The general preparative route and the bonding properties of transition metal complexes with acyclic carbene ligands are discussed. Phenylmethoxycarbene pentacarbonylcobalt(0) forms 1,2-dimethoxy-1,1,2,2-tetraphenylethane with phenyllithium. This reaction is in accord with the $\Delta^+$ charged C$_{\text{carbene}}$ atom in the complex. Thiolysis and selenolysis of methoxyorganylcarbene pentacarbonylcobalt(0) or tungsten(0) yield thio- and selenocarbene complexes, respectively. IR. and dipole measurements of the complexes (CO)$_5$W–C(XCH$_3$)CH$_3$ (X = O, S, Se, NH) show that the negative charge transfer from the carbene ligand to the W(CO)$_5$ residue increases in the sequence O < Se < S < NH. The x-ray structure on the novel ethoxydimethylaminocarbene pentacarbonylcobalt(0) confirms for the first time a trans effect of the carbene ligand. The bond distances exhibit a stronger $\pi$-character for the C$_{\text{carbene}}$–N bond than for the C$_{\text{carbene}}$–O bond. The reaction of Cr(CO)$_5$ with (CH$_3$)$_2$PLi in ether at $-80^\circ$C and the subsequent alkylation with [(C$_2$H$_5$)$_3$O][BF$_4$] yielded a complex with the formula CrC$_{14}$H$_{22}$O$_6$P$_2$. Instead of the expected dimethylphosphinoethoxycarbene pentacarbonylcobalt(0), a complex which we suggest to be cis-(bisdimethylphosphinoethoxycarbene) tetracarbonylcobalt(0) is formed. According to x-ray results methoxyphenylcarbene enneacarbonyldimanganese has the carbene ligand in the equatorial position like its technetium and rhenium homologues and the methoxymethylcarbene analogues. Several preparative routes are given for mononuclear carbene tetracarbonylsiron complexes. The addition of 2,6-dimethoxyphenyllithium to Fe(CO)$_5$ and the subsequent ethylation yields binuclear Fe$_2$(CO)$_7$C(OCC$_2$H$_5$)$_3$C$_6$H$_3$(OCH$_3$)$_2$, whose structure was proved by x-ray analysis. Details of the preparation and properties of tetracoordinated mixed transition metal carbene complexes of Ni, Co and Fe follow. Cleaved methoxyphenylcarbene ligands form with organic substrates such as methyl trans-crotonate, ethyl vinyl ether and diethyl fumarate cyclopropane derivatives. The isomer ratio of the cyclopropane derivatives is shown to depend on the metal of the parent carbene complex. Insertion of methoxyphenylcarbene ligands occurs with diphenylsilane and methanol.

The taming of shortlived organic intermediates by complexation with transition metals is one of the present-day challenges of organometallic chemists. The $\pi$-complexes of cyclobutadiene, and of allyl, cyclopentadienyl and cyclohexadienyl radicals show the success of the international efforts in this field. Our exertions have been devoted to the carbenes for a couple of years. In 1964 we reported the preparation of the first stable transition metal complex...
carbene complexes, recognized as such, namely \((\text{CO})_5\text{WC(OCH}_3\text{)CH}_3\) and \((\text{CO})_5\text{WC(OCH}_3\text{)C}_6\text{H}_5\).

**PREPARATION OF METAL CARBONYL CARBENE COMPLEXES**

The general preparative route was the reaction of \(\text{W(CO)}_6\) with organolithium reagents \(\text{RLi}\), such as \(\text{CH}_3\text{Li}\) or \(\text{C}_6\text{H}_5\text{Li}\). The nucleophilic attack of the carbanion on the \(\delta^+\) charged carbon atom of one of the CO ligands yielded a lithium acylmetallate which was soluble in water and formed a rather unstable hydroxycarbene complex with acids. In a second step a \(\text{CH}_2\) insertion from \(\text{CH}_2\text{N}_2\) into the \(\text{O—H}\) bond of the hydroxycarbene ligand gave methoxymethyl- or methoxyphenylcarbene pentacarbonyltungsten(0). The use of trimethyloxoniumtetrafluoroborate\(^2\) improved the synthesis. Extensions to \(\text{Cr(CO)}_6\), \(\text{Mo(CO)}_6\) and substituted metal hexacarbonyls followed very soon yielding a great variety of acyclic carbene carbonyl transition metal complexes. At the present time there is a great deal of international research activity directed towards other types of carbene complexes. Schöllkopf\(^3\), Wanzlick\(^4\), Richards\(^5\), Clark\(^6\), Crociani\(^7\) and their co-workers may be mentioned in this connection.

The structure of methoxyphenylcarbene pentacarbonylchromium(0), disclosed by the x-ray investigations of Mills\(^8\), has shown that in the crystalline state only the *trans* isomer exists. The term ‘*trans*’ is applied by definition
RECENT ASPECTS OF TRANSITION METAL CARBONYL CARBENE COMPLEXES

to the partial double bond $\text{C}_{\text{carbene}}-\text{O}$, which proves the transfer of electron density from $\text{O}$ to $\text{C}_{\text{carbene}}$ and furthermore to the $\text{Cr(CO)}_5$ residue.

To a lesser extent the vacant $\pi$-orbital of $\text{C}_{\text{carbene}}$ is also filled up by $d_\pi-p_\pi$ backbonding from the metal. In my lecture at the XIIth International Conference on Coordination Chemistry$^9$, CO and carbene substitutions, ester type cleavage, addition and rearrangement reactions, and H substitution of such carbene complexes were discussed in more detail. Among other things a $\delta^+$ charged carbene ligand was postulated while the $\delta^-$ centre should be located on the $\text{Cr(CO)}_5$ part of the molecule. The dipole moment of $\text{(CO)}_5\text{CrC(OCH}_3\text{)}\text{C}_5\text{H}_5$, 4.08 D, is rather high. The formation of 1,2-dimethoxy-1,1,2,2-tetraphenylethane, among other products, from the reaction of $\text{(CO)}_5\text{CrC(OCH}_3\text{)}\text{C}_5\text{H}_5$ with $\text{C}_6\text{H}_5\text{Li}^{10}$ is additional chemical proof for a $\delta^+$ charged $\text{C}_{\text{carbene}}$ atom. Possibly this will provide a new route for the synthesis of ethane derivatives.

