carbon ("carbene plane"). By π interaction between the carbene carbon atom and its substituents, electron deficiency at the carbene carbon is reduced. In principle, only one sufficiently π-donating substituent (R, R′ or L_nM in **1**) is necessary to yield stable compounds. In vinyl or related complexes one of the organic substituents (R or R′) is the sole π donor (B in Scheme 1). If only L_nM is π donating, carbene complexes in a very narrow sense, with a pure metal–carbon double bond, are obtained (A in Scheme 1). The more common situation is that two or all of the substituents bonded to the carbene carbon have π-donor properties (C–E in Scheme 1). In this case the π-donating groups compete with each other for π bonding with the carbene carbon. As will be discussed in more detail in Section C, the bond order between the carbene carbon and a particular substituent is not only determined by the π-donor ability of this very substituent, but also by the π-donor abilities of the other carbene substituents. Between A–E (Scheme 1) any transition is possible. The magnitude and kind of partial charge remaining on the carbene carbon atom depends on the electronic properties of its substituents. In most of the carbene complexes investigated so far the carbene carbon atom is more or less electrophilic. However, in Schrock's electron deficient carbene complexes of tantalum, niobium and tungsten [25] the carbene carbon is nucleophilic. MO calculations have shown that this is a consequence of the extremely good overlap between metal and carbene orbitals in these complexes [23i,n].



SCHEME 1

C. BOND LENGTHS BETWEEN THE CARBENE CARBON AND ITS SUBSTITUENTS

In closely related complexes, bond lengths between the carbene carbon and its substituents should correlate with "bond orders". A comparison of bond lengths should therefore provide information about bonding. For example, in $(CO)_5CrC(OMe)Ph$ [6a] (Fig. 1) the methoxy group and the $(CO)_5Cr$ moiety act as π-donating substituents. Therefore the Cr–C(carbene) (204(3) pm) and C(carbene)–O bond lengths (133(2) pm) are shorter than

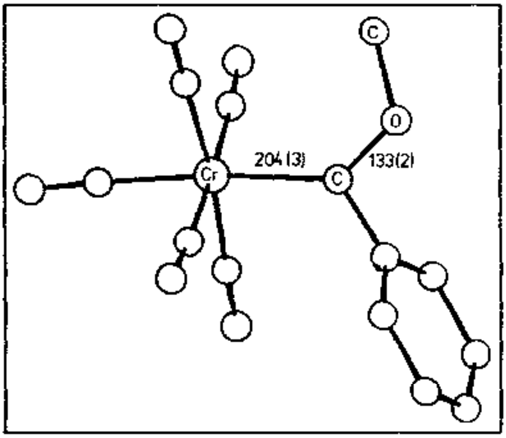


Fig. 1. $(CO)_5CrC(OMe)Ph$ [6a]. The phenyl ring is approximately perpendicular to the carbene plane.

expected for single bond distances. The third substituent, the phenyl group, does not π-interact with the carbene carbon [26]. If the latter substituent is replaced by another with good π-donor properties, like an amino group or a phosphorus ylide function, the degree of π bonding between the carbene carbon and both the metal and oxygen atoms is diminished. The reduced backbonding from the metal results in a lengthening of the Cr–C(carbene) distance in $(CO)_5CrC(OEt)NMe_2$ (213.4(4) pm) [6h] (Fig. 2) and $(CO)_5CrC(OSiMe_3)CHPMe_3$ (213.7(7) pm) [6g] compared with $(CO)_5CrC(OEt)Ph$. Also the C(carbene)–O distances in these complexes are

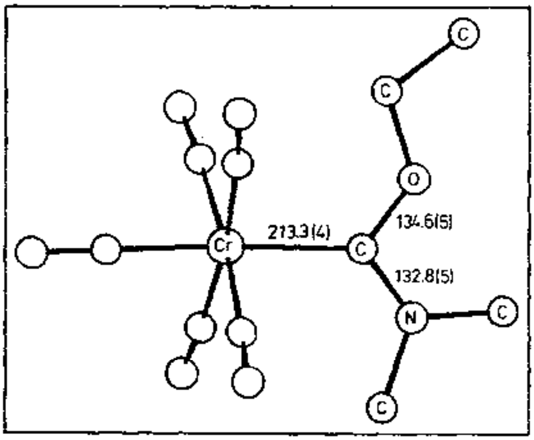


Fig. 2. $(CO)_5Cr(OEt)NMe_2$ [6h]. All atoms of the carbene ligand are more or less coplanar.

lengthened (134.6(5) pm in $(CO)_5CrC(OEt)NMe_2$ and 137.8(8) pm in $(CO)_5CrC(OSiMe_3)CHPMe_3$). Though this is in agreement with the previous statement, emphasis has to be put on the fact that differences between the distances of two light atoms are not always significant and therefore are less suited for a thorough discussion. The reason for this is that the positional parameters of light atoms have higher standard deviations than heavier ones, along with smaller absolute alterations of the distances. In this case spectroscopic methods often provide more precise information about bonding (see ref. 27c, for example).

In $(CO)_5CrC(XR)R'$ complexes replacement of an alkoxy group (XR = OR) by an amino group ($XR = NR_2$), which is a much better π donor, results in a distinct lengthening of the Cr–C(carbene) distance from about 200–205 pm to about 210–215 pm (Table 1).

