

ON THE ROAD TO CARBENE AND CARBYNE COMPLEXES

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by

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Translation from the German text

INTRODUCTION

In the year 1960, I had the honour of giving a talk at this university* about sandwich complexes on which we were working at that time. I think I do not have to repeat the results of those investigations today. I would like to talk instead about a field of research in which we have been intensely interested in recent years: namely, the field of carbene complexes and, more recently, carbyne complexes. If we substitute one of the hydrogen atoms in a hydrocarbon of the alkane type - for example, ethane - by a metal atom, which can of course bind many more ligands, we arrive at an organometallic compound in which the organic radical is bound to the metal atom by a σ -bond (Fig. 1a). The earliest compounds of this kind were prepared more than a hundred years ago; the first was cacodyl, prepared by R. Bunsen (1), and then zinc dialkyls were prepared by E. Frankland (2). Later V. Grignard was able to synthesise alkyl magnesium halides by treating magnesium with alkyl halides (3). Grignard was awarded the Nobel Prize in 1912 for this effort. We may further recall the organo-aluminium compounds (4) of K. Ziegler which form the basis for the low pressure polymerisation, for example of ethylene. Ziegler and G. Natta were together honoured with the Nobel Prize in 1963 for their work on organometallic compounds.

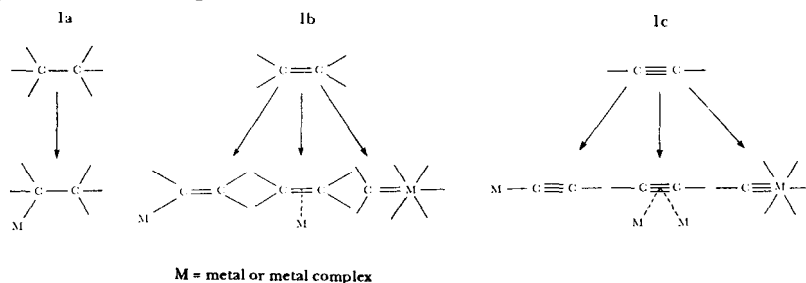


Fig. 1. Derivation of organometallic compounds from hydrocarbon derivatives.

If we then go over to a system with two carbon atoms connected by a double bond, i.e. a molecule of the alkene type, the roads leading to organometallic

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compounds branch out (Fig. 1b). In the first place, on substituting a radical by a metal atom, we get, as before, the σ compounds, for example, the vinyl lithium derivatives. In the second type, only the π electrons of the double bond are used for binding the organic molecule to the metal atom. In this way, we obtain π complexes (5,6) (Fig. 1b), the first representative of this being Zeise's salt $K[PtCl_3(C_2H_4)]$, which was prepared as early as 1827 (7). Such metal π complexes of olefins appear especially with transition metals. Main group elements are less capable of forming such a bond. The sandwich complexes (8,9) in which the bond between the metal and ligand takes place not only through two π electrons alone but also through a delocalised cyclic π electron system, may also be included in this type of compound. As an example of this we may mention dibenzene chromium(0) (10), in which the chromium atom lies between two parallel benzene rings that face each other in a congruent fashion.

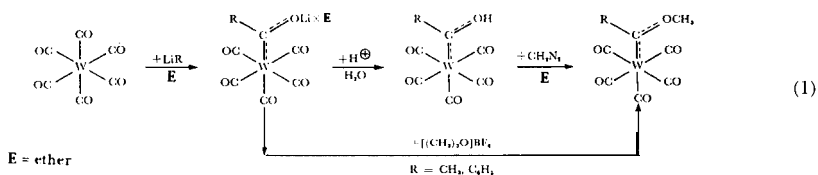
We get a third type of compound by formally separating the double bond and by fixing one of the halves to a transition metal radical. This idea is realised in the transition metal carbene complexes, in which carbenes CRR' that have a short life in the free state are stabilised by being bound to the metal. The first part of my lecture will be devoted to complexes of this type.

Finally, if we consider molecules with a carbon-carbon triple bond, of the kind that is present in alkynes, we find here also three paths towards metal derivatives (Fig. 1c). As in the earlier cases, we can build up σ compounds and then utilise the two π bonds to synthesise, for example, complexes in which the two metal-ligand bonds are situated more or less perpendicular to each other. Finally, if we imagine the triple bond to be separated and one half to be substituted by a metal complex radical, we arrive at carbyne complexes. I shall deal with these complexes in the second part of my lecture.

TRANSITION METAL CARBENE COMPLEXES

PREPARATION OF THE EARLIEST CARBENE COMPLEXES

A. Maasböl and I reported some stable carbene complexes for the first time in the year 1964 in a short communication (12). We had treated hexacarbonyl tungsten with phenyl (and methyl) lithium in ether with the intention of adding the carbanion to the carbon ion of a CO ligand which has been positivised with respect to the oxygen ion. By this reaction we did in fact get lithium acyl pentacarbonyl tungstates, which could then be converted into pentacarbonyl [hydroxy(organyl)carbene] tungsten(0) complexes by acidifying in aqueous solution (Eq. 1).



However, we very soon found that these complexes are not very stable. They tend to cleave the carbene ligand with a simultaneous hydrogen displacement/shift. We then get aldehydes - as also independently found by Japanese researchers (13). Only recently we have managed to prepare these hydroxy carbene complexes in an analytically pure form (14). However, even without isolating them, these complexes could be converted into the much more stable methoxy carbene compounds by treating them at an early stage with diazomethane (12).

We soon found a more elegant method of getting the methoxy carbene compounds by directly alkylating (15) the lithium acyl carbonyl metallates with trialkyl oxonium tetrafluoroborates (16) (Eq. 1). H. Meerwein had also synthesised these compounds in a similar manner. This method of preparation combines several advantages: the method is clear and easy to carry out and gives very high yields. It also makes it possible to prepare a wide spectrum of carbene complexes. Thus, for example, instead of phenyl lithium, many other organolithium compounds (17-23) can be used. Similarly, instead of the hexacarbonyl tungsten used first, one can use hexacarbonyl chromium (17), hexacarbonyl molybdenum (17), the di-metal decacarbonyls of manganese (24,25), technetium (25) and rhenium (25), pentacarbonyl iron (26) and tetracarbonyl nickel (27). However, the corresponding carbene complexes become increasingly unstable in the above sequence. Finally, substituted metal carbonyl (27-30) can also be subjected to carbanion addition followed by alkylation. The carbene complexes are generally quite stable, diamagnetic, easily soluble in organic solvents, and sublimable. Before going into the details about their reactions, I would like to deal briefly with the binding conditions of the carbene ligand/metal bond.

OUR UNDERSTANDING OF THE NATURE OF THE BOND AND SPECTROSCOPIC RESULTS

SPECULATIONS ABOUT THE BONDS AND SPECTROSCOPIC RESULTS

The first X-ray structure determination (31), carried out by O. S. Mills in collaboration with us, on pentacarbonyl [methoxy (phenyl) carbene] chromium (0) confirmed our notion about the bonds postulated earlier. Our notion was that the carbon atom of carbene is present in the sp^2 -hybridised form. It should therefore have a vacant p-orbital and should hence show an electron deficit.

This strong electron deficiency is compensated mainly through a $p\pi-p\pi$ bond between one of the free electron pairs of the oxygen atom of the methoxy group and the unoccupied p-state of the carbene carbon atom. A $d\pi-p\pi$ reverse bonding takes place - to a smaller yet appreciable extent - from an occupied central metal orbital with a suitable symmetry to this vacant p-orbital of the carbene carbon. This can be deduced from the distances between the carbene carbon atom and the oxygen atom on the one hand, and between the carbene carbon atom and the central chromium atom on the other hand.

The $C_{\text{carbene}}-O$ distance, which was found to be 1.33\AA , lies between the numerical values for a single bond (1.43\AA in diethyl ether) and a double bond (1.23\AA in acetone). While the $Cr-C_{\text{CO}}$ distance in the carbene complex is 1.87\AA on average, the $Cr-C_{\text{carbene}}$ distance was found to be 2.04\AA . For a pure chromium-carbon (σ bond, one would expect the distance to be 2.21\AA according to the arguments of F. A. Cotton (32). According to these arguments, the bond order for the $Cr-C_{\text{carbene}}$ bond is much smaller than for the chromium- C_{CO} bond in the same complex, but greater than the bond order in a single bond. That the phenyl group does not form any $p\pi-p\pi$ bond with the carbene carbon - at least in the lattice - is clear from the intense twisting of the plane formed by the atoms Cr, C and O and the twisting of the phenyl ring. We can see at the same time that the double bond character of the $C_{\text{carbene}}-O$ bond is so strong that cis and trans isomers with respect to the CO bond can easily occur (Fig. 2). In the case of pentacarbonyl [methoxy(phenyl)carbene]chromium(0) we only find molecules of the trans type in the lattice, but at low temperatures the cis isomer can also be detected by $^1\text{H-NMR}$ spectroscopy (33,34).