![Reaction Equation]

Properties of $\text{C}_2(\text{OCH}_3)_2(\text{C}_6\text{H}_5)_4$

- Light-yellow crystals
- m.p. 163°C, soluble in organic solvents
- mol. wt. calc: 394.5; found: 394
- $^1\text{H}$ n.m.r., CDCl$_3$, internal TMS standard:
  - $\tau = 2.90$ (10) $\text{C}_6\text{H}_5$
  - $\tau = 7.00$ (3) $\text{OCH}_3$
- Analysis:
  - calc: C 85.25; H 6.64; O 8.11% 
  - found: C 85.38; H 6.60; O 8.00%

Cationic $\pi$-cyclopentadienyl metal carbonyl carbene complexes

The success of Green and his group in preparing cationic $\pi$-carbene carbonyl cyclopentadienyl metal complexes seems to be important$^{11,12}$. 

![Diagram of Cationic $\pi$-Cyclopentadienyl Metal Carbonyl Carbene Complexes]
E. O. FISCHER

Suitable acyl complexes are susceptible to protonation and react subsequently with \( \text{CH}_2\text{N}_2 \) in a similar manner to the hydroxycarbene complexes. The direct addition of an alkyl cation via oxonium salts is also possible and cationic carbene complexes are formed.

**Thiocarbene pentacarbonyl metal complexes**

Since our finding that the OCH\(_3\) group in \((\text{CO})_5\text{CrC(OCH}_3)\text{R'}\) complexes undergoes aminolysis with primary or secondary amines, cleaving CH\(_3\)OH and forming \((\text{CO})_5\text{CrC(NHR)}\text{R'}\) complexes\(^{13}\), we have tried to expand the range of heteroatoms in carbene ligands beyond O and N. Recently, a wide variety of thiocarbene complexes of chromium and tungsten have been obtained by thiolysis in thiol solvents\(^{14}\).

\[
\text{(CO)}_5\text{M} \equiv \text{C}[\text{OCH}_3] + \text{HSR}^\ast \xrightarrow{\text{room temperature}} \text{(CO)}_5\text{M} \equiv \text{C}[\text{SR}^\ast] + \text{HOCH}_3
\]

\(M = \text{Cr, W}
\)

\(R' = \text{CH}_3, \text{C}_6\text{H}_5
\)

\(R^\circ = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5
\).

**Properties of thiocarbene complexes**

<table>
<thead>
<tr>
<th>Colour</th>
<th>State</th>
<th>m.p.</th>
<th>Decomp.</th>
<th>Subl. dipole moment (HV) (C(<em>6)H(</em>{12}), 20(^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CO})_5\text{CrC}[\text{OCH}_3])</td>
<td>deep-red</td>
<td>34(^\circ)C</td>
<td>&gt;65(^\circ)C</td>
<td>RT</td>
</tr>
<tr>
<td>((\text{CO})_5\text{CrC}[\text{SCH}_3])</td>
<td>deep-red</td>
<td>34(^\circ)C</td>
<td>&gt;65(^\circ)C</td>
<td>RT</td>
</tr>
<tr>
<td>((\text{CO})_5\text{CrC}[\text{SC}_2\text{H}_5])</td>
<td>deep-red</td>
<td>67(^\circ)C</td>
<td>&gt;85(^\circ)C</td>
<td>RT</td>
</tr>
<tr>
<td>((\text{CO})_5\text{CrC}[\text{S}\phi])</td>
<td>red-brown</td>
<td>—</td>
<td>&gt;75(^\circ)C</td>
<td>RT</td>
</tr>
<tr>
<td>((\text{CO})_5\text{CrC}[\text{SC}_2\text{H}_5])</td>
<td>red-brown</td>
<td>—</td>
<td>&gt;75(^\circ)C</td>
<td>RT</td>
</tr>
<tr>
<td>((\text{CO})_5\text{CrC}[\text{S}\phi])</td>
<td>red-brown</td>
<td>—</td>
<td>&gt;45(^\circ)C</td>
<td>RT</td>
</tr>
<tr>
<td>((\text{CO})_5\text{W} \equiv \text{C}[\text{OCH}_3])</td>
<td>deep-red</td>
<td>34(^\circ)C</td>
<td>&gt;90(^\circ)C</td>
<td>RT</td>
</tr>
</tbody>
</table>

* All these complexes are very soluble in all organic solvents.
RECENT ASPECTS OF TRANSITION METAL CARBONYL CARBENE COMPLEXES

The thiocarbene complexes are less stable than the O- and N-carbene complexes and have intermediate dipole moment values. There is an effective negative charge transfer (mixed from \( \sigma \)- and \( \pi \)-contributions) from the thiocarbene ligands to the extremely electronegative M(CO)\(_5\) residue.

\[
\begin{align*}
\text{CH}_3 & \quad \text{very} \\
\text{SCH}_3 & \quad \text{soon.}
\end{align*}
\]

Methylselenomethylcarbene pentacarbonyltungsten (0)\(^{15}\)

In spite of our experience with sulphur derivatives it took us more than a year to prepare the first selenocarbene complex. This was achieved by selenolysis of (CO)\(_5\)WC(OCH\(_3\))CH\(_3\) at low temperatures in the dark.

\[
\begin{align*}
\text{(CO)}_5\text{W} &= \begin{array}{c}
\text{OCH}_3 \\
\text{CH}_3
\end{array} + \text{HSeCH}_3 \quad \text{10°C} \quad \text{(CO)}_5\text{W} &= \begin{array}{c}
\text{SeCH}_3 \\
\text{CH}_3
\end{array} + \text{HOCH}_3
\end{align*}
\]

Properties of (CO)\(_5\)WC(SeCH\(_3\))CH\(_3\)
- Black crystals
- Light and temperature sensitive
- Diamagnetic, m.p. 38°C
- Mol. wt. calc.: 445.0; found: 445 (mass spectra)
- I.r.: \( \nu_{\text{CO}} \) (n-hexane, LiF): 2066 s, 1954 ss cm\(^{-1}\)
- \(^1\)H n.m.r.: (CDCl\(_3\), 20°C)
  - \( \tau \) 6.63 (1, s) CCH\(_3\)
  - \( \tau \) 7.47 (1, s) SeCH\(_3\) satellites according to \(^{77}\)Se

Analysis
- calc.: C 21.60 H 1.36 Se 17.75 O 17.98 W 41.32% 
- found: C 21.72 H 1.36 Se 17.20 O 18.30 W 41.10%

COMPARISON OF THE CHARGE TRANSFER IN (CO)\(_5\)W–C(XCH\(_3\))CH\(_3\) COMPLEXES

It is now possible to compare, for the first time, the effective charge transfer in (CO)\(_5\)WC(XCH\(_3\))CH\(_3\) complexes (X = O, S, Se, NH) from the carbene ligand to the W(CO)\(_5\) residue, by means of their \( A_1 - \nu_{\text{CO}} \) i.r. frequencies referring to the CO trans to the carbene ligand, and by their dipole moments.