Comparison of bond lengths in $(CO)_5CrC(OMe)Ph$ [6a] (Fig. 1) and $(\eta^6\text{-}C_6H_6)(CO)_2CrC(OMe)Ph$ [7e] shows that the metal complex fragment is not privileged compared with the organic groups in the electronic cooperation of the substituents at the carbene carbon. Replacement of the $(CO)_5Cr$ moiety by the better π-donating $(\eta^6\text{-}C_6H_6)(CO)_2Cr$ moiety (while keeping

TABLE 1

Bond lengths (pm) in carbene complexes $(CO)_5CrC(XR)R'$ with non-cyclic alkoxy-, thio- or (di)alkylaminocarbene ligands

XR	R′	Cr–C(carbene)	C(carbene)–X	Ref.
OMe	Ph	204 (3)	133 (2)	6a
OEt	C≡CPh	200 (2)	132 (2)	6b
OEt	$SiPh_3$	200 (2)	133 (2)	6c
SPh	Me	202.0 (3)	169.0 (3)	6s
SCH=C(OMe)Ph	Ph	202.9(10)	167.1 (10)	6t
$SCH_2SCH_2SCH{=}C(OMe)Ph$	Ph	202.7 (5)	167.3 (5)	6t
NHMe	Me	209	133	6i
NEt_2	Me	216 (1)	131 (1)	6j
NEt_2	H	208.4 (2)	130.0 (3)	6k
NEt_2	Cl	211.0 (5)	129.9 (8)	6l
NEt_2	NCO	212 (1)		6m
NEt_2	NCS	211 (1)		6m
NEt_2	$SnPh_3$	211 (1)	133 (2)	6p
NHC_6H_{11}	$C(OMe){=}CH_2$	215 (1)	132 (1)	6o
NEt_2	SePh	217.1 (8)	128 (1)	6q
NMe_2	OEt	213.3 (4)	O: 134.6 (5) N: 132.8 (5)	6h
NMe_2	N=C(OMe)Ph	213.5 (4)	134.0 (6)	6r
NEt_2	$C(NEt_2)Cr(CO)_5$	219.0 (7)	130.6 (9)	6n

the carbene ligand constant) has the same consequences as an analogous replacement of one of the organic substituents: π bonding between the metal and the carbene carbon is strengthened at the cost of the π bond between the carbene carbon and the oxygen atom. Thus in $(\eta^6\text{-}C_6H_6)(CO)_2CrC(OMe)Ph$ the Cr–C(carbene) distance is about 10 pm shorter and the C(carbene)–O distance about 3 pm longer than in $(CO)_5CrC(OMe)Ph$.

Shortening of a metal–C(carbene) bond length by substitution of CO ligands by a π-bonded aromatic (usually a cyclopentadienyl) ligand is a general trend (for rhenium see [17a,b,f], for molybdenum see [6c,12d], for tungsten see [21b,l], for example).

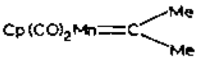
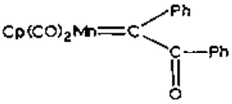
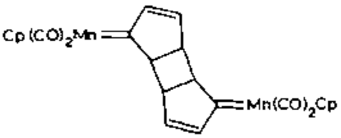
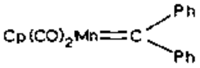
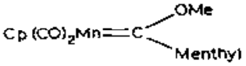
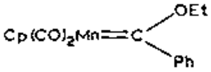
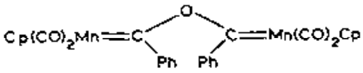
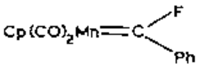
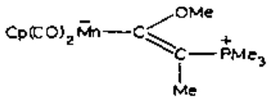
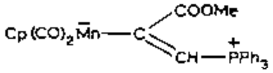
Generally, a high metal–carbon bond order in carbene complexes (ideally, a double bond (A in Scheme 1)) can only be expected if the metal complex fragment is a much better π donor than both organic substituents at the carbene carbon. The structural consequences of this bonding situation can best be substantiated for $Cp(CO)_2Mn$–carbene complexes ($Cp = \eta^5\text{-}C_5H_5$ or $\eta^5\text{-}CH_3C_5H_4$), for which a relatively large number of structure analyses is available (see Table 2). The most important consequence of the high Mn–C(carbene) bond order is that stable complexes can be obtained even if none of the organic carbene substituents has π-donor properties (see Table 2 for examples). Analogous complexes with weaker backbonding metal complex fragments, like $(CO)_5Cr$ or $L_3Pt(II)$, would be non-existent or, at least, very unstable.

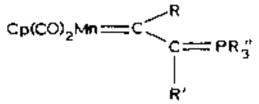
Structural evidence for the high metal–carbene carbon bond order in $Cp(CO)_2Mn$–carbene complexes is obtained from the fact that the Mn–C(carbene) distances are not significantly influenced by the nature of the organic carbene substituents. The contrary would be expected for carbene complexes with weaker backbonding metal complex moieties. In $Cp(CO)_2$ Mn–carbene complexes the Mn–C(carbene) distances are in the range 185–189 pm, whether there is an oxy substituent or not (Table 2), because oxy substituents can hardly compete with the $Cp(CO)_2Mn$ fragment for π bonding with the carbene carbon. Consequently, the C(carbene)–O distances in such $Cp(CO)_2Mn$–carbene complexes are in the range of $C(sp^2)$–O single bond lengths. $Cp(CO)_2MnC(F)Ph$ is a special case and will be discussed in Section H.