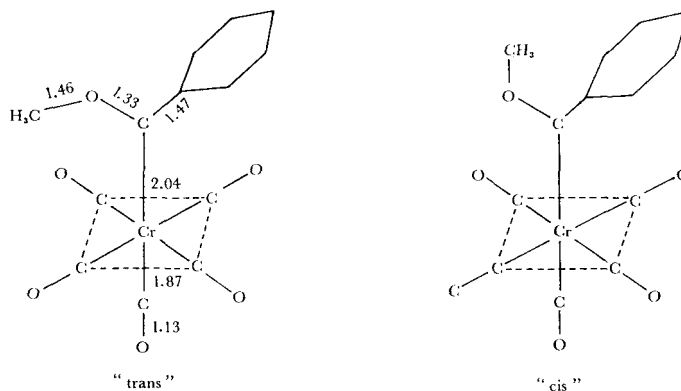


Fig. 2. Structure of pentacarbonyl[methoxy(phenyl)carbene]chromium(0)

Further important insights into the bond situations in carbene complexes are provided by the ν_{CO} spectra (20,35-37). As we know, the carbon monoxide ligands in metal carbonyls can be regarded as weak donor systems. They provide electron density from the free electron pair of the carbon to unoccupied orbitals of the metal atom. This would lead to a formally negative charging of the metal. This negative charge is broken down to a great extent by a reverse transport of charge density from the metal to the carbon monoxide through $d\pi-p\pi$ back bonding; that is, the carbon has an acceptor function in addition to its donor function. This donor/acceptor ratio of the CO ligands of a complex represents a very sensitive probe for the electronic properties of the other ligands bonded to the metal. This ratio can be qualitatively estimated by determining the CO stretching vibrations (ν_{CO}).

Let us now compare carbon monoxide and methoxy (phenyl) carbene as ligands in complexes of the type $(\text{CO})_5\text{CrL}$ ($L=\text{CO}$ or $[\text{C}(\text{OCH}_3)_2\text{C}_6\text{H}_5]$) with

regard to their ν_{∞} absorptions: while the total symmetrical Raman-active ν_{∞} stretching vibration in $\text{Cr}(\text{CO})_6$ appears at 2108 cm^{-1} (Al.) (38) we find that the CO absorption of the CO group in the trans-position with respect to the carbene ligand is shifted drastically towards lower wave numbers, namely 1953 cm^{-1} (A.) (17); that is, the carbene ligand has a much greater (σ donor/ π acceptor) ratio than CO. In other words the carbene ligand is on the whole positively polarised, and the $\text{Cr}(\text{CO})_5$ part is negatively polarised. The dipole moments of the complexes are therefore also relatively high, about 5 Debye.

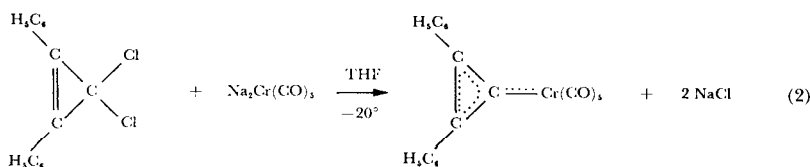
In what follows, I would not like to go into the details of the spectroscopic studies as such. It may, however, be pointed out briefly that ^{13}C -NMR measurements are extremely useful for research in this area of chemistry. In one such early study on pentacarbonyl [methoxy(phenyl)carbene]chromium(0), C. G. Kreiter (39) could show that the carbene carbon atom is highly positivised. The chemical shift that was found, namely 351.42 ppm, is in fact; within the range of values of carbonium ions in organic chemistry. This modern method has thus confirmed our original proposal once again.

With its high "positive" charge character, the carbene carbon acts as an electrophilic centre. This is of great importance when one is looking at the reactions of these compounds. We shall come back to these reactions in the course of this lecture.

SYNTHESES OF OTHER CARBENE COMPLEXES

Our first paper on metal carbene complexes was published in 1964. This area of work has expanded rapidly since then. A number of fairly extensive review articles (40-43) on the chemistry of carbene complexes have now appeared. I shall therefore pick out only a few examples, particularly of those involving interesting syntheses.

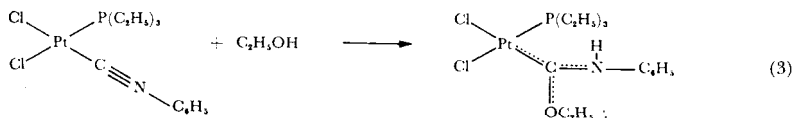
In 1968, K. Öfele treated 1,1-dichloro-2,3-diphenyl cyclopropene (2) with disodium pentacarbonyl chromate in our laboratory and obtained pentacarbonyl (2,3-diphenyl cyclopropenyldiene) chromium (0) with the elimination of sodium chloride (44). This carbene compound is stable up to 200°C and has the characteristic property that the carbene ligand no longer has any hetero atom. The electronic saturation of the carbene carbon takes place in this reaction through the three-ring π system (Eq. 2).



X-ray structural analysis (45) showed that the three C-C distances in the ligand are not identical: the distance between the two phenyl substituted C atoms is somewhat shorter than the other two. The carbene carbon-chromium

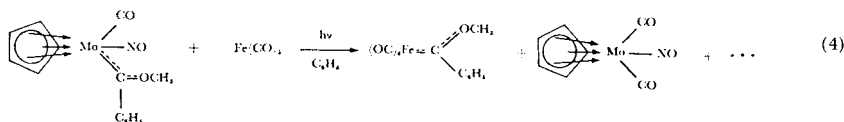
distance is 2.05 Å and lies in the range of the values found for our carbene complexes, i.e. this complex must be a genuine carbene complex.

Another fine method of synthesis was published by R. L. Richards *et al.* in 1969 (46). They found that in the reaction of alcohols with certain isonitrile complexes, for example the isonitrile platinum complex, addition of the alkoxy group at the carbon atom and the hydrogen at the nitrogen atom of the isonitrile ligand takes place, resulting in the corresponding carbene complexes, for example (Eq. 3).

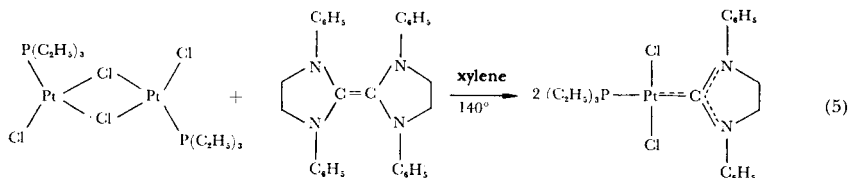


This method of synthesis has since led to several such compounds. We notice here the similarity between the chemistry of isonitrile complexes and carbon monoxide complexes.

In 1971 we succeeded, for the first time once again, in transferring a carbene ligand from one complex to another (26, 47). For example, if we irradiate a solution of cyclopentadienyl(carbonyl) [methoxy(phenyl) carbene] nitrosylmolybdenum(0) in the presence of an excess of pentacarbonyl iron, we get tetracarbonyl [methoxy(phenyl) carbene] iron (0) with the simultaneous formation of cyclopentadienyl (dicarbonyl) nitrosylmolybdenum (Eq. 4).



Finally, another method of synthesis was developed recently (1971) by M. F. Lappert *et al.* (48). They treated an electron-rich olefinic system, such as N.N.N'.N'-tetraphenyl bis dihydroimidazolyidene, with a suitable complex. In this way, they were able to split the double bond and fix the carbene halves at the metal, for example (Eq. 5).



This was a brief survey of other methods for the synthesis of carbene complexes found independently by other workers.

POSSIBLE REACTIONS OF CARBENE COMPLEXES

In what follows, I shall confine myself to carbene complexes of our type and I shall show, with some examples from recent times, the kinds of reactions that we could observe with these complexes.

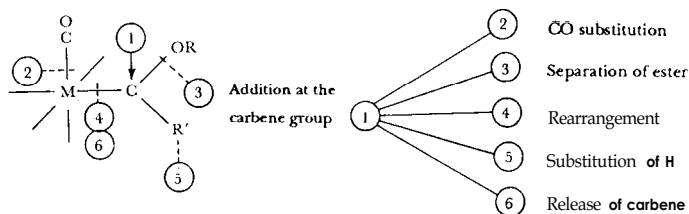


Fig. 3. Possible reactions of alkoxy carbene complexes.