The sequence O < Se < S < NH for the increasing negative charge transfer from the carbene ligands to the W(CO)\(_5\) residue is clearly shown.
Some time ago we prepared the first complex with a carbene ligand stabilized by two heteroatoms, namely (CO)₅Cr(CO₂H₅)N(C₂H₅)₂, by adding (C₂H₅)₂NLi to Cr(CO)₆ in the first step and then [(C₂H₅)₃O]BF₄ in the second step. Nevertheless, our intention to obtain bond angles and distances from this compound by x-ray investigation failed because of its low melting point. Therefore we treated Cr(CO)₆ with (CH₃)₂NLi in THF. Subsequent ethylation in CH₂Cl₂ with [(C₂H₅)₃O]BF₄ yielded (CO)₅Cr(CO₂H₅)N(CH₃)₂.  

\[
\text{Cr}(\text{CO})₆ + R₂NLi \xrightarrow{\text{ether or THF, } 0°C} (\text{CO})₅\text{Cr} \equiv \begin{array}{c}
\text{O}\text{Li} \\
\text{NR}_2
\end{array}
\]

\[
(\text{CO})₅\text{Cr} \equiv \begin{array}{c}
\text{O}\text{Li} \\
\text{NR}_2
\end{array} + [(\text{C}_₂\text{H}_₅)₃\text{O}]\text{BF}_₄ \xrightarrow{\text{CH}_₂\text{Cl}_₂, 0°C} (\text{CO})₅\text{Cr} \equiv \begin{array}{c}
\text{OC}_{\text{H}}₂ \\
\text{NR}_2
\end{array}
\]

\[
+ \text{LiBF}_₄ + 2 \text{O}(\text{C}_₂\text{H}_₅)_₂
\]

\( R = \text{CH}_₃, \text{C}_₂\text{H}_₅ \)

Properties

Pale-yellow crystals

m.p. 29°C, subl., diamagnetic,
mol. wt. calc.: 321; found: 321 (mass spectrum)
I.r. (n-hexane): \( \nu_{\text{CO}} \) 2057 (A₁), 1927 (A₁, E) cm⁻¹
dipole moment: \( \mu_{\text{C}_₆\text{H}_{₁₂}, 20°C} \) = 5.75 ± 0.1 D

1H n.m.r. (C₆D₆): \( \tau \) 5.49 (OCH₂), \( \tau \) 6.29 and \( \tau \) 7.09 (NCH₂) \( \tau \) 8.96, \( \tau \) 9.07 and \( \tau \) 9.25 (CH₃)

Pale-yellow crystals

m.p. 45°C. subl., diamagnetic,
mol. wt. calc.: 293; found: 293 (mass spectrum)
I.r. (n-hexane): \( \nu_{\text{CO}} \) 2050 (A₁), 1929 (A₁, E) cm⁻¹

1H n.m.r. (C₆D₆): \( \tau \) 5.70 (OCH₂), \( \tau \) 7.13 and \( \tau \) 7.86 (NCH₃) \( \tau \) 9.09 (O—CH₂—CH₃)
The C\textit{carbene} atom is sp\textsuperscript{2} hybridized. The carbene ligand is found to be \textit{trans} configurated and its plane forms a 45° angle with the axes of the four \textit{cis} CO ligands. There is a distinct double bond character of the C\textit{carbene}-O as well as of the C\textit{carbene}-N bond, the latter one definitely stronger, as one would expect. For the first time a significant \textit{trans} effect from the carbene ligand to the \textit{trans} CO ligand is observed. The Cr—C\textsubscript{0} trans distance of 1.85 Å is shortened compared with an average of 1.89 Å for the Cr—C\textsubscript{0} equatorial bonds. This is additional proof for our original concept that acyclic carbene ligands with heteroatoms are stronger donors and weaker acceptors than CO. All our efforts to substitute the \textit{0C\textsubscript{2}H\textsubscript{5}} group in the carbene ligand with an amino group have failed. This indicates that the C\textit{carbene}-O bond is not sufficiently polarized to allow substitution with NR\textsubscript{2}. In other words, the electron deficiency in the ‘empty’ p-orbital of the C\textit{carbene} atom is mainly compensated by the N atom, resulting in a comparatively smaller p\textsubscript{π}-p\textsubscript{π} interaction in the O—C\textit{carbene} bond.

The x-ray result on (CO)\textsubscript{5}CrC(OC\textsubscript{2}H\textsubscript{5})N(CH\textsubscript{3})\textsubscript{2} is in accord with six other structures of carbene pentacarboxylchromium(0) complexes.
### Selected x-ray data of carbene metal carbonyl complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Cr–C&lt;sub&gt;Carb&lt;/sub&gt;</th>
<th>C&lt;sub&gt;Carb&lt;/sub&gt;–C</th>
<th>C&lt;sub&gt;Carb&lt;/sub&gt;–O(N)</th>
<th>Cr–C&lt;sub&gt;CO&lt;/sub&gt;</th>
<th>C≡O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO)&lt;sub&gt;5&lt;/sub&gt;Cr=CH/OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.04</td>
<td>1.47</td>
<td>1.33</td>
<td>1.88</td>
<td>1.14</td>
</tr>
<tr>
<td>(CO)&lt;sub&gt;2&lt;/sub&gt;p(CO)&lt;sub&gt;2&lt;/sub&gt;Cr=CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.00</td>
<td>1.53</td>
<td>1.32</td>
<td>1.87</td>
<td>1.16</td>
</tr>
<tr>
<td>(CO)&lt;sub&gt;5&lt;/sub&gt;Cr=CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.09</td>
<td>1.51</td>
<td>1.33</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>(CO)&lt;sub&gt;5&lt;/sub&gt;Cr=CH(N(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2.16</td>
<td>1.50</td>
<td>1.31</td>
<td>1.90</td>
<td>1.14</td>
</tr>
<tr>
<td>(CO)&lt;sub&gt;5&lt;/sub&gt;Cr=CH(OH)</td>
<td>2.15</td>
<td>1.51</td>
<td>1.31</td>
<td>1.88</td>
<td>1.14</td>
</tr>
<tr>
<td>(CO)&lt;sub&gt;5&lt;/sub&gt;Cr=CH/C=O</td>
<td>2.05</td>
<td>1.40</td>
<td>1.39</td>
<td>1.90</td>
<td>1.13</td>
</tr>
<tr>
<td>(CO)&lt;sub&gt;5&lt;/sub&gt;Cr=CH(N(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2.13</td>
<td>1.346(O)</td>
<td>1.847 ax</td>
<td>1.158 ax</td>
<td>1.1141 eq</td>
</tr>
</tbody>
</table>