Constant Mn–C(carbene) bond lengths of course can be expected only as long as none of the organic substituents competes effectively with the metal complex fragment as a π donor. Whether an amino substituent would be sufficiently π donating cannot be answered, because no structure of a $Cp(CO)_2Mn$–aminocarbene complex is known. However, in the phosphorus ylide-substituted complexes $Cp(CO)_2MnC(OMe)C(Me)PMe_3$ [11i] and $Cp(CO)_2MnC(CO_2Me)CHPPh_3$ [11j] a pronounced lengthening of the Mn–C("carbene") distances (Table 2) shows that the ylide substituent is a much better π donor than the $Cp(CO)_2Mn$ moiety. Shortening of the C(carbene)–C(ylide) distance with respect to a single bond and lengthening of the C(ylide)–P distances with respect to a double bond additionally proves that the vinylic form **3** is a better description of the bonding situation in these complexes than the carbene-like form **2**. The chemical properties of these complexes support this interpretation [6g].

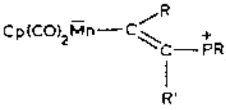
TABLE 2

$Cp(CO)_2Mn$–carbene complexes ($Cp = \text{-}\eta^5C_5H_5$ or $\text{-}\eta^5CH_3C_5H_4$)

Carbene complex	Mn–C(carbene) (pm)	Approx. conformation	Ref.
	186.8 (10)	**10**	11a
	188.2 (2)	**10**	11b
	187.8 (8)	**10**	11d
	188.5 (2)	**10**	11c
	189 (2)	**9**	11e
	186.5 (14)	**10**	11f
	187 (2)	**10**	11g
	183.0 (5)	**10**	11h
	199 (1)	**9**	11i
	198.5 (3)	**9**	11j



(2)



(3)

Comparison of $Cp(CO)_2MnC(OEt)Ph$ (Fig. 3) [11f], which is a typical carbene complex, with the vinyl-like $Cp(CO)_2MnC(OMe)C(Me)PMe_3$ shows that, by (formal) replacement of a single substituent (–Ph by –C(Me)PMe_3), transition from one type of organometallic compound to another (from A to B in Scheme 1) is achieved. This example demonstrates that all compounds in which an sp^2-hybridized carbon atom is bonded to a transition metal atom should be treated as a single class of compounds from a bonding point of view.

Carbene complexes, in which the metal–carbene carbon bond corresponds more or less to a single bond (B and D in Scheme 1) are not uncommon. D (Scheme 1) is mainly found in diaminocarbene and related complexes, many of which are known (Fig. 4, for example). It was pointed out very early on the basis of the metal carbon bond lengths (which are close to single bond distances) that these complexes are better regarded as metallated amidinium ions [28].

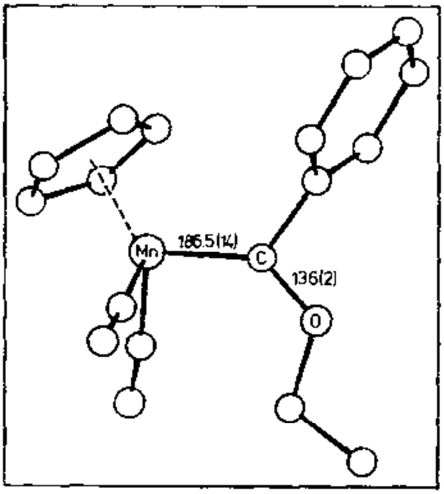


Fig. 3. $Cp(CO)_2MnC(OEt)Ph$ [11f]. The dihedral angle between the carbene plane and the mirror plane of the $Cp(CO)_2Mn$ fragment is 14°. Phenyl ring and carbene plane are approximately perpendicular to each other.

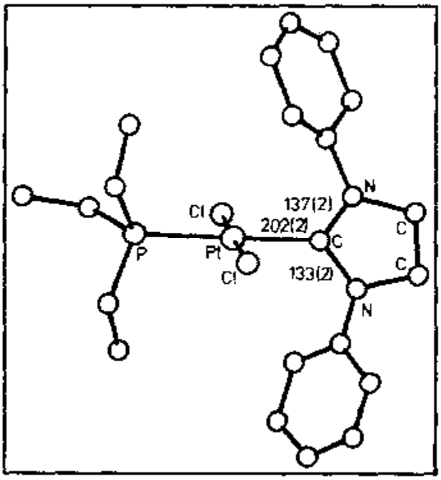


Fig. 4. *trans*-$Cl_2(PEt_3)Pt\overline{CN(Ph)CH_2CH_2N}Ph$ [16d]. The carbene plane and the coordination plane of Pt are approximately perpendicular to each other.

Up to this point mainly $(CO)_5Cr$– and $Cp(CO)_2Mn$–carbene complexes have been mentioned, for which the most systematic and comprehensive structural data are available. Furthermore, these complexes are particularly well suited as models, since by the symmetry of the metal complex fragments and by the favourable steric properties of both CO and Cp ligands steric interactions between substituents at the carbene carbon and ligands at the metal are usually not a crucial issue. For octahedral aminocarbyne complexes of chromium, in which bonding of the aminocarbyne ligand is very carbene-like, a sterically demanding *cis* ligand, like triphenylphosphine, was shown to cause considerable distortion of the bond angles at chromium and to weaken the metal–carbyne carbon bond [29]. Since phosphines are very often used as co-ligands, particularly in noble metal carbene complexes, similar steric effects on the metal–carbene carbon bond cannot be neglected. Apart from steric effects, which may render an analysis of the structural parameters more difficult, the structural consequences of the bonding situation in other types of carbene complexes should be the same as in $(CO)_5Cr$– or $Cp(CO)_2Mn$–carbene complexes.