We have already pointed out that the carbene carbon atom is an electrophilic centre and should therefore have a high nucleophilic reactivity. Hence, according to our present understanding, in most reactions a nucleophile would be added to the carbene carbon atom in the primary reaction stage. In some cases, for example in the case of some phosphines (49) and tertiary amines (50), such addition products can be isolated in an analytically pure form under certain conditions (① in Fig. 3). Another possible reaction is that the nucleophilic agent substitutes a carbon monoxide group in the complex while preserving the carbene ligand (② in Fig. 3). The carbene complex can also be regarded in a very formal way from the point of view of an ester-like system ($X = C \begin{matrix} \diagup \\ \text{OCH}_3 \\ \diagdown \\ \text{R} \end{matrix}$, where $X = M(CO)_5$, instead of $X = O$) since the oxygen atom as well as the metal atom in the $M(CO)_5$ radical have two electrons less than the number of electrons required for attaining the rare gas configuration. Therefore, it is not surprising that the OR radical can be substituted by amino, thio and seleno groups (③ in Fig. 3). This leads us to the synthesis of amino (organyl) carbene complexes (36, 51-54) thio (organyl) carbene complexes (51, 55) and seleno (organyl) carbene complexes. The synthesis of the last two series of complexes requires some experimental skill.

We can also observe reactions which lead to a more stable arrangement of the entire system through a primary addition followed by a rearrangement (④ in Fig. 3). It can be noticed further that the hydrogen atoms of alkyl groups in the α position with respect to the carbene carbon atom are so acidic - because of the electron pull of the $M(CO)_5$ radical - that their acidity is similar to that of the hydrogen atoms in nitromethane (⑤ in Fig. 3). Finally the separation of the carbene ligand from the metal complex opens up new synthetic routes in organic chemistry (⑥ in Fig. 3).

ADDITION AND CO SUBSTITUTION

If we treat trialkyl phosphines with pentacarbonyl [alkoxy (organyl) carbene] complexes of chromium(0) and tungsten(0), for example, in hexane at

temperatures below -30°C , the corresponding phosphorylide complexes (which are addition compounds) can be isolated in an analytically pure form and studied (49). The erstwhile carbene carbon is now sp^3 hybridised and now has only a σ -bond at the central metal. In the case of triaryl and mixed alkyl aryl phosphines, the addition-dissociation equilibrium (57) (Fig. 4) lies to a great extent on the side of the starting materials, so that the ylide complexes can be detected only by spectroscopy. Figure 4 shows the reaction scheme for pentacarbonyl[methoxy(methyl)carbene]chromium(0) and tertiary phosphines.

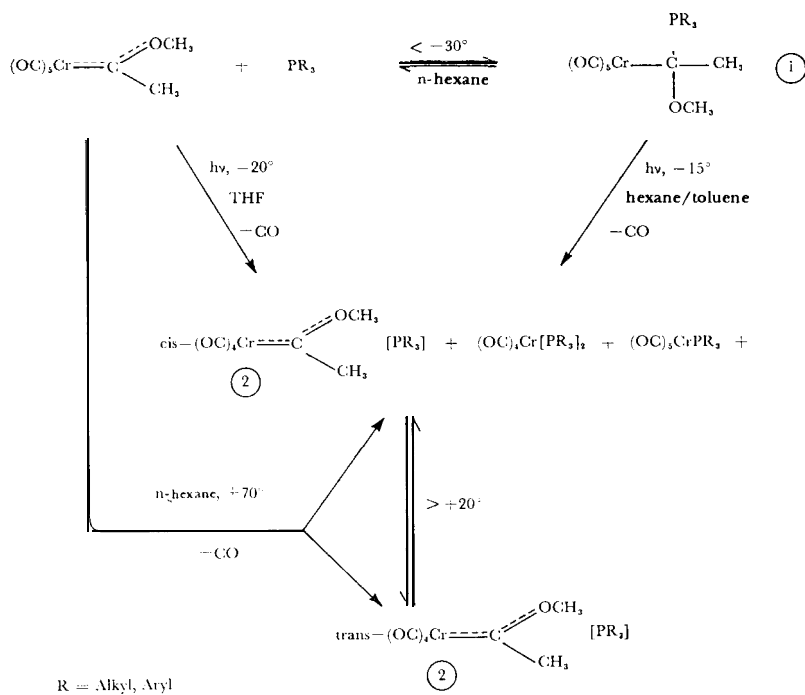


Fig. 4. Reaction of pentacarbonyl[methoxy(methyl)carbene]chromium(0) with tertiary phosphines.

On irradiating solutions of these ylide complexes in hexane-toluene mixtures at -15°C , we get the cis-tetracarbonyl[alkoxy(organyl)carbene] phosphine complexes (58) with elimination of a CO ligand from the cis position. That is, the phosphine which is at first added to the carbene carbon of the starting complex, substitutes a CO ligand at the metal atom and the carbene grouping is formed once again. To a smaller extent, the carbene ligand is also substituted by phosphine. We arrive at the same products if we employ only the equilibrium mixtures of pentacarbonyl carbene complexes and phosphines under slightly modified conditions (at -20°C in THF) instead of the isolated ylide complexes (58). But, if the reaction is carried out thermally - at 70°C in hexane - mixtures of the cis and trans isomers are formed instead of the pure cis tetracarbonyl carbene phosphine complexes (59, 60). We were able to isolate

the cis and trans isomers in pure form (60). On heating solutions of either of these components (separately) isomerisation takes place until an equilibrium is attained (61). We were especially interested in the mechanism and found that the isomerisation reaction (62) follows first order kinetics, that the reaction rate is not influenced by the presence of the free ligands, phosphine and carbon monoxide, and that the isomerisation rate is greater in tetracarbonyl[methoxy(methyl)carbene] triethyl phosphine chromium(O) than in the corresponding tricyclohexyl phosphine complex. Now, how do we visualise this process of isomerism? The findings suggest an intramolecular mechanism in which none of the bonds of the six monodentate ligands with the metal are broken or formed afresh during the change from the cis isomer to the trans isomer and vice versa. Instead there could be a twist in the two planes formed by any three ligands, by 120° in opposite directions (twist mechanism) (Fig. 5).

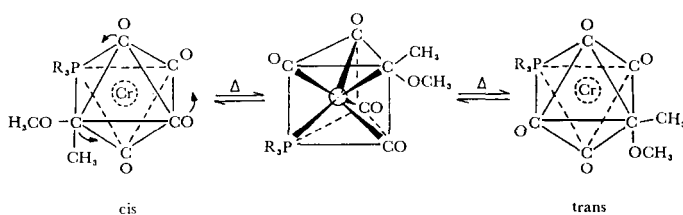


Fig. 5. Hypothesis regarding the isomerisation of tetracarbonyl[methoxy(methyl)carbene] phosphine chromium(O).

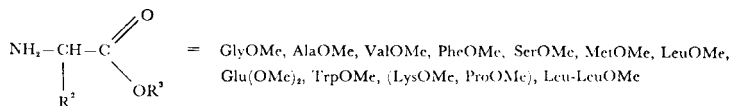
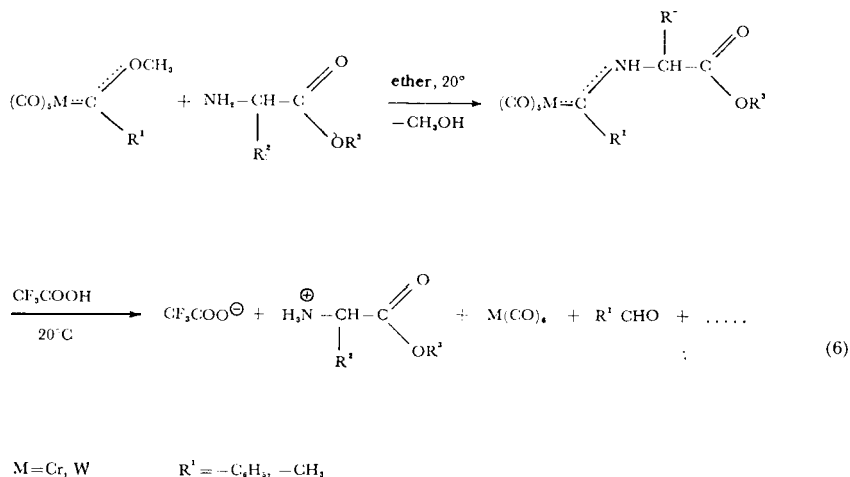
Since this process passes through a trigonal-prismatic transition state with an increased steric inhibition, it is also quite understandable that the compound with the highly cumbersome tricyclohexyl phosphine ligand isomerises at a slower rate than the corresponding triethyl phosphine complex.

