

# STRUCTURE, BONDING AND REACTIVITY OF (STABLE) TRANSITION METAL CARBONYL CARBENE COMPLEXES

E. O. FISCHER

*Inorganic Chemistry Laboratory, Technical University, 8 Munich 2*

## ABSTRACT

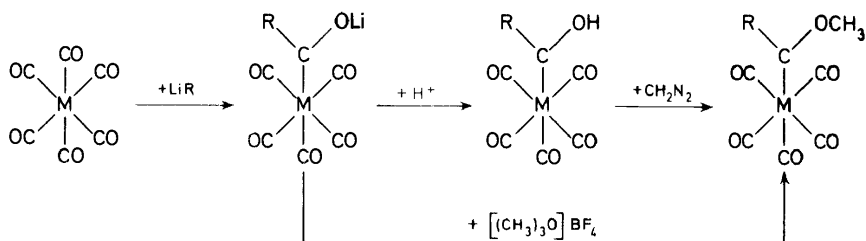
The generally applicable method for the preparation of stable metal carbonyl carbene complexes by nucleophilic addition of a carbanion from an organolithium reagent to a carbonyl group with subsequent methylation of the resulting acylcarbonyl metallate by diazomethane or trimethyloxonium-tetrafluoroborate is described. The i.r. and  $^1\text{H-n.m.r.}$  spectra of new cyclopentadienyl carbonyl nitrosyl carbene complexes of chromium, molybdenum and tungsten confirm the idea of the bonding of methoxyorganylcarbene ligands as being predominantly a donation of electron density from the ligand to the rest of the molecule, with only a very much weaker  $\pi$ -acceptance of electrons.

Five types of reaction of carbonyl carbene complexes, CO substitution, carbene substitution, ester cleavage, addition and rearrangement, and H substitution are described with representative examples. The kinetic results on the aminolysis of phenylmethoxycarbene pentacarbonyl chromium, and the conclusions which can be drawn from the i.r. and  $^1\text{H-n.m.r.}$  spectra of some *o*-, *m*- and *p*-substituted derivatives and arene chromium dicarbonyl carbene complexes are discussed. Results obtained from the analogous iron carbonyl system are briefly given. Some of the general features of bonding of this type of compound are summarized by the x-ray results obtained for six carbene complexes.

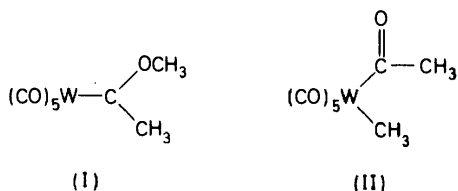
Finally, an account of the secondary reactions of cleaved carbene ligands with themselves and olefins close this survey of this new field of organometallic chemistry.

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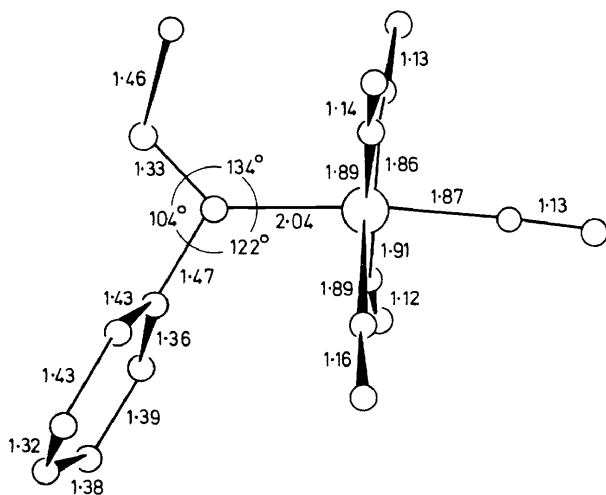
In 1964 we published a short note<sup>1</sup> 'On the existence of a tungsten carbonyl carbene complex'. The general principle behind the preparation of the carbene complex was the reaction of  $\text{W(CO)}_6$  with organolithium reagents. Nucleophilic attack and addition of a carbanion to one of the CO ligands gave an adduct  $(\text{CO})_5\text{WC(OLi)R}$ , from which a rather unstable hydroxy complex,  $(\text{CO})_5\text{WC}_R^{\text{OH}}$  could be obtained in solution by treatment with acid. The final step in the reaction was then a  $\text{CH}_2$ -insertion from  $\text{CH}_2\text{N}_2$  into the O—H bond to give  $(\text{CO})_5\text{WC}_R^{\text{OCH}_3}$  as a novel type of stable organometallic compound. The procedure was later improved by using  $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ <sup>2</sup> as immediate methylating agent for the RLi adduct, and extended to  $\text{Cr(CO)}_6$ <sup>3</sup>,  $\text{Mo(CO)}_6$ <sup>3</sup>, some of their monosubstituted hexacoordinated derivatives and similar derivatives of  $\text{W(CO)}_6$ <sup>4</sup>. We obtained carbene complexes also from  $\text{C}_6\text{H}_6\text{Cr(CO)}_3$ <sup>5</sup>,  $\text{C}_5\text{H}_5\text{Mn(CO)}_3$ <sup>3</sup> and  $\text{C}_5\text{H}_5\text{Re(CO)}_3$ <sup>6</sup>.



The first compounds obtained by this procedure were  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  and  $(\text{CO})_5\text{W}(\text{OCH}_3)\text{CH}_3$ . From the two possible structures (I, II), I was shown to be correct for  $(\text{CO})_5\text{W}(\text{OCH}_3)\text{CH}_3$  by  $^1\text{H}$ -n.m.r. measurements and by the absence of any characteristic  $\text{>C=O}$  vibrations in the i.r. between  $1500$  and  $1800\text{ cm}^{-1}$ .

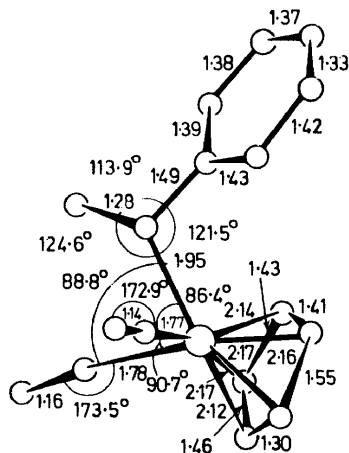


The x-ray structure of  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$ <sup>