A relatively large number of structure analyses was performed for square-planar Pt(II) carbene complexes [16] (Fig. 4). Though the ligands L of the L_3Pt fragment vary considerably, a few general trends can be established: (1) Pt–C(carbene) distances are shortest when (π-donating) chloride is *trans* to the carbene ligand (182–201 pm). This distance increases to 200–213 pm if chloride is replaced by a phosphine or methyl ligand (which render the L_3Pt fragment a weaker donor). (2) Since in alkoxy- and aminocarbene complexes of this type, with only one π-donating organic substituent present, the C(carbene)–O (122–133 pm) and C(carbene)–N distances (125–129 pm) are rather short, L_3Pt fragments have to be considered as poor π donors.

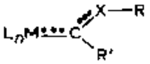
D. ORIENTATION OF ORGANIC SUBSTITUENTS

π bonds between the carbene carbon and its substituents are only possible if the orbitals concerned have the right symmetry and orientation to provide sufficient overlap. A prerequisite is a proper orientation of each π-interacting substituent relative to the carbene plane. On the other hand, the orientation of the substituents provides data concerning their π-interaction with the carbene carbon.

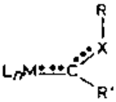
Quite a lot of carbene complexes with alkoxy and (di)alkylamino substituents have been investigated. The corresponding oxygen or nitrogen atom is sp^2-hybridized, with a filled p orbital perpendicular to the plane C(carbene)–O–C(alkyl) or the plane of the (planar) amino group, respectively. For π interaction between the filled orbital at the heteroatom and the empty carbene carbon p orbital the alkoxy or amino plane has to be (roughly) coplanar with the carbene plane, i.e. the σ-bonds between the heteroatom and its substituents must be located within the carbene plane.

If large torsional angles are observed instead, the conclusion must be drawn that there is no, or at least only a very weak, π bond between the carbene carbon and the corresponding substituent (see ref. 26, for instance). Thus, in the "ylide carbene" complexes $(CO)_5CrC(OSiMe_3)CHPMe_3$ [6g] and $Cp(CO)_2MnC(OMe)C(Me)PMe_3$ [11i] only the ylidic P–C bond is coplanar with the carbene plane, not the silicon atom of the siloxy group or the methoxy carbon, respectively. In addition to bond lengths arguments, as discussed in Section C, this is additional evidence that in these particular complexes the siloxy or alkoxy substituent does not (or does not have to) make a substantial contribution to the electronic stabilization of the carbene carbon. A converse example is $(CO)_5CrC(NEt_2)SePh$ [6q], in which no clear-cut answer concerning π participation of the SePh group could be derived from the C(carbene)–Se distance. However, the Se-bonded carbon atom of the phenyl group is located within the carbene plane, though this brings about steric problems. From this fact the conclusion was drawn that the SePh group is probably also engaged in π bonding with the carbene carbon.

π bonding between the carbene carbon and organic substituents results in the possibility of E/Z isomers (**4**,**5**) along the C(carbene)–X bond.



E-isomer(4)(see fig.6)



Z-isomer(5) (see fig.1,2,3 and 7)

(X = O, S, Se, NR″, etc.)

From the very beginning of carbene complex chemistry the existence of both isomers had been established by ^1H NMR spectroscopy [27,30], mainly for alkoxy, amino and related substituents. The energies required for thermal isomerization are in the typical range of 11.5–14 kcal mol^{-1} for $(CO)_5CrC(OMe)R$ (R = alkyl, aryl) [27a]. For aminocarbene complexes, $L_nMC(NRR')R''$, they are usually large enough (> 25 kcal mol^{-1} for $(CO)_5CrC(NMe_2)Me$ [27c]) to permit coexistence of both isomers at room temperature [30]. If R = R′, two ^1H NMR signals are observed for the amine substituents. Naturally, the isomerization energy of a particular C(carbene)–O or C(carbene)–N bond depends on its bond order. Thus, in $(CO)_5CrC(OEt)NMe_2$ (Fig. 2) the rotational barrier for the C(carbene)–O bond is reduced to less than 8 kcal mol^{-1} and that of the C(carbene)–N bond to 20.8 kcal mol^{-1} [27c], due to the mutual weakening of these bonds, as discussed earlier in this article.

Which isomer will be energetically favoured in a particular complex is hard to predict and depends on the steric properties of the groups attached to the carbene carbon. In the absence of steric influences, the Z isomer (**5**) has been shown to prevail in $(CO)_5MC(OR)R'$ (M = Cr, Mo, W) [27c] (see also [23a]), whereas bulky R substituents tend to reinforce the E isomer (**4**). As a matter of fact, in crystal structures of methoxy- or ethoxy-substituted carbene complexes (R = Me, Et) of octahedrally coordinated metals Z isomers (**5**) (see Figs. 1–3 and 7) have been observed twice as frequently as E isomers (**4**) (see Fig. 6). However, in the analogous complexes of square-planar coordinated metals only Z isomers have been found until now. This difference is easily understood from the stereochemistry of these complexes: in octahedral complexes there may be steric interactions between R and R′ in E isomers (**4**) or between R and *cis* ligands at the metal in Z isomers (**5**); in square-planar complexes the carbene plane is (at least roughly) perpendicular to the coordination plane of the metal (see Section F and Fig. 4). Thereby in Z isomers (**5**) the R group is hardly obstructed, whereas in E isomers (**4**) there would be the same steric interactions between R and R′ as in octahedral complexes.