TRANSITION METAL/CARBENE COMPLEX RADICALS AS PROTECTIVE AMINO GROUPS FOR AMINO ACIDS AND PEPTIDES

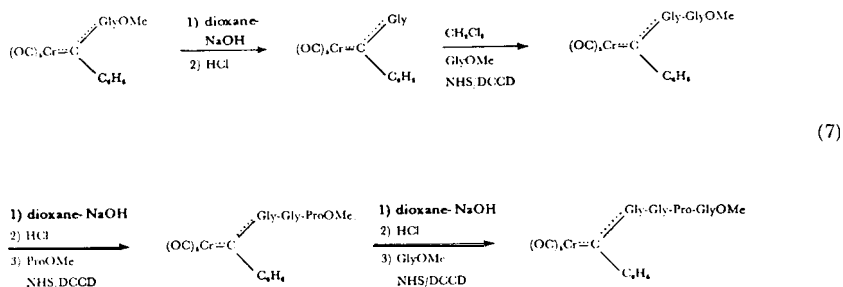
If we treat the alkoxy carbene complexes with primary or secondary amines, instead of phosphines, we observe a new type of reaction which is similar to the reactions of esters. We have been greatly interested in this type of reaction in recent times and it has shown us a new approach to the chemistry of peptides - quite a surprising approach for a chemist dealing with complexes. We could show that the alkoxy group of alkoxy (organyl) carbene complexes can be substituted not only by mono or dialkyl amino radicals but also by free amino groups of amino acid esters and peptide esters (63, 64). The principle of this reaction is shown in Eq. 6.

Even at 20°C , not only simple amino acid esters but also polyfunctional amino acid esters react with alkoxy (organyl) carbene complexes in ether solution without protection of the third function. The organometallic radical thus represents a new and interesting protecting group, especially because it can be easily separated again by treatment with trifluoro acetic acid. In some

cases, this separation can be done even with acetic acid, in a milder reaction.



I shall now show, with another example, that one can add further amino acid groups to an amino ester carbene complex by the usual methods of peptide chemistry (64). Starting with pentacarbonyl (phenyl carbene) GlyOMe chromium (0) we were able to synthesise, for example, the sequence 14 to 17 of the human proinsulin C peptide - as shown by Eq. 17 - by the NHS/DCCD method (N-hydroxy succinimide/dicyclohexylcarbodiimide) .

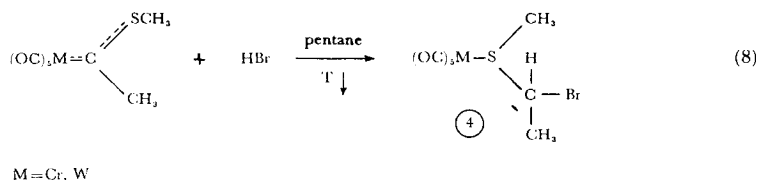


We are now working with E. Wiensch in this area and we believe that the utilisation of such carbene complexes could offer a number of new routes and advantages to the peptide chemist:

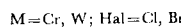
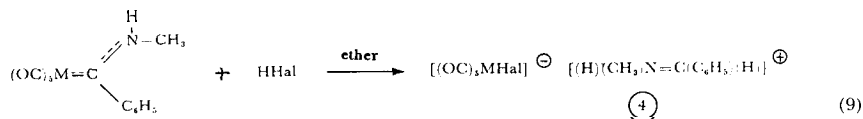
- (1) Such amino acid or peptide derivatives are yellow and hence easy to distinguish, for example in chromatographic methods.
- (2) This protecting group can be separated under milder conditions; the reaction products that are formed in addition to the amino acid or peptide esters - mainly aldehydes and metal hexacarbonyls - are volatile and can therefore be easily separated.
- (3) Most carbene complexes of amino acid esters and many dipeptide esters are volatile and can be studied by mass spectroscopy.
- (4) We have here a method by which heavy metal atoms like tungsten can be incorporated in peptides and free amino groups can thus be marked.

ADDITION AND REARRANGEMENT REACTIONS

Here are two recent examples to illustrate this type of reaction of carbene complexes. Pentacarbonyl [methyl(thiomethyl)carbene] chromium (0) and tungsten(0) react at low temperatures with hydrogen bromide to form pentacarbonyl[(1-bromoethyl) methylsulfide] complexes (65) (Eq. 8).



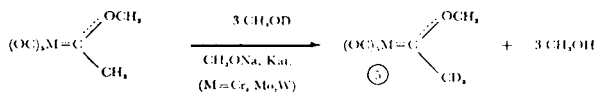
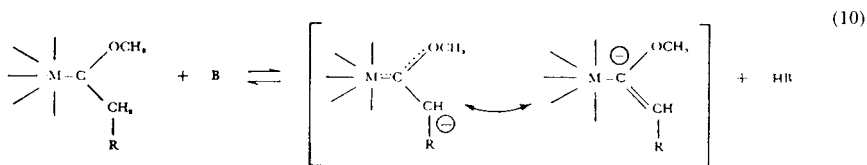
In this process, the original carbene carbon loses its bond with the transition metal and sulphur occupies this position. The second example shows that such a reaction need not always result in an uncharged system. That is, instead of thiocarbene complexes, if we use aminocarbene complexes in the reaction with hydrogen halides, salt-like compounds can be isolated (66). After the reaction we find the halogen at the metal, the hydrogen at the eliminated carbene ligand, and we get imonium halogeno pentacarbonyl metallates.



We thus have a method for synthesising such cations and this method allows great variations in this type of compound, which are not easily accessible.

HYDROGEN SUBSTITUTION AT THE α -C ATOM

C. G. Kreiter (67) was the first to show the acidity of hydrogen atoms bound to the α -C atom of alkoxy (alkyl) carbene complexes by $^1\text{H-NMR}$ spectroscopic studies. Solutions of pentacarbonyl[methoxy(methyl)carbene]chromium(0) in CH_3OD , in the presence of catalytic quantities of sodium methylate, exchange all the hydrogen atoms at the methyl group bound to the carbene carbon with deuterium (Eq. 10).

**Explanation:**

The base is thus evidently in a position to form an anion through reversible elimination of a proton in the α position with respect to the carbene carbon. This reaction can also be utilised to introduce new groups into the carbene ligand at this position (40, 68).

By its nature, this acidity is closely connected with the strong positively charged character of the carbene carbon atom. Let me once again therefore take up at this point the unusual $^{13}\text{C-NMR}$ spectroscopic shifts of this atom, with the examples of some characteristic chromium(0) complexes.

$(\text{OC})_5 \text{CrC}[\text{N}(\text{CH}_3)_2] \text{C}_6\text{H}_5$	270,6 ppm ^{b)}
$(\text{OC})_5 \text{CrC}(\text{OCH}_3) \text{C}_6\text{H}_5$	351,4 ppm ^{a)}
$(\text{OC})_5 \text{CrC}(\text{C}_6\text{H}_5) \text{C}_6\text{H}_5$	399,4 ppm ^{b)}
a) in C_6D_6	
b) in CD_3COCD_3	

Fig. 6. $^{13}\text{C-NMR}$ shifts of $\text{C}_{\text{carbene}}$ atoms of some carbene complexes (values of δ relative to int. TMS)

If we start with the methoxy (phenyl) carbene complex, for which a shift of 351.4 ppm was measured (39) and replace the methoxy group with the dimethyl amino group which has a better stabilising effect, the value of δ drops as expected to 270.6 ppm (66). On the other hand, in the diphenyl carbene complex, δ has a value of 399.4 ppm (69). We have been working on this compound recently and we have in this compound an extremely highly positivised carbon atom, even when composed to the values found for organic carbonium ions. The two phenyl groups are therefore now hardly capable of

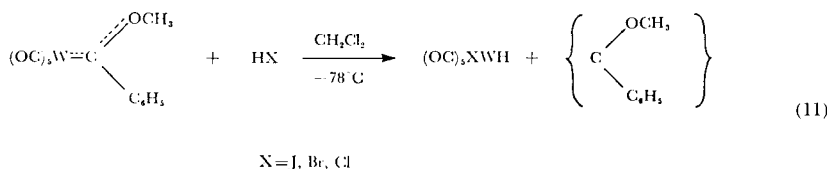
compensating for the electron deficit at the carbene carbon. This chromium carbene complex is much more unstable than the homologous tungsten compound reported recently by C. P. Casey (70).

ELIMINATION OF THE CARBENE LIGAND

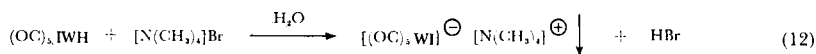
Reaction with acids

I do not want to try the patience of the organic chemists present here with too many details about the chemistry of complex compounds. I shall therefore mention here some applications of carbene complexes that may be of interest to organic chemists. I think the epoch of "inorganic" and "organic" chemistry as watertight compartments is now over. We must now consider all possible avenues that nature offers us.

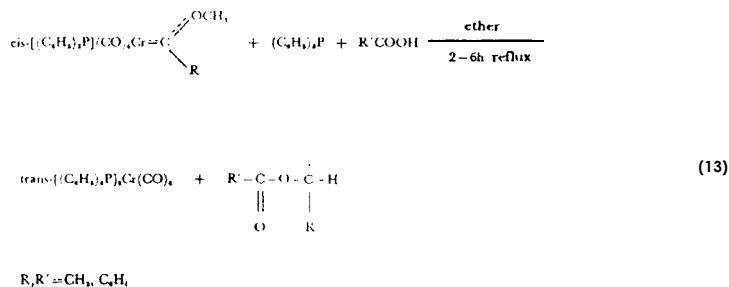
The road to organic chemistry will be open when it becomes possible to separate the carbene ligand from the metal under conditions that are not too drastic. This is now possible with hydrogen halides in methylene chloride at a temperature as low as -78° (71) (Eq. 11).