**methyl acetate**  

- CH<sub>3</sub>  
  - O=C/<sub>1.52</sub>  
  - 1.22/<sub>1.36</sub>  
  - O/C<sub>1.46</sub>  

**acetamide**  

- CH<sub>3</sub>  
  - O=C/<sub>1.53</sub>  
  - 1.2/<sub>1.36</sub>  
  - NH/<sub>H</sub>  

**ethyl carbamate**  

- H  
  - N–H/<sub>1.22</sub>  
  - 1.33/<sub>C<sub>2</sub>H<sub>5</sub></sub>  
  - O=C/<sub>1.47</sub>  

360
REACTION OF Cr(CO)$_6$ WITH (CH$_3$)$_2$PLi AND [(C$_2$H$_5$)$_3$O]BF$_4$

Unexpected results were obtained during preliminary investigations using (CH$_3$)$_2$PLi instead of (CH$_3$)$_2$NLi to expand our experience with stabilizing heteroatoms.

\[
\text{Cr(CO)$_6$} \xrightarrow{(1)(\text{CH$_3$})$_2$PLi, (C$_2$H$_5$)$_2$O, $-80^\circ$C} \text{CrC$_{14}$H$_{22}$O$_6$P$_2$} \\
\text{(2) [(C$_2$H$_5$)$_3$O]BF$_4$, CH$_2$Cl$_2$, $-20^\circ$C}
\]

Properties of CrC$_{14}$H$_{22}$O$_6$P$_2$

- Reddish-orange crystals
- Diamagnetic, m.p. 94°C
- Mol. wt.: calc: 400.3; found: 400 (mass spectrum)
- Dipole moment: $\mu_{\text{calc}}$: 20°C 8.30 ± 0.1 D
- $\nu_{\text{CO}}$(n-hexane, LiF): 2008 m, 1917 m, 1894 ss cm$^{-1}$
- $^1$H n.m.r. (C$_6$D$_5$CD$_3$, 40°C):
  - $\tau$: 6.24 OCH$_2$ (2, q);
  - $\tau$: 8.67, $\tau$: 8.73, $\tau$: 8.80 PCH$_3$ (6);
  - $\tau$: 9.04 OCH$_2$CH$_3$ (3, t)

Analysis

- Calc: C 42.01, H 5.54, O 23.98, P 15.48, Cr 12.99%
- Found: C 42.14, H 5.54, O 24.20, P 15.20, Cr 13.28%

When Cr(CO)$_6$ is treated with an equivalent amount of (CH$_3$)$_2$PLi and subsequently with [(C$_2$H$_5$)$_3$O]BF$_4$, instead of the expected dimethylphosphinoethoxycarbene pentacarbonylchromium(0), a red-orange, volatile compound of the formula CrC$_{14}$H$_{22}$O$_6$P$_2$ is formed.

Hypothetical structure of 'CrC$_{14}$H$_{22}$O$_6$P$_2$'

\[
\text{[cis-(CO)$_4$Cr} \text{N=CH} \text{N=CH} \text{CH}_3 \text{]} \text{2} \]

\[
\nu_{\text{CO}}$(CHCl$_3$, LiF) 1986 w 1870 s 1847 s 1825 sh cm$^{-1}$

\[
\text{['CrC$_{14}$H$_{22}$O$_6$P$_2$']} \quad \nu_{\text{CO}}$(CHCl$_3$, LiF) 2008 m 1912 m 1883 ss cm$^{-1}$
\]

The i.r. and $^1$H n.m.r. data suggest a cis-(bisdimethylphosphinoethoxycarbene) tetracarbonylchromium(0) structure. There is a slight possibility of additional P–P bonding, but we hope to be able to exclude this alternative very soon.
E. O. FISCHER

In contrast to all our earlier findings a double addition to a metal carbonyl seems to occur with (CH₃)₂PLi. This is a further warning that one should not transfer, too formally, experience with heteroatoms from the first short period, to higher homologues. CrC₁₄H₂₂O₆P₂ is the second example of a biscarbene tetracarbonyl metal complex. The first one, bis(1,3-dimethyl-4-imidazolinylidene) tetracarbonylchromium(0)¹⁹, with cyclic carbene ligands, was prepared last year by Dr Öfele in our laboratories by irradiation or heating with subsequent disproportionation of the monocarbene complex into the biscarbene compound and the metal hexacarbonyl.

**METHOXYORGANYLCARBENEC ENNEACARBONYL DIMETAL COMPLEXES OF MANGANESE, TECHNETIUM AND RHENIUM**²⁰

I now wish to consider the carbene complexes derived from the binuclear decacarbonyl dimetals of manganese, technetium and rhenium. An interesting problem is whether CH₃Li or C₆H₅Li attacks one of the two axial or one of the eight equatorial CO ligands, resulting in, after formal addition of a CH₃⁺ cation, a carbene ligand in the axial or equatorial position.

\[
\text{M}_2(\text{CO})_{10} + \text{RLi} \rightarrow (\text{CO})_9\text{M}_2\text{C(O)Li}_\text{R} + \text{LiBF}_4 + (\text{CH}_3)_2\text{O}
\]

\(M = \text{Mn, Tc, Re; R} = \text{CH}_3, \text{C}_6\text{H}_5\)