$(CO)_5CrC(OSiMe_3)CHPMe_3$ exists as an E isomer relative to the C(carbene)–C(ylide) partial double bond (there are no isomers relative to the C(carbene)–O bond, since there is no π interaction between C(carbene) and the siloxy group). In solution the E isomer can be photochemically converted to the Z isomer, which thermally reisomerizes rapidly [6g].

A very unusual kind of π bonding between the carbene carbon and an organic substituent is observed in $(CO)_5CrC(NMe_2)N{=}C(OMe)Ph$ (Fig. 5) [6r]. From spectroscopic investigations π interaction of both the amino and the imino groups with the carbene carbon was postulated. However, a

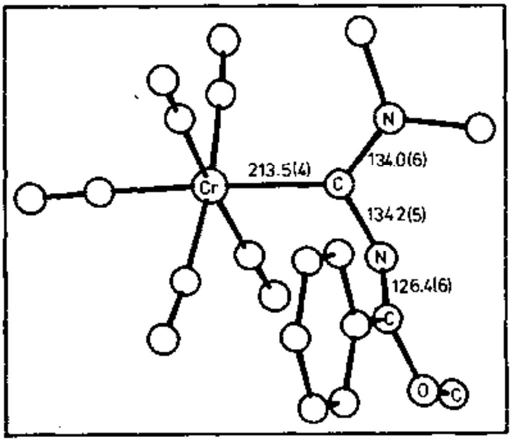


Fig. 5. $(CO)_5CrC(NMe_2)N{=}C(OMe)Ph$ [6r]. The dihedral angle between the carbene plane and the plane of the imino function is 100.6°.

coplanar arrangement of both substituents within the carbene plane is not possible for steric reasons. X-Ray structures analysis indicated that the imino group is rotated relative to the carbene plane is such a way that the electron lone pair at the imino nitrogen can interact with the carbene *p* orbital. The dihedral angle between both planes is 101°. Judged from the C–N bond lengths (134.0(6) and 134.2(5) pm) both nitrogens contribute equally to the electronic stabilization of the carbene carbon. The bond between the carbene carbon and the imino nitrogen must be regarded as a p_π–n_π bond. If the imino nitrogen were *sp* hybridized, the bonding situation would be similar to allenes. In a related tungsten complex, $(CO)_5WC(SEt)N{=}CPh_2$ [21g], a similar bonding situation is observed. However in the tungsten complex the SEt group is a poorer π donor than the dimethylamino group in the chromium complex. Therefore the imino group has to take over a larger share of π bonding. The increased overlap between the carbene carbon and the imino nitrogen is obtained by an increased rehybridization towards *sp* (C(carbene)–N=C: 149(2)° in $(CO)_5WC(SEt)N{=}CPh_2$, 134.6(4)° in $(CO)_5CrC(NMe_2)N{=}C(OMe)Ph$).

E. BOND ANGLES AT THE CARBENE CARBON ATOM

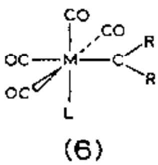
The mutual steric influence of the carbene substituents is also reflected in the bond angles at the carbene carbon atom. In octahedral alkoxy-substituted monocarbene complexes the mean metal–C(carbene)–O bond angle is 118° (based on 6 cases) for E isomers (**4**), but 132° (10 cases) for Z isomers (**5**). Steric interactions between group R and *cis* ligands at the metal seem to be responsible for the bond angle in the Z isomer since the same mean angle of 132° (11 cases) is found in analogous dialkylaminocarbene complexes. A pair of E/Z isomers was investigated. In $(CO)_5Re(CO)_4ReC(OMe)SiPh_3$ the Z isomer is found but the E isomer occurs in the analogous ethoxy carbene complex. Structural parameters of both complexes are alike, exept the Re–C(carbene)–O bond angle, which is 133(1)° in the methoxycarbene complex (Z isomer) and 120(3)° in the ethoxycarbene complex (E isomer), these bond angles being in good agreement with the mean values.

Because of reduced steric interaction between group R and the ligand sphere of the metal in Z-configurated alkoxycarbene complexes of square-planar metals the mean metal–C(carbene)–O bond angle is decreased to 125° (5 cases) and the mean metal–C(carbene)–N bond angle in analogous mono- or dialkylaminocarbene complexes to 123° (7 cases). Emphasis has to be put on the fact that the metal–C(carbene)–O or –N bond angles in the individual complexes are not much different to the average values, i.e. they are quite independent of the second organic carbene substituent R′ (in **4** and **5**).

Not unexpectedly, these numbers show that bond angles at the carbene carbon are easily deformed and, contrary to the bond lengths, are mainly determined by the steric situation within the carbene plane. However, in special cases, which will be discussed in Section H, deformation of bond angles may also occur for electronic reasons.