This reaction leads to pentacarbonyl halogeno tungsten hydrides. Unlike the corresponding anions, these compounds were not known earlier, as far as we know. The neutral hydride complexes are very unstable and are almost completely dissociated in aqueous solution into hydronium cations and pentacarbonyl halogen tungstate anions. The anions can be precipitated in the form of tetramethyl ammonium salts (71) for example (Eq. 12).



We found some indications concerning the fate of the cleaved carbene ligand from other studies. That is, if we treat tetracarbonyl [methoxy(organyl) carbene] triphenyl phosphine chromium(O) with benzoic acid or acetic acid in boiling ether, we can isolate the α -methoxy organyl esters of these acids (72) (Eq. 13).

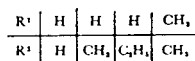
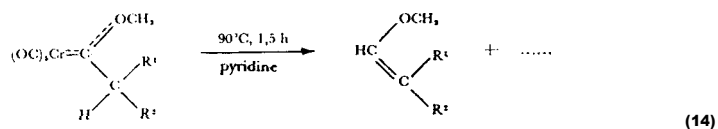


This secondary reaction amounts to a formal insertion of the carbene radical into the OH group of the carboxylic acid. Triphenyl phosphine, which is added to the reaction mixture, merely serves to improve the separation of the organometallic radical in the form of the poorly soluble tetracarbonyl bis (triphenyl phosphine) chromium(0) complex. The reaction with HCl proceeds similarly; but the insertion products formed, namely, α -halogen organyl (methyl) ethers, react immediately with the phosphine present to form the corresponding phosphonium salts (72).

The following question of course arises in this connection: What happens to the eliminated carbene ligand when no suitable reaction partner is available? The reaction conditions employed are of decisive importance in answering the question.

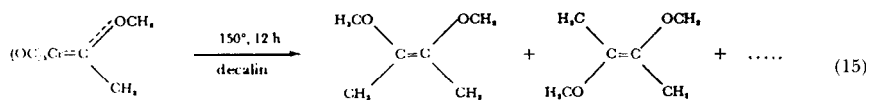
Reaction with pyridine

Right at the beginning of our studies on carbene complexes, we observed that the carbene radical can be easily broken off from the metal with the help of pyridine, and that the metal fragment can be separated in the form of carbonyl pyridine chromium complexes (73). In the case of alkoxy (alkyl) carbene complexes, a hydrogen atom of the eliminated carbene radical shifts, with the help of the base, towards the original carbene carbon atom, with the formation of enol ether (73, 74) (Eq. 14).



Thermal decomposition

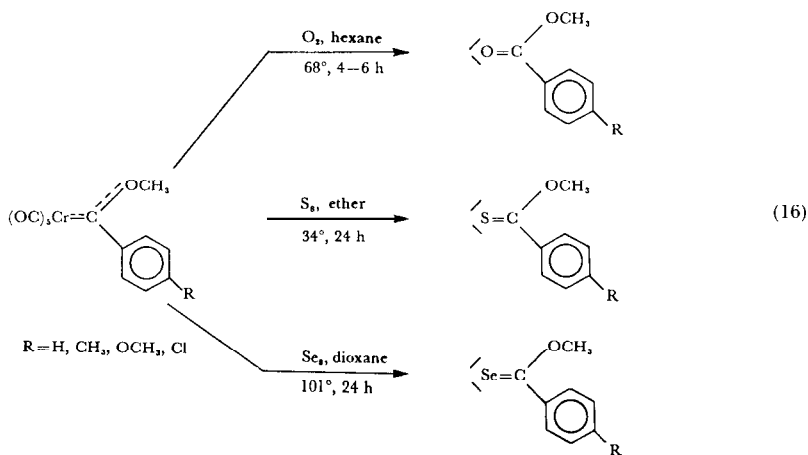
To check whether the base has an effect on the (secondary) reaction of the carbene ligand, we decomposed pentacarbonyl[methoxy(methyl) carbene] chromium(0) purely thermally at 150°C in decalin. Under these conditions we observed the exclusive formation of the dimer; to be precise, as a mixture of the cis and trans isomers (74). The reaction must therefore be as follows (Eq. 15).



Since the shifting of a hydrogen atom is not possible in the case of the methoxy (phenyl) carbene ligand, only dimerisation takes place in the reactions with bases as well as with thermal decomposition.

Reactions with elements of the sixth group in the periodic table

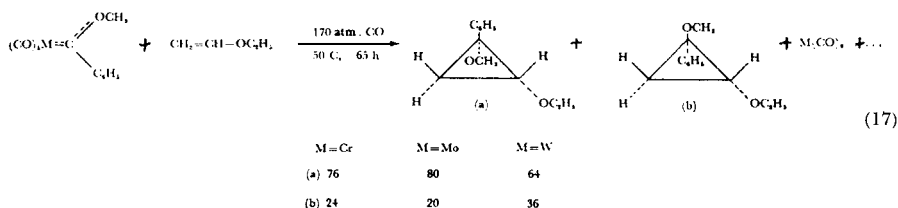
We are of course especially interested in those reactions which lead to products that are not easily accessible by the conventional methods of organic chemistry and which can be prepared easily with our complexes. We found such an example in the reaction of pentacarbonyl[methoxy(aryl)carbene]chromium(0) complexes with oxygen, sulphur and selenium (76). By this reaction we can easily get the corresponding methyl esters, thio-O-methyl esters and seleno-O-methyl esters. The latter two types of compounds seem important to us from the synthetic point of view (Eq. 16).



Reactions with vinyl ethers and N-vinyl pyrrolidones

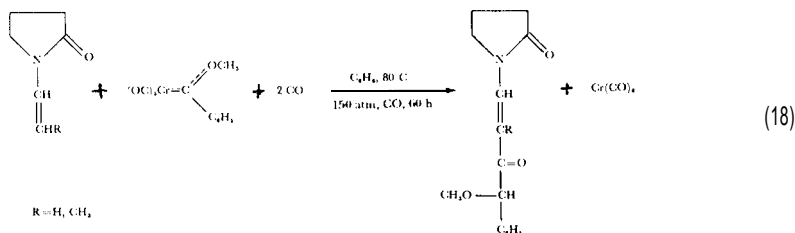
At quite an early stage of our studies on carbene complexes, we had argued that these compounds would deserve their name only if they underwent reactions typical of carbenes.

In this connection the organic chemist will immediately recall the formation of cyclopropane derivatives from olefins and carbenes. We very soon found that this reaction was also possible with our complexes and those $C = C$ double bonds which are deficient in electrons and are either polarised or easily polarisable (77-81). As an example of this, I would like to mention the reaction of pentacarbonyl [methoxy(phenyl)carbene] chromium(0), molybdenum(0) and tungsten(0) with ethylvinyl ether (79). However, we get the corresponding cyclopropane derivatives only if we cleave the carbene ligand in an autoclave at $50^\circ C$ under CO atmosphere at a pressure of 170 atm. (Eq. 17).



As expected, we find two isomers [(a) and (b) in Eq. 17]. Under the same reaction conditions, the ratio of the two isomers depends on the choice of the central metal. This seems to us to be a rather definite pointer that this reaction takes place not through a "free" methoxy (phenyl) carbene, but that, to the contrary, the metal atom is involved at the decisive stage of the reaction.

When we try to carry out this reaction, under similar conditions, with vinyl pyrrolidone (2) as the olefin component, we get, instead of the expected cyclopropane derivative, quite surprisingly, 1-[4methoxy-4-phenyl-butene (1)-on(3)yl] pyrrolidone(2) (82) (Eq. 18).



How do we explain the formation of this unexpected product, in which we find carbon monoxide also added to the carbene ligand and pyrrolidone? (Fig. 7).

We now believe that the carbene ligand first reacts with carbon monoxide to form methoxy(phenyl)ketene. This forms a cyclobutanone derivative with the polarised olefin, which is converted into the product found - via a ring opening.

This hypothesis has been reinforced by the subsequent finding that on using N-(β-methyl vinyl) pyrrolidone (2) instead of N-vinyl-pyrrolidone (2) we could isolate the postulated four-ring system in addition to the open-chain end product (82).

Our original idea of using carbon monoxide only for cleaving the carbene ligand thus led us to an unexpected result and showed at the same time that the reactivity of carbon monoxide with respect to organic systems should not be ignored.