Properties and \(v(\text{CO})\) frequencies of methoxyorganylcarbene complexes of Mn, Tc and Re (n-hexane, LiF optics)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>m.p. °C</th>
<th>(v(\text{CO}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO)₉Mₙ(C(OCH₃))CH₃</td>
<td>orange crystals</td>
<td>82</td>
<td>2092 w, 2024 s, 2008 s, 1996 ss, 1989 m, 1966 m, 1956 m, 1949 m cm⁻¹</td>
</tr>
<tr>
<td>(CO)₉Mₙ(C(OCH₃))C₆H₅</td>
<td>orange crystals</td>
<td>68</td>
<td>2089 m, 2024 s, 1996 ss, 1971 m, 1954 m cm⁻¹</td>
</tr>
<tr>
<td>(CO)₉Tc₂(C(OCH₃))C₆H₅</td>
<td>yellow crystals</td>
<td>83</td>
<td>2020 w, 2043 m, 2009 m, 1993 ss, 1989 m, 1979 m, 1960 sh, 1957 s cm⁻¹</td>
</tr>
<tr>
<td>(CO)₉Re₂(C(OCH₃))CH₃</td>
<td>yellow crystals</td>
<td>110</td>
<td>2010 w, 2046 s, 2019 m, 2000 ss, 1992 s, 1973 m, 1957 s, 1951 s cm⁻¹</td>
</tr>
<tr>
<td>(CO)₉Re₂(C(OCH₃))C₆H₅</td>
<td>yellow crystals</td>
<td>94</td>
<td>2010 w, 2048 s, 2019 w, 2001 ss, 1993 m, 1973 m, 1957 sh, 1952 s cm⁻¹</td>
</tr>
</tbody>
</table>

\[C(9)\]

\[C_{4v}(5)\]
Eight or in one case seven \( \nu_{\text{CO}} \) absorptions of the well-characterized methoxymethyl- or methoxyphenylcarbene complexes are observed according to the symmetries of the \( \text{M}_2(\text{CO})_9 \) fragments, when the carbene ligands are in the equatorial position. Only \( (\text{CO})_9\text{Mn}_2\text{C(OCH}_3\text{)}\text{C}_6\text{H}_5 \) showed five \( \nu_{\text{CO}} \) bands as one would expect for an axial position of the methoxyphenylcarbene ligand in this compound. Speculation about the small Mn atom, the bulky methoxyphenylcarbene ligand and the less crowded axial position in \( \text{M}_2(\text{CO})_9\text{L} \) compounds was tempting. Nevertheless, according to our past experience that 'one method is no method' an x-ray investigation was carried out in our laboratories.\(^{21}\)

\[
\text{X-ray structure of } \text{Mn}_2(\text{CO})_9\text{C(OCH}_3\text{)}\text{C}_6\text{H}_5
\]

In \( (\text{CO})_9\text{Mn}_2\text{C(OCH}_3\text{)}\text{C}_6\text{H}_5 \) the carbene ligand was also found to be in the equatorial position: we have postulated this equatorial positioning for all the other related carbene complexes. The carbene ligand is cis configured and there is no significant change in all of the remaining bond distances compared to those of \( \text{Mn}_2(\text{CO})_{10} \). This was investigated by Rundle and Dahl. Obviously nine \( \text{CO} \) ligands are less sensitive towards a charge of the electron density on the central atoms, than five or less, in the mononuclear carbene complexes.
CARBENE TETRACARBONYLIRON COMPLEXES

The addition of lithiumorganyls to Fe(CO)₅, as a representative pentacoordinated metal carbonyl, yields acyl tetracarbonyltertates. By subsequent treatment with oxonium salts, or even better with trityl chloride, asymmetric dimers of the type [Fe(CO)₃COR]₂ with bridging acyl groups are obtained. We have found a number of preparative methods to isolate the mononuclear carbene tetracarbonyliron complexes.

Preparative methods

(1) C₅H₅M(CO)(NO)C₆H₅ + Fe(CO)₅ \text{u.v.} \rightarrow C₅H₅M(CO)₂NO

M = Mo, Cr
X = OCH₃, OC₂H₅, N(CH₃)₂

(2) Cr(CO)₂C₆H₅ + Fe(CO)₅ \rightarrow Cr(CO)₃ + (CO)₄FeC₆H₅

(3) Fe(CO)₅ + RLi \rightarrow (CO)₄FeC(OLi)R

R = C₆H₅, C₆F₅, C₆Cl₅

(4) (CO)₄FeC₆H₅ + (CH₃)₂NH \rightarrow (CO)₄FeC₆H₅ + C₂H₅OH

R = C₆H₅, C₆F₅

(5) Fe(CO)₅ + (C₂H₅)₂N Li \rightarrow (CO)₄FeC(O)(N(C₂H₅)₂)

Some properties of the iron carbene complexes including their ν_CO bands are given below.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>State at r.t.</th>
<th>m.p.</th>
<th>I.r. ν_{CO} solution spectra:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CO)₄FeC(O₇H₅)₆F₅</td>
<td>deep-red</td>
<td>crystalline</td>
<td>46°C</td>
<td>2065 m 2000 m 1971 s 1960 s</td>
</tr>
<tr>
<td>(CO)₄FeC(O₇H₅)₆Cl₅</td>
<td>light-red</td>
<td>crystalline</td>
<td>121°C</td>
<td>2065 m 2000 m 1971 s 1960 s</td>
</tr>
<tr>
<td>(CO)₄FeC(O₇H₅)₆H₅*</td>
<td>red-brown</td>
<td>oily</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(CO)₄FeC(O₇H₅)₆H₅</td>
<td>red-brown</td>
<td>oily</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(CO)₄FeC[N(CH₃)₂]₆F₅</td>
<td>yellow-orange</td>
<td>crystalline</td>
<td>129°C</td>
<td>2048 m 1981 m 1950 s 1941 s</td>
</tr>
<tr>
<td>(CO)₄FeC[N(CH₃)₂]₆H₅</td>
<td>white-yellow</td>
<td>crystalline</td>
<td>†</td>
<td>2049 m 1980 m 1951 s 1934 s</td>
</tr>
<tr>
<td>(CO)₄FeC[N(CH₃)₂]₆H₅</td>
<td>light-yellow</td>
<td>crystalline</td>
<td>†</td>
<td>2042 m 1974 m 1945 s 1923 s</td>
</tr>
<tr>
<td>(CO)₄FeC[N(C₂H₅)₂]₆H₅</td>
<td>red-brown</td>
<td>oily</td>
<td>—</td>
<td>2043 m 1950 s 1936 vs 1928 sh</td>
</tr>
</tbody>
</table>

Solubility: good—very good in all organic solvents.
* μ_{CH₃} 20°C = 3.19 ± 0.1 D.
† = no m.p.; on heating sinters with no noticeable decomposition.
E. O. FISCHER

The i.r. spectra support an apical position of the carbene ligand in a slightly distorted trigonal bipyramidal arrangement of the complexes. The influence of the growing charge transfer capacity of the carbene ligands can be seen from the second column of $\nu_{\text{CO}}$ bands, referring to the trans CO in this case, and from the decrease of all $\nu_{\text{CO}}$ absorptions.