F. ORIENTATION OF THE METAL COMPLEX FRAGMENT

The spatial arrangement of metal complex fragment orbitals, π interacting with the carbene carbon, i.e. the energetically most favourable orientation of the metal complex moiety relative to the carbene plane, is often less obvious than for organic substituents. By comparison of the structures of a number of carbene complexes of the same type the preferred orientation of the carbene plane can be determined, but there is no answer to the question why the carbene plane is oriented in a specific way. However, fragment orbital calculations have provided decisive contributions to an understanding of these questions [23]. For example, in most of the structurally characterized $(CO)_5M$–carbene complexes (M = Cr, Mo, W) [6;21a–e] the carbene plane is roughly staggered with the *cis* carbonyl ligands (see Figs. 1, 2 and 5). MO calculations indicate an identical π interaction between the carbene ligand and the $(CO)_5M$ moiety for any conformation [31] and that therefore interactions between the carbene substituents and *cis* CO ligands seem to be responsible for the observed structures [29]. The same is true for square-planar carbene complexes, in which the carbene plane and the coordination plane of the metal are (roughly) perpendicular [23b] (see Fig. 4), unless the carbene carbon is part of a chelating ligand (13a,b;15d;16l,n]. Independence of the π overlap between the metal and the carbene ligand from the conformation of these complexes results from degenerate metal orbitals. If the symmetry of the metal complex fragment is lowered, degeneracy of the orbitals is cancelled and an electronically preferred orientation of the carbene plane is to be expected. For example, in *cis*-$(CO)_4LM$–carbene complexes (M = Cr, Mo, W), in which L has different electronic properties to CO, the carbene plane should be eclipsed with *cis* ligands. Depending on the σ- and π-bonding properties of the ligand L (relative to CO), this ligand L will either be within the carbene plane (**6**) or perpendicular to it (**7**). The difference in energy between both conformations will be the smaller the poorer the back-bonding



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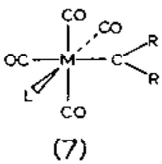

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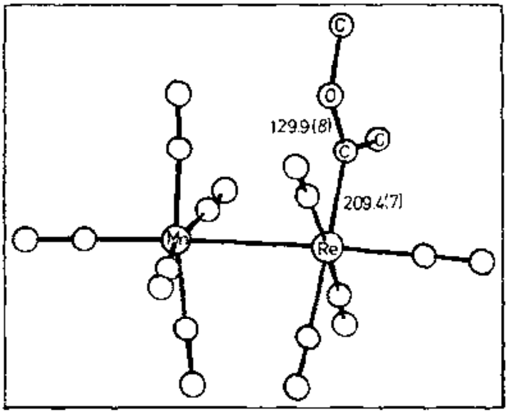


Fig. 6. $(CO)_5Mn(CO)_4ReC(OMe)Me$ [17a].

from the metal to the carbene carbon and the smaller the electronic difference between CO and L (generally, between L and L′ in $L'L_4M$–carbene complexes), i.e. the smaller the energy gap between the metal orbitals providing π overlap in both orientations. If the energetic difference is small enough, packing forces and intramolecular steric interactions may cause considerable deviations from the conformation, in which π overlap would be most effective. In octahedral complexes the best agreement between theoretical considerations and real structures is found in *cis*-$R_3Ge(CO)_4M$–carbene [11o;17c] and *cis*-$(CO)_5M(CO)_4M$–carbene complexes (M = Mn, Re) [11l;17a,b] which all adopt the sterically less demanding conformation **7** (see Fig. 6). In these complexes the *cis* ligand R_3Ge or $(CO)_5M$ is electronically quite different from CO. Contrary to this, conformation **6** is only found

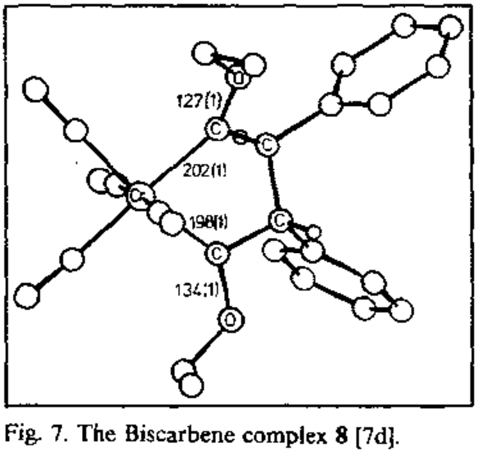
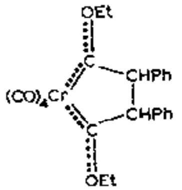


Fig. 7. The Biscarbene complex **8** [7d].

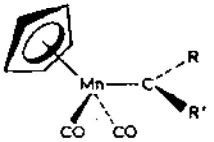
without major distortion if both the carbene carbon and L are members of the same chelate ring [7b,c;11m;21e,f].

If, for steric reasons, a conformation is enforced which allows no optimal π overlap between the carbene carbon and the metal orbitals, the metal–carbene carbon distance should be longer than in complexes with a more suitable conformation. However, such alterations of bond length are usually difficult to observe. In the crystals of **8** [7d] (Fig. 7) a situation is "frozen", in which there are different torsional angles between the coordination plane of the metal and the carbene planes (16° vs. 37°), i.e. in which there is different π overlap between the metal orbitals and the *p* orbitals of both carbene carbons. Since the same substituents are bonded to both carbene carbon atoms, bond lengths of both carbene units can be compared within the same molecule and their changes traced back to the different torsional angles. As a matter of fact, two significantly different Cr–C(carbene) distances are found (197.6(13) and 202.4(10) pm), the shorter of which belongs to the carbene unit with the smaller torsional angle. Because of the stronger metal–carbene π interaction in this unit only a weaker π interaction between the carbene carbon and the ethoxy group is necessary (C–O 133.8(12) pm) compared with the other carbene unit (C–O 127.3(13) pm).