In an attempt to obtain the cyclopropane derivatives which we wanted, we reacted the same starting materials thermally in benzene in the absence of CO. But in this attempt also, we did not get the desired compounds,

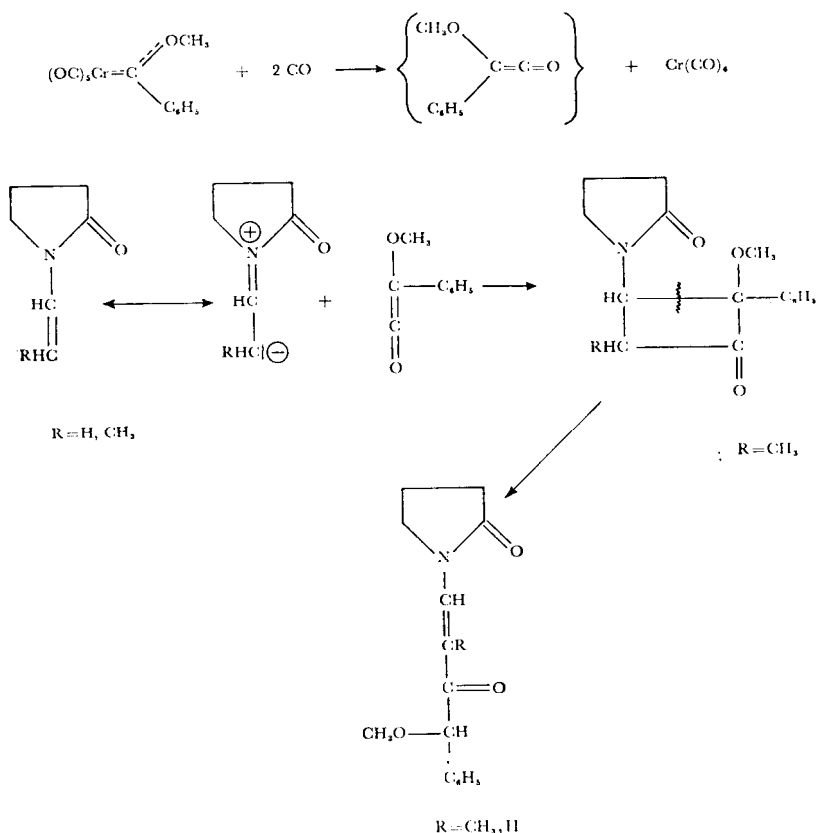
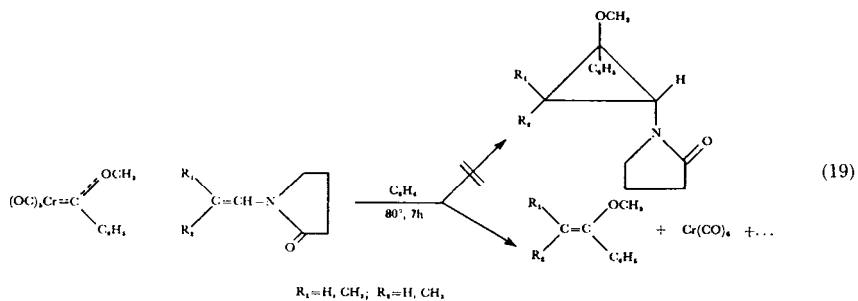


Fig. 7. Hypothesis regarding the course of the reaction of pentacarbonyl[methoxy(phenyl)carbene] chromium(0) with N-vinyl-pyrrolidone(2) under 150 atm. CO pressure.

but, surprisingly, the corresponding substituted α -methoxy styrenes (83) (Eq. 19).



A possible course of the reaction might be as follows:

N-vinyl-pyrrolidone(2) also has a nucleophilic centre at the oxygen atom. This nucleophilic centre could attack the electrophilic carbene carbon and separate the carbene ligand from the metal. The intermediate product thus

formed - irrespective of whether it has an open chain form or a six-membered ring - then undergoes a cleavage similar to the heterolytic fragmentation reported by C. A. Grob (84) (Fig. 8).

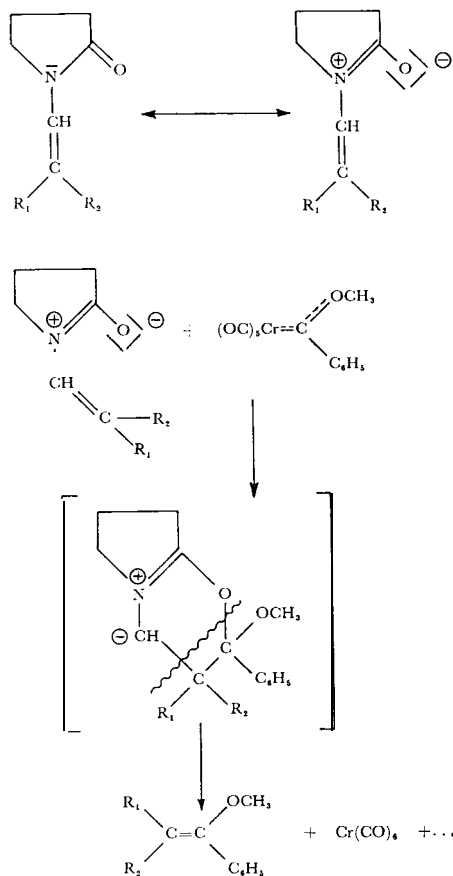
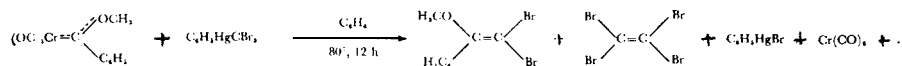
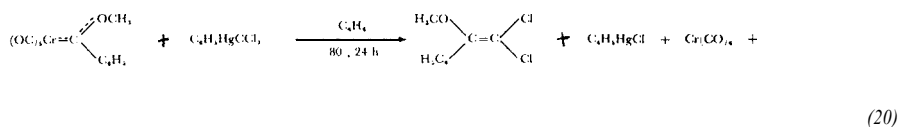


Fig. 8. Hypothesis regarding the course of the reaction of pentacarbonyl [methoxy(phenyl) carbene] chromium(0) with N-vinyl-pyrrolidone(2) and P-substituted N-vinyl-pyrrolidones under normal pressure.

Reactions with electrophilic carbenes

As shown right at the beginning of this lecture, the carbene ligand in carbene complexes of our type provides a "nucleophilic" behaviour with respect to the metal fragment. One of our pet ideas was thus to combine the carbene ligand with an electrophilic carbene. We therefore treated pentacarbonyl [methoxy(phenyl)carbene] chromium (0) with phenyl (trichloromethyl) mercury (85). Compounds of this kind have been studied in detail by D. Seyferth and they are recognised as starting materials for dihalo carbenes (86). The carbene complex and the carbenoid compound could be made to react at 80°C in benzene to form β,β -dichloro- α -methoxy styrene (85) (Eq. 20).



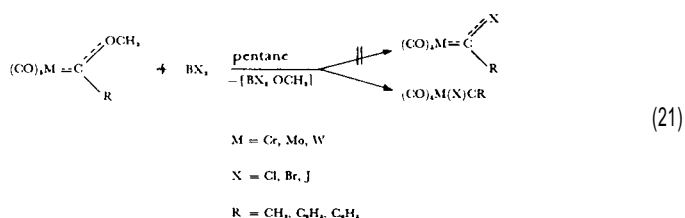
This combination reaction is very sensitive to temperature conditions. Even greater complications arose on using phenyl (tribromomethyl) mercury, with the formation of mixtures of olefins.

With this small selection from our recent research results, I think I have been able to show you the wide variety of possible reactions offered by the chemistry of transition metal carbene complexes.

I would now like to report to you our findings in another related area on which we have been working very intensively recently: the chemistry of transition metal carbene complexes.

TRANSITION METAL CARBYNE COMPLEXES

To explore all the possible reactions of transition metal carbene complexes, we had attempted some years ago to make our complexes react with electrophilic reaction partners in addition to nucleophilic reaction partners. Our idea was to exchange the methoxy group of methoxy (organyl) carbene complexes by a halogen with the help of borontrihalides and thus to arrive at halogeno (organyl) carbene complexes. We did observe a fast reaction but found only decomposition products. But recently, in collaboration with G. Kreis, we carried out this reaction at very low temperatures and could isolate well-defined compounds which were, however, thermally quite unstable (87). Their composition was equivalent to the sum of a metal tetracarbonyl fragment, a halogen and the carbene ligand minus the methoxy group (Eq. 21).



The IR spectra indicated the presence of disubstituted hexacarbonyls with two different ligands in the trans position (trans $(\text{CO})_4\text{MR}^1\text{R}^2$). Moreover, the cryoscopic determination of molecular weight showed the presence of a monomer complex. Together with other spectroscopic findings, especially

from ^{13}C and $^1\text{H-NMR}$ studies, this could be interpreted only if we assumed that, besides the four CO ligands, a halogen and a CR group bonded to the metal had to be present (Fig. 9).

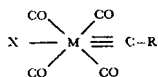


Fig. 9. Structure and model of bonds for $(\text{CO})_4(\text{X})\text{MCR}$.