**$\mu$-Ethoxy(2,6-dimethoxyphenyl)carbene heptacarbonyldiiron**

An unexpected result was obtained from the reaction between Fe(CO)$_5$ and 2,6-dimethoxyphenyllithium at $-50^\circ$C with subsequent ethylation in CH$_2$Cl$_2$.

$$\text{Fe(CO)}_5 + \text{Li} \rightarrow \text{ether} \rightarrow -50^\circ\text{C} \rightarrow + (\text{C}_2\text{H}_5)_3\text{OBF}_4 \rightarrow \text{CH}_2\text{Cl}_2 \rightarrow -20^\circ\text{C} \rightarrow \text{Fe}_2(\text{CO})_7\text{C}=(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_3(\text{OCH}_3)_2 +$$

Properties of Fe$_2$(CO)$_7$C(OC$_2$H$_5$)C$_6$H$_3$(OCH$_3$)$_2$

- black-red crystals
- diamagnetic
- m.p.: 98°C (decomp.)
- $\mu_{\text{C}_{6}\text{H}_{12}}$, $20^\circ\text{C} = 5.92$ D
- mol. wt. calc.: 502, found: 502 (mass spectrum)
- $\nu_{\text{CO}}$(n-hexane) 2077, 2022, 2012, 1990, 1972, 1945 cm$^{-1}$

The binuclear Fe$_2$(CO)$_7$C(OC$_2$H$_5$)C$_6$H$_3$(OCH$_3$)$_2$ complex raised structural problems which could not be settled by spectroscopic methods such as i.r. $^1$H n.m.r. and mass spectrometry. The final structure was obtained by x-ray investigations in our laboratories.

**X-ray structure of Fe$_2$(CO)$_7$C(OC$_2$H$_5$)C$_6$H$_3$(OCH$_3$)$_2**
In \( \text{Fe}_2(\text{CO})_7\text{C(OCH}_3\text{)}\text{C}_6\text{H}_3(\text{OCH}_3)_2 \) an ethoxy-2,6-dimethoxyphenyl-carbene tetracarbonyliron part can be assumed. This fixes an additional tricarbonyliron group with its 'allylic' \( \pi \)-cloud encompassing the iron, the carbene carbon, and the oxygen.

A higher electron density, caused by the two \( \text{OCH}_3 \) groups in ortho position on the phenyl ring, may possibly be of importance in the suggested \( \pi \)-bonding capacity. The compound itself is rather labile in solution.

**TETRA-COORDINATED MIXED TRANSITION METAL CARBENE COMPLEXES**

During our search for carbene complexes with lower coordination numbers we observed that the coordination number five is less stable than six. We encountered enhanced difficulties with the coordination number four. The preparation of such complexes only seemed possible with carbene ligands containing two heteroatoms. A representative metal tetracarbonyl, \( \text{Ni}(\text{CO})_4 \), yielded, with \( \text{(C}_2\text{H}_5)_2\text{NLi} \), a very unstable carbamoyl metallate which reacted with \( [(\text{C}_2\text{H}_5)_3\text{O}]\text{BF}_4 \) in \( \text{CH}_2\text{Cl}_2 \) at \(-30^\circ\text{C} \) to form ethoxydiethylaminocarbene tricarbonylnickel(0)\(^24 \), an oily compound. This compound slowly decomposes at \(-60^\circ\text{C} \).

\[
\text{Ni}(\text{CO})_4 \xrightarrow{(1) \text{C}_2\text{H}_5\text{NLi, ether, THF, } -78^\circ\text{C}} (\text{CO})_3\text{Ni} \equiv \text{C} = \text{OC}_2\text{H}_5
\]

Properties of \( (\text{CO})_3\text{Ni} \{\text{OC}_2\text{H}_5\} \text{Ni}\{\text{OC}_2\text{H}_5\}_2 \)

- pale-red oil
- diamagnetic, decomp. above \(-60^\circ\text{C} \)
- \( \nu_{\text{CO}} \{\text{hexane, LiF} \} : 2058 \text{ m, } 1976 \text{ ss cm}^{-1} \)

\[ \begin{align*}
\text{H n.m.r. (C}_6\text{D}_6) : \\
\tau 5.86 \text{ OCH}_2 (2, q) \tau 6.62 \text{ NCH}_3 (2, q) \tau 7.11 \text{ NCH}_2 (2, q) \\
\tau 9.02 \text{ OCH}_2\text{CH}_3 (3, t) \tau 9.16 \text{ NCH}_2\text{CH}_3 (3, t) \tau 9.25 \text{ NCH}_2\text{CH}_3 (3, t)
\end{align*} \]

**Analysis**

\[
\begin{align*}
\text{calc.} & : \text{C} 44.17, \text{ H} 5.56, \text{ N} 5.15, \text{ Ni} 21.58 \% \\
\text{found} & : \text{C} 44.60, \text{ H} 5.76, \text{ N} 4.96, \text{ Ni} 20.92 \%
\end{align*}
\]

Subsequently we were able to prepare a number of tetra-coordinated carbene complexes with ligands such as \( \text{CO} \), \( \text{NO} \) and \( \text{P(C}_6\text{H}_5\}_3 \). Their preparation and isolation in all cases required low temperature techniques.
<table>
<thead>
<tr>
<th>Compound</th>
<th>State at $-30^\circ$C</th>
<th>Colour</th>
<th>Decomposition starts at</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)NHCH$_3$</td>
<td>oily</td>
<td>red-brown</td>
<td>$\sim -30^\circ$C</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)NHCH$_3$</td>
<td>oily</td>
<td>orange</td>
<td>$\sim -30^\circ$C</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)NHCH$_3$</td>
<td>oily</td>
<td>yellow</td>
<td>$\sim -40^\circ$C</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)N(CH$_3$)$_2$</td>
<td>oily</td>
<td>red</td>
<td>$\sim -20^\circ$C</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)N(CH$_3$)$_2$</td>
<td>oily</td>
<td>orange</td>
<td>$\sim -20^\circ$C</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)N(CH$_3$)$_2$</td>
<td>oily</td>
<td>yellow</td>
<td>$\sim -25^\circ$C</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)Ni(C$_2$H$_5$)$_2$</td>
<td>oily</td>
<td>red-brown</td>
<td>$\sim -20^\circ$C</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)Ni(C$_2$H$_5$)$_2$</td>
<td>oily</td>
<td>red</td>
<td>$\sim -15^\circ$C</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)Ni(C$_2$H$_5$)$_2$</td>
<td>oily</td>
<td>yellow</td>
<td>$\sim -60^\circ$C</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)C$_6$H$_5$</td>
<td>crystalline</td>
<td>orange</td>
<td>$\sim -30^\circ$C</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)C$_6$H$_5$</td>
<td>crystalline</td>
<td>orange</td>
<td>$\sim -30^\circ$C</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)C$_6$H$_5$</td>
<td>solid</td>
<td>red-brown</td>
<td>$\sim -35^\circ$C</td>
</tr>
</tbody>
</table>

$\nu_{CO}$ and $\nu_{NO}$ absorptions in n-hexane of tetra-coordinated carbene complexes (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{CO}$</th>
<th>$\nu_{NO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CO)$_2$(NO)$_2$</td>
<td>2082 vs</td>
<td>1810 vs</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)C$_6$H$_5$</td>
<td>2024 vs</td>
<td>1765 vs</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)NHCH$_3$</td>
<td>2022 s</td>
<td>1768 s</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)N(CH$_3$)$_2$</td>
<td>2006 vs</td>
<td>1751 vs</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(OC$_2$H$_5$)Ni(C$_2$H$_5$)$_2$</td>
<td>2002 vs</td>
<td>1752 vs</td>
</tr>
<tr>
<td>Co(CO)$_3$NO</td>
<td>2101 s</td>
<td>1805 vs</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)C$_6$H$_5$</td>
<td>2032 s</td>
<td>1764 s</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)NHCH$_3$</td>
<td>1988 sh</td>
<td>1754 sh</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)N(CH$_3$)$_2$</td>
<td>1980 vs</td>
<td>1751 s</td>
</tr>
<tr>
<td>Co(CO)$_2$(NO)(OC$_2$H$_5$)Ni(C$_2$H$_5$)$_2$</td>
<td>2038 s</td>
<td>1745 s</td>
</tr>
<tr>
<td>Ni(CO)$_4$</td>
<td>1965 vs</td>
<td>1742 vs</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)NHCH$_3$</td>
<td>2052 s</td>
<td>1742 vs</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)N(CH$_3$)$_2$</td>
<td>1963 vs</td>
<td>1742 vs</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)Ni(C$_2$H$_5$)$_2$</td>
<td>2058 s</td>
<td>1742 vs</td>
</tr>
<tr>
<td>Ni(CO)$_3$(OC$_2$H$_5$)C$_6$H$_5$</td>
<td>1976 vs</td>
<td>1742 vs</td>
</tr>
<tr>
<td>Fe(CO)(NO)$_2$(P(C$_6$H$_5$)$_3$)</td>
<td>2008 s</td>
<td>1766 s</td>
</tr>
<tr>
<td>Fe(NO)$_2$(P(C$_6$H$_5$)$_3$)C(OC$_2$H$_5$)N(C$_2$H$_5$)$_2$*</td>
<td>2008 s</td>
<td>1726 vs</td>
</tr>
<tr>
<td>Fe(NO)$_2$(P(C$_6$H$_5$)$_3$)C(OC$_2$H$_5$)N(C$_2$H$_5$)$_2$*</td>
<td>1702 s</td>
<td>1658 vs</td>
</tr>
</tbody>
</table>

* Measured in toluene—values compensated.
RECENT ASPECTS OF TRANSITION METAL CARBONYL CARBENE COMPLEXES

Also in this group of closely related complexes the introduction of a carbene ligand lowers the $\nu_{\text{CO}}$ and $\nu_{\text{NO}}$ valence vibrations because of the greater $\sigma$-donor/$\pi$-acceptor ratio of the carbene ligands compared with CO and NO. This can also be seen in the nickel tricarbonyl derivatives, by comparison of the arithmetic mean value of the two resulting $\nu_{\text{CO}}$ bands with the original one from Ni(CO)$_4$.

CARBENE LIGANDS AS REACTIVE INTERMEDIATES

The last part of my lecture will deal with new results on the interaction of methoxyphenylcarbene ligands cleaved from (CO)$_5$CrC(OCH$_3$)C$_6$H$_5$, as a representative carbene complex, with organic substrates. An interesting pathway to organic chemistry seems to be opened.

**Reaction of methoxyphenylcarbene pentacarbonylchromium(0), -molybdenum(0), and -tungsten(0) with methyl trans-crotonate**

![Diagram showing possible stereoisomers and properties of C$_{13}$H$_{16}$O$_3$]

- **trans-C$_{13}$H$_{16}$O$_3$**
  - Colourless crystals
  - Molecular weight: Calc: 220.2; found: 220
- **trans-C$_{13}$H$_{16}$O$_3$**
  - Colourless oily liquid
  - Molecular weight: Calc: 220.2; found: 220

**Properties of C$_{13}$H$_{16}$O$_3$**

- $^1$H N.M.R. spectrum (CDCl$_3$):
  - $\tau$(C$_6$H$_5$) 2.64 (5 s); $\tau$(COOCH$_3$) 6.54 (3 s);
  - $\tau$(OCH$_3$) 6.83 (3 s); $\tau$(H$_a$) 7.82 (1 m);
  - $\tau$(H$_b$) 8.10 (1 d); $\tau$(CH$_3$) 8.58 (3 d);
- $J_{\text{trans}}$ $\sim$ 6.5 Hz
- $J_{\text{trans}}$ $\sim$ 5–7 Hz; $J_{\text{cis}}$ $\sim$ 9–11 Hz