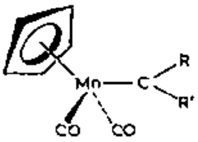


(8)

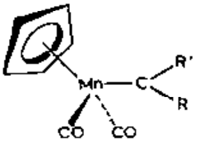
How much the conformation of a given carbene complex can be influenced by the steric properties of the organic carbene substituents can be substantiated by a comparison of the structures of $Cp(CO)_2Mn$–carbene complexes [11a–h] (Table 2, see also [11f] for a detailed discussion). MO calculations for $Cp(CO)_2MnCH_2$ (or the isoelectronic $[Cp(CO)_2FeCH_2]^+$) [23c] and $Cp(CO)_2MnC(OMe)Ph$ [23d] indicate that conformation **9**, in which the carbene plane is perpendicular to the mirror plane of the $Cp(CO)_2Mn$ fragment is higher in energy than conformation **10**, but only by a few kcal mol^{-1} (6.2 kcal mol^{-1} for $[Cp(CO)_2FeCH_2]^+$. Though **10** is more



(9)



(10a)



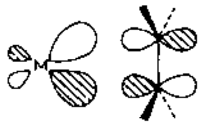
(10b)

favourable than **9**, intra- or intermolecular steric requirements may force the molecule to adopt the "wrong" conformation **10**. Because of the small difference in energy the metal–C(carbene) bond will not noticeably be affected. As a matter of fact, in one out of eight structurally characterized manganese complexes of this type (see Table 2) and in both [Cp(CO)$_2$ Fe–carbene]$^+$ complexes [8j] the electronically unfavourable, yet sterically advantageous, conformation **9** is observed. (Cp(CO)$_2$MnC(OMe)C(Me)PMe$_3$ [11i] and Cp(CO)$_2$MnC(CO$_2$Me)CHPPh$_3$ [11j] are not considered in this context because of their vinyl-like character **3**).

In complexes with two different organic substituents (R and R′) either **10a** or **10b** should be more favoured on electronic grounds, depending on the electronic properties of R and R′. However, the observed solid state structures will again strongly depend on the steric properties of R and R′ (see [11f] for an example). Because of the small energetic differences between the various conformations they sometimes coexist in solution and can be observed IR-spectroscopically [32]. Of [Cp(NO)(PPh$_3$)ReCHR]$^+$ two conformers (which are different from **9** and **10** due to the lower symmetry of the metal complex fragment) could be prepared separately for the first time [33].

Although the preceding examples have dealt with carbene complexes in which different conformations are similar in energy and more or less convertible, there are other types of carbene complexes in which only one orientation of the carbene ligand should result in stable complexes according to MO calculations [23]. Cp$_2$M–carbene, Cp$_2$(X)M–carbene and Cp(CO)$_2$ (X)M–carbene complexes are of this type. Although comprehensive structural data are lacking for these complexes, all available X-ray structures [12d,e; 20a–c; 21i,k,l] are consistent with the theoretically predicted geometries.

In this connection, emphasis has to be placed on the fact that the orbitals of a carbene ligand which are involved in bonding with a metal, are topologically very similar to the corresponding orbitals of an olefin [23b] (see the acceptor orbital of an olefin, **11**, and of a carbene, **12**, interact in a very similar way with an (arbitrarily drawn) metal orbital). Since many theoretical investigations have been performed for various types of olefin complexes, including rather complicated ones (e.g. [34] for five coordinate complexes), the results of these calculations can easily be applied to carbene complexes.



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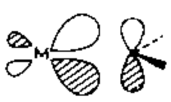

(12)

G. *TRANS* EFFECT

A more detailed investigation of the *trans* influence of carbene ligands has been performed mainly for square-planar complexes of Pt(II) [35]. However, this effect is also observed in octahedral complexes (see [6h,l,s;11i,r;12b;16r] for examples). For Pt(II) carbene complexes the effect of a carbene ligand on a *trans*-Pt–Cl bond is between that of an alkyl group and a CO or isonitrile ligand and is similar to those of phosphine ligands [16d,k;35]. The same order is true for octahedral Pt(IV) [16r], Rh(III) [18c,d] and Ru(III) carbene complexes [19c]. The similarity of carbene ligands to phosphines indicates that they are good σ donors but poor π acceptors in these particular complexes. Unfavourable back-bonding properties of the metal atoms in positive oxidation states and the presence of at least one organic π donor substituent at the carbene carbon in the complexes investigated are responsible for this observation.

Decreasing π-acceptor properties of a carbene ligand increases the bond length of a *trans* metal–Cl bond (by strengthening metal–Cl antibonding), but decreases the bond length of a *trans* metal–CO bond (by increased population of bonding orbitals). However, in carbonyl complexes the *trans* effect of a carbene ligand is often not so easily observed, because the rather small changes in the metal–CO(*trans*) bond lengths get lost in their standard deviations. Therefore, in $(CO)_5Cr$–carbene complexes significant shortening of these distances is normally found only if π-donating organic substituents at the carbene carbon effectively weaken the π-acceptor ability of the whole carbene ligand. For instance, in $(CO)_5CrC(OSiMe_3)CHPMe_3$ Cr–C(CO, *trans*) is 3 pm shorter than the average Cr–C(CO, *cis*) [6g]. *Trans* effects of similar magnitude are reported for aminocarbene complexes $(CO)_5CrC(NR_2)R'$ [6h–r]. The same is true for $Cp(CO)_2Mn$–carbene complexes, where a significant *trans* influence of the carbene ligand on the Mn–C(Cp) distances is only observed for the vinyl-like complex $Cp(CO)_2MnC(OMe)C(Me)PMe_3$ (4) [11i], in which Mn–C(Cp, *trans*) is about 11 pm shorter than Mn–C(Cp, *cis*).