We would like to propose the name “carbyne complexes” for this new type of compound, for two reasons: (1) on the analogy of “carbene complexes” and (2) on the analogy of the term “alkyne”, because on the basis of the diamagnetism of these compounds, we must postulate a formal metal-carbon triple bond.

X-RAY STRUCTURE ANALYSES

Such a triple bond should result in a very short distance between the metal and the carbyne carbon. To answer this question and to confirm the proposed structure, X-ray structural analyses have been carried out in our institute by G. Huttner *et al.* on three carbyne complexes so far (88).

The first such study was done on *trans*-(iodo)tetracarbonyl(phenylcarbyne) tungsten (0) (87, 88) (Fig. 10).

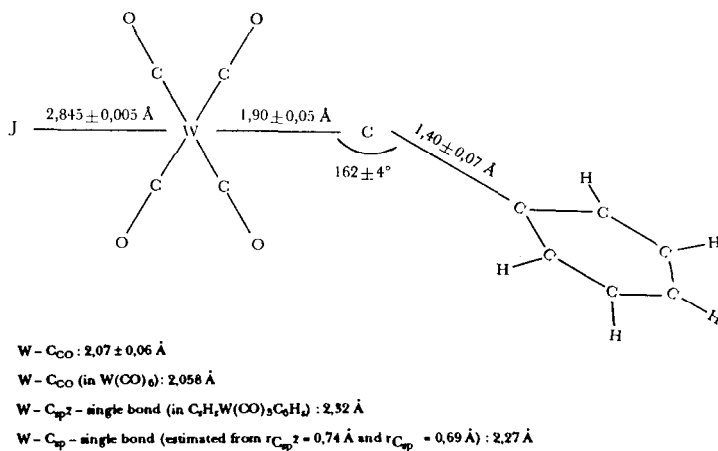


Fig. 10. Molecular structure of *trans*-(iodo) tetracarbonyl(phenylcarbyne) tungsten (0).

This study essentially confirmed our ideas and gave an extremely short tungsten-carbon distance of 1.90 Å. Instead of the linear arrangement of metal, C_{carbyne} and C_{1,4 (phenyl)} atoms, however, we found a clear bending of about 162°. Since we could not explain at this stage whether this bending was due to

electronic or lattice effects, we immediately undertook the study of another complex. Figure 11 shows the result: the structure of trans-(iodo)-tetracarbonyl(methyl carbyne)chromium(0) (88).

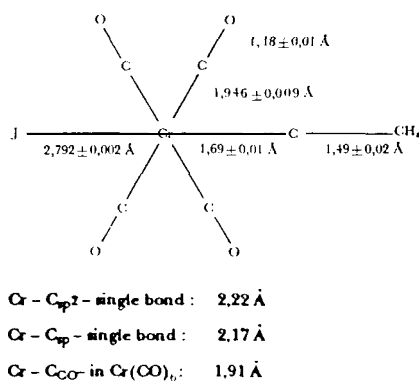
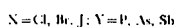
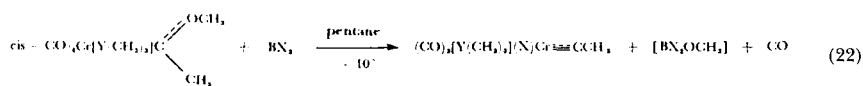


Fig. 11. Molecular structure of trans-(iodo) tetracarbonyl(methylcarbyne)chromium(0).

In this compound we found not only the expected linear arrangement of the chromium, carbon and methyl group, but also the shortest distance between chromium and carbon found so far, namely 1.69 Å. This value is appreciably shorter than the Cr-C_{co} distance in the same complex (1.946 Å or in hexacarbonyl chromium (1.91 Å).

Subsequently we were interested in the question whether second substituents in the starting carbene complex can influence the orientation of the halogen in the resulting carbyne complex. To answer this question, we first treated cis-tetracarbonyl[methoxy(methyl)carbene]trimethylphosphine, arsine and stibine chromium (0) with borontrihalides (89) (Eq. 22).



The reaction proceeded as smoothly as before, but in the compounds with the composition (CO)₅[Y(CH₃)₃](X)Cr = CCH₃ (X = Cl, Br, I and Y = P, As, Sb) that were formed, the mutual spatial arrangement of the ligands could not at first be clearly determined. An X-ray structural analysis was therefore carried out on a representative compound of this type (88-90) (Fig. 12).

For (bromo)tricarbonyl (methylcarbyne) trimethylphosphinechromium(0), we found a meridional arrangement of the three substituents and, again, a trans-arrangement of the halogen and carbyne ligand. We are at present studying how a carbene complex with an initial trans-configuration behaves in the reaction with borontrihalides (89).

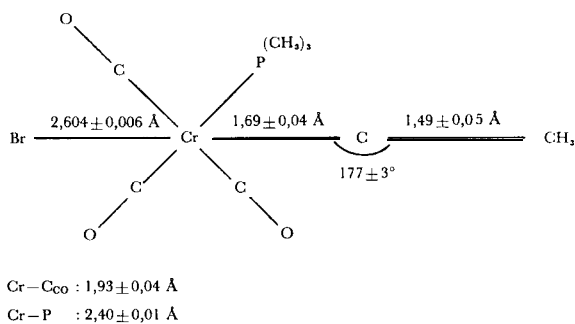
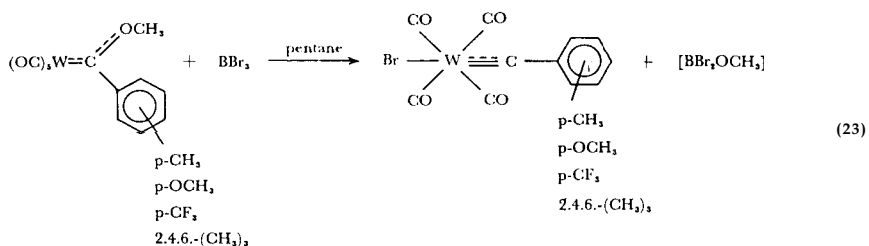


Fig. 12. Molecular structure of mer-(bromo)tricarbonyl(methylcarbene)trimethylphosphine chromium(0).

REACTIONS OF OTHER PENTACARBONYL CARBENE COMPLEXES WITH BORONTRIHALIDES

We thought it would also be interesting to study the effects of changes in the organic radical of the carbyne ligand on the stability and behaviour of these compounds. For this purpose, we treated a number of phenyl-substituted pentacarbonyl[methoxy(aryl)carbene]tungsten(0) complexes with borontribromide (91) (Eq. 23).



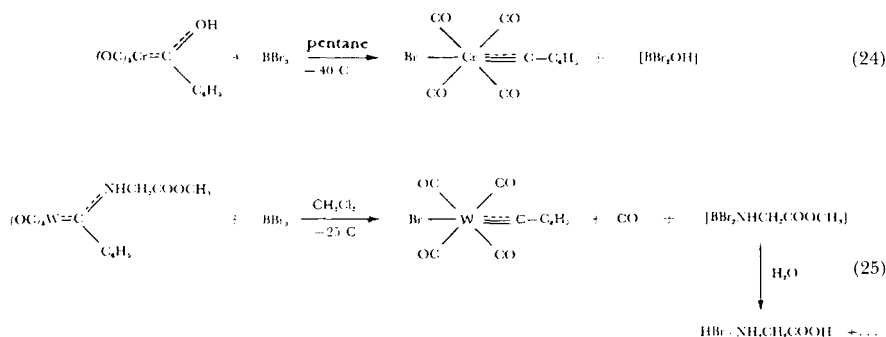
¹³C-NMR spectroscopy seemed to us to be a suitable tool for studying electronic changes in this case. Figure 13 compares the chemical shifts of the carbyne carbon atoms of the resulting trans-(bromo) tetracarbonyl(aryl) carbyne) tungsten (0) complexes (87,92).

$\equiv \text{C} - \text{C}_6\text{H}_4 - \text{CF}_3$	266,15
$\equiv \text{C} - \text{C}_6\text{H}_5$	271,30
$\equiv \text{C} - \text{C}_6\text{H}_4 - \text{CH}_3$	271,43
$\equiv \text{C} - \text{C}_6\text{H}_4 - \text{OCH}_3$	273,16
$\equiv \text{C} - \text{C}_6\text{H}_2(\text{CH}_3)_3$	275,13

Fig. 13. ¹³C-NMR shifts of C_{carbyne} atoms of some trans-Br(CO)₄WC-Ar complexes (values of δ , CD₂Cl₂ relative to int. TMS).