**Possible stereoisomers**

- **trans**: $\delta_{\text{CH}_3}$ $\sim$ 75–95 Hz; found $\delta_{\text{CH}_3}$ = 85 Hz
- **cis**: $\delta_{\text{CH}_3}$ $\sim$ 50–65 Hz; found $\delta_{\text{CH}_3}$ = 72 Hz

**Influence of the central metal**

- Reaction time: 2–6 hours, temp. 90–140°C
- **trans cis**
  - M = Cr: 70:30 (±3%)
  - M = Mo: 85:15 (±3%)
  - M = W: 68:32 (±3%)
We have shown earlier that this carbene ligand, cleaved from the Cr(CO)$_5$ residue by different methods, forms with methyl trans-crotonate the two isomeric 1-methoxy-1-phenyl-2-carbomethoxy-3-methylcyclopropanes by stereospecific addition of the carbene to the polarized double bond$^{25}$. The structures of the cyclopropanes were assigned from $^1$H n.m.r. measurements. Whether we were dealing in these experiments with free carbenes or not is still an open question. However, starting from the Cr, Mo and W methoxyphenylcarbene pentacarbonyl complexes under exactly the same reaction conditions we found a rather strong dependence of the ratio of the two isomers on the transition metal$^{26}$. We think therefore, that the complexed carbene interacts with the substrate and not the free carbene.

Reactions of methoxyphenylcarbene pentacarbonylchromium(0) with carbon monoxide in ethyl vinyl ether

Similarly, the same carbene ligand reacts with ethyl vinyl ether, when substituted with CO, to give the two isomeric 1-methoxy-1-phenyl-2-ethoxycyclopropanes (I) and (II), the ratio of which depends on the metal$^{26}$.

\[
\text{(CO)}_3\text{M} \overset{\equiv}{\text{C}} \overset{\text{OCH}_3}{\text{C}_6\text{H}_5} + \text{CH}_2=\text{CH} \overset{\text{OC}_2\text{H}_5}{\text{H}} \overset{170 \text{ atm. CO}}{\text{50°C 65 h}} \overset{\text{50°C 65 h}}{\text{H}} \overset{\text{OC}_2\text{H}_5}{\text{H}} \overset{\text{OC}_2\text{H}_5}{\text{H}} \overset{\text{M(CO)}_6}{\text{M(CO)}_6} + \ldots
\]

\[
\begin{array}{ccc}
M = \text{Cr} & M = \text{Mo} & M = \text{W} \\
(\text{I}) & 76 & 80 \\
(\text{II}) & 24 & 20 \\
\end{array}
\]

These results seem to exclude once again free methoxyphenylcarbene as reactive agent since a considerable influence of the metal on the ratio of (I) to (II) is observed.

Reaction of methoxyphenylcarbene pentacarbonylchromium(0) with diethyl fumarate

We found that the diethyl ester of fumaric acid also formed a cyclopropane derivative with methoxyphenylcarbene pentacarbonylchromium(0), namely 3-methoxy-3-phenyl-trans-1,2-dicarboxylic ethyl ester$^{26}$. Only one isomer was observed as expected. This shows that in no way is a push–pull combination of substituents in the 1,2-positions of the C=C double bond necessary for the reaction, but a small $\pi$-electron density of the double bond seems to be important.

\[
\text{(CO)}_3\text{Cr} \overset{\equiv}{\text{C}} \overset{\text{OCH}_3}{\text{C}_6\text{H}_5} + \text{H}_5\text{C}_2\text{OOOC} \overset{110\text{°C}}{\overset{2.5 \text{ h}}{\text{H}}} \overset{\text{H}_5\text{C}_2\text{OOOC}}{\text{H}} \overset{\text{H}_5\text{C}_2\text{OOOC}}{\text{H}} \overset{\text{Cr(CO)}_6}{\text{Cr(CO)}_6} + \ldots
\]
Recent Aspects of Transition Metal Carbonyl Carbene Complexes

Reaction of methoxyphenylcarbene pentacarbonylchromium(0) with cyclohexane, diphenylmethane and diphenylsilane

Further experiments have proved that there is no insertion of the methoxyphenylcarbene into the C—H bonds of cyclohexane or diphenylmethane; cis- and trans-α,α′-dimethoxystilbene were the only reaction products. In contrast, diphenylsilane, which contains much more polar Si—H bonds, reacts with methoxyphenylcarbene pentacarbonylchromium(0) within 15 minutes at 55°C to give α-methoxybenzyldiphenylsilane. This is the formal insertion product of the carbene ligand into the Si—H bond.

\[
\begin{align*}
&\text{cis} \\
&\text{trans} \\
&1.3 : 1
\end{align*}
\]

\[
\begin{align*}
&\text{cis} \\
&\text{trans} \\
&1.3 : 1
\end{align*}
\]

Reaction of methoxyphenylcarbene pentacarbonylchromium(0) with carbon monoxide in methanol

Finally, substitution of the carbene ligand in methoxyphenylcarbene pentacarbonylchromium(0) with CO in methanol also yields the formal O—H insertion product, namely benzaldehyde dimethylacetal.

I should mention that the crude products of the reaction of carbene complexes with organic substrates are always accompanied to some extent by other products. Nevertheless, this part of carbene complex chemistry also seems promising from the aspect of organic chemists. Sawa, Ryang and Tsutsumi and also Connor have opened additional routes to interesting products.

I would like to end my lecture, which has given some aspects of our research on acyclic carbene carbonyl transition metal complexes, with especial thanks to my group and my colleagues in Munich.
E. O. FISCHER

Co-workers

Dr H.-J. Beck    Dr J. Lynch    Dipl. Chem. G. Kreis
Dr K. H. Dötz    Dr E. Offhaus Dipl. Chem. F. Kreißl
Dr M. Leupold    Dr E. Winkler Dipl. Chem. S. Riedmüller

in collaboration with

Doz. Dr C. G. Kreiter    Doz. Dr J. Müller    Dr K. Öfele

Dr G. Huttner
Dipl. Chem. D. Regler
Dipl. Chem. B. Krieg
Dipl. Chem. S. Lange

REFERENCES

10 E. O. Fischer and S. Riedmüller, unpublished results.
15 E. O. Fischer and G. Kreis, unpublished results.
18 E. O. Fischer and F. Kreißl, unpublished results.
21 G. Huttner and D. Regler, unpublished results.
24 E. O. Fischer and E. Winkler, unpublished results.
26 E. O. Fischer and K. H. Dötz, unpublished results.