H. HYPERCONJUGATIVE INTERACTIONS

As was discussed in Section E, bond angles at the carbene carbon can easily be adjusted to steric requirements of the carbene substituents. Bond lengths are not significantly influenced by such distortions. However, in a number of 14- to 16-electron complexes of tantalum and tungsten with CHR ligands (R = CMe_3 [20d,f,g;21m–p], Ph [20e], Li [20h], AlR_3[21q]) metal–C(carbene)–R bond angles up to 170° are observed (Table 3) along with shortened metal–carbene carbon distances and lengthened carbene

TABLE 3

Bond angles (°) and NMR coupling constants $^1J_{CH\alpha}$ (Hz) in neopentylidene complexes of tantalum and tungsten (L = C(H)CMe$_3$, dmpe = Me$_2$P(CH$_2$)$_2$PMe$_2$)

Complex	Formal electron count at metal	M–C(carbene)–C	M–C(carbene)–H	$^1J_{CH\alpha}$ [a]	Ref.
(η^5-C$_5$Me$_5$)(PMe$_3$)(η^2-C$_2$H$_4$)TaL [b]	16	170.0 (2)	78.1 (3)	74	20d
Cl$_2$(CO)(PMe$_3$)$_2$WL	16	168.7 (3)		73	21p
(Mesityl)(PMe$_3$)$_2$TaL$_2$	14	154.0 (6) 168.9 (6)		104 91	20f
[Cl$_3$(PMe$_3$)TaL]$_2$ [b]	14	161.2 (1)	84.8 (2)	101	20d
[(CH$_2$CMe$_3$)(PMe$_3$)$_2$TaL]$_2$N$_2$	14	158.2 (7) 160.3 (7)		91	20g
Cp$_2$ClTaL	18	150.4 (5)	111 (4)	121	20c
(CCMe$_3$)(CH$_2$CMe$_3$)(dmpe)WL	16	150.44 (7)		90	21m
Cl$_2$(O)(PMe$_3$)$_2$WL	16	142.4 (19)		126 [c]	21n
Cl$_2$(O)(PEt$_3$)WL	14	140.6 (11)		115	21o

[a] Coupling constants not given in the structural papers see [37]. [b] Neutron diffraction. [c] For the analogous PEt$_3$ complex.

carbon–hydrogen distances. Weakening of the carbene carbon–hydrogen bond was also inferred from the lowered ν_{CH} frequencies and NMR coupling constants [25]. The latter decrease with increasing metal–C(carbene)–C angle (Table 3). The most accurate crystallographic data are available for the neopentylidene complexes $[Cl_3(PMe_3)TaCHCMe_3]_2$ and $(\eta^5\text{-}C_5Me_5)(PMe_3)(\eta^2\text{-}C_2H_4)TaCHCMe_3$ (Fig. 8) [20d]. For these complexes the exact hydrogen positions were determined by neutron diffraction. According to these investigations the large Ta–C(carbene)–C bond angles of 161.2(1)° and 170.0(2)° are not only a consequence of the different size of the carbene substituents (in the 18-electron complex $Cp_2ClTaCHCMe_3$ [20c] Ta–C(carbene)–C is 150.4(5)°). Instead, the carbene ligand seems to pivot in its place: the Ta–C(carbene)–H angles are reduced to 84.8(2)° and 78.1(3)°, while the C–C(carbene)–H angles (113.7(2)° and 111.5(3)°) are more or less uninfluenced. Structural investigations on 14- and 16-electron complexes of tungsten [21m–q] have shown that only in the absence of strongly π-donating ligands can extreme distortions be expected [21p]. MO analyses of such complexes [23i,n] have traced the unusual structural parameters back to the electron deficiency of the corresponding metal by which an intramolecular electrophilic interaction between an acceptor orbital of the metal and the σ(C–H) orbital of the carbene ligand becomes possible in addition to the usual metal–carbene interactions. The magnitude of this additional interaction, i.e. the magnitude of the structural deformations, will depend on the actual electron deficiency. Accordingly, in formal 14- or 16-electron complexes there are only small deformations of the metal–C(carbene)–C angle if strong σ- or, particularly, π-donor ligands are present (see Table 3).

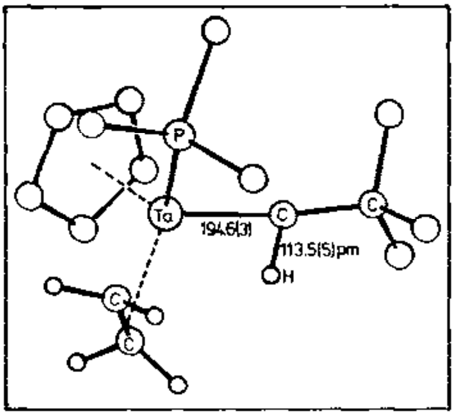

Fig. 8. $(\eta^5\text{-}C_5Me_5)(PMe_3)(\eta^2\text{-}C_2H_4)TaCHCMe_3$ [20d], neutron diffraction. For clarity the methyl groups at the Cp ring have been omitted.

While structural phenomena caused by hyperconjugation have been well investigated for electron-deficient carbene complexes, analogous phenomena are nearly unknown for electron-rich carbene complexes. Only in $Cp(CO)_2MnC(F)Ph$ have similar distortions (to a smaller extent, however) been observed [11h]: the Mn–C(carbene) distance is shorter than in other $Cp(CO)_2Mn$–carbene complexes (Table 2), the C(carbene)–F distance (139.2(6) pm) is longer than expected for $C(sp^2)$–F (135 pm) and the Mn–C(carbene)–C(phenyl) bond angle is somewhat wider than in comparable complexes. These changes indicate a hyperconjugative interaction between the electron-rich $Cp(CO)_2Mn$ fragment and the C(carbene)–F bond. Accordingly, the reactivity of this complex is very similar to that of carbyne complexes [36].

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