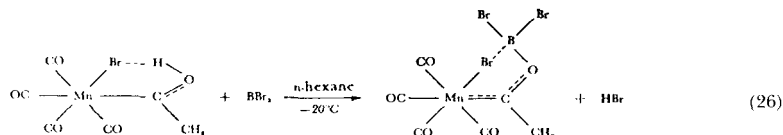
Quite unexpectedly, we find in this series that the p-CF₃ derivative has the lowest value of δ , i.e. the strongest screening for the carbyne carbon atom; we find a much weaker screening for the 2,4,6-trimethyl phenyl compound. We need more data to interpret this result exactly and experiments for this purpose are in progress.

We could further show that not only methoxy(organyl)carbenecomplexes react with borontrihalides in the manner described above. We found that trans-(bromo) tetracarbonyl (phenyl carbyne) chromium(0) and trans-(bromo) tetracarbonyl(phenyl carbyne) tungsten(0) can also be obtained by treating pentacarbonyl[hydroxy(phenyl)carbene]chromium(0) (93) as well as pentacarbonyl(phenyl carbene)glycinemethyltungsten(0) (64) (Eqs. 24 and 25) with borontrihalides.



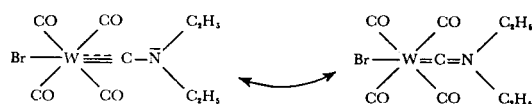
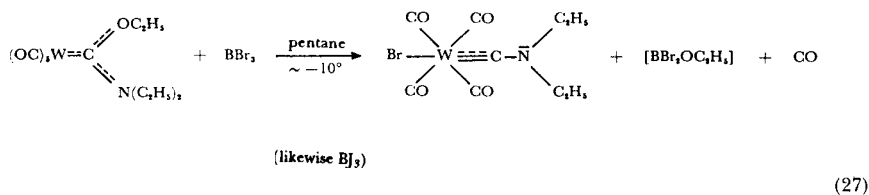
I would like to point out especially that the reaction of the aminoacidcarbene complex with borontribromide offers another convenient way of cleaving the metal pentacarbonyl (phenyl carbene)yl protecting group - under very mild conditions, namely, even at -25°C.

The fact that experimental results cannot always be generalised is shown by the reaction of cis-(bromo)tetracarbonyl[hydroxy(methyl)carbene]manganese with borontribromide. The reaction does not lead to the analogous carbyne complex, but to a product in which the hydrogen atom of the hydroxy group is replaced by the BBr₂ radical (92) (Eq. 26).



The situation here does not seem to be conducive to the formation of a carbyne complex because of the "fixation" of the OH group by the formation of a bridge with the bromide ligand in the cis position. Another interesting question was how pentacarbonyl[ethoxy(diethylamino)carbene] tungsten(0) would react with borontrihalide, because - as we have seen earlier - in principle the alkoxy group as well as the amino group can be cleaved. The

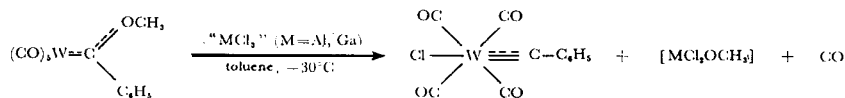
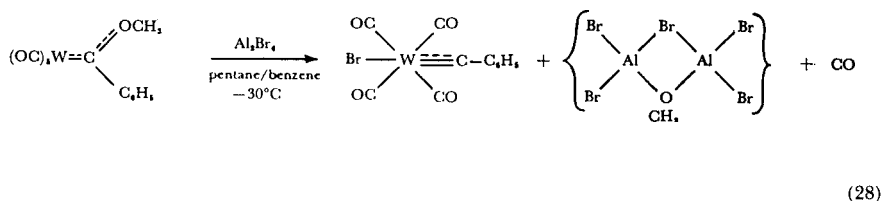
experiment led to the exclusive formation of *trans*-(bromo) tetracarbonyl(diethyl amino carbene) tungsten (0) (95) - a compound that can be handled relatively easily. Its stability is probably due to the interaction of the metal/carbon bond with the free electron pair of nitrogen. This explanation is also supported by ^{13}C -NMR measurements (Eq. 27).



$\delta_{\text{C}_{\text{carbene}}} = 235,6 \text{ ppm (CD}_2\text{Cl}_2, \text{ int. TMS)}$

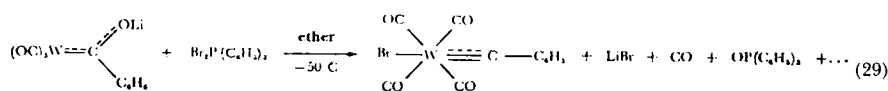
REACTIONS OF PENTACARBONYL CARBENE COMPLEXES WITH ALUMINIUM AND GALLIUM HALIDES

We could extend the scope of our method of synthesis by using aluminium trichloride, aluminium tribromide and gallium trichloride instead of borontrihalides (96) (Eq. 28). With these compounds we also obtained carbene complexes in good yields.



REACTIONS OF LITHIUM BENZOYL PENTACARBONYL TUNGSTATES WITH TRIPHENYLPHOSPHINE DIBROMIDE

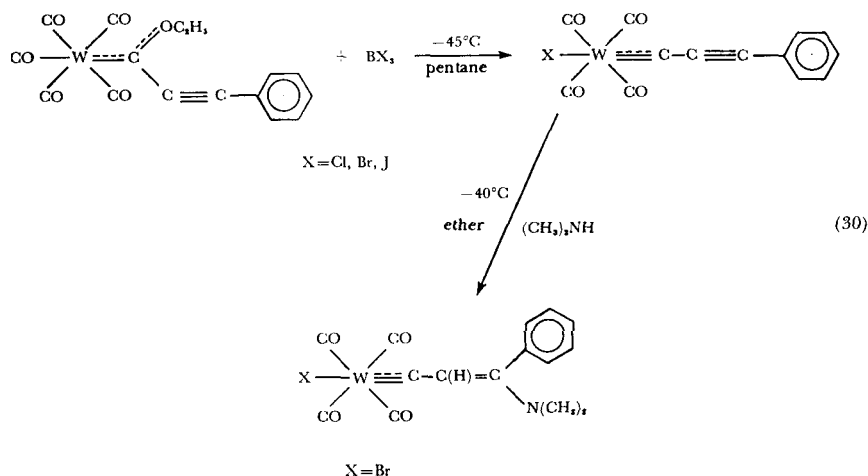
A new method of synthesis - new in principle - was discovered from the reaction of lithium benzoyl pentacarbonyl tungstate with triphenyl phosphine dibromide, at low temperatures in ether (97) (Eq. 29).



The first step is presumably the establishment of a $C_{\text{carbene}}\text{-O-P}$ bond with the formation of lithium bromide. The intermediate product thus formed could then be stabilised by reaction between the second bromine atom and the metal, elimination of a CO ligand and the cleavage of triphenyl phosphine oxide under thermodynamically favourable conditions to form the carbyne complex.

REACTIVITY OF THE CARBYNE LIGAND

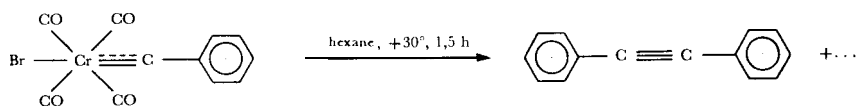
With the carbyne complexes also, we did not wish to confine ourselves to the preparation and spectroscopic study of new representatives of this type of compound. We therefore began, in the meantime, to study their reactivity. We first looked for a possible way of comparing such a metal-carbon triple bond with a carbon-carbon triple bond. We found this in the reaction of dimethyl amine with *trans*-(bromo) tetracarbonyl (phenyl acetylenyl carbyne) tungsten (0) (98). This latter compound can be obtained by treating pentacarbonyl [ethoxy(phenylacetylenyl)carbene] tungsten(0) (21) with borontribromide. We found that at -40°C in ether only addition to the organic triple bond takes place while the carbyne-metal bond remains unchanged (99) (Eq. 30).



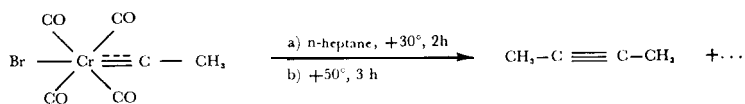
At the same time we also tried to study how the carbyne ligand behaves when it is cleaved from the metal. As with the carbene complexes, a dimerisation takes place in the absence of a suitable reaction partner, but alkynes are formed in this case (100). The conditions for the decomposition are very mild.

Tolane or dimethyl acetylene can be obtained in this way in non-polar solvents even at 30°C . We get the same result on heating the solid methyl carbyne complex to 50°C (Eq. 31).

We think that the path is now open for utilising carbyne complexes to synthesise organic compounds. As far as we know, no systematic source of "carbyne complexes" is now available for the purpose of synthesis. Because the



(31)



cleavage conditions are mild, there is a wide scope here for interesting applications.

That brings me to the end of my lecture. I hope I have shown you that organometallic chemistry offers many more interesting possibilities.

ACKNOWLEDGEMENTS

The research results that I have had the honour to report are largely the work of my colleagues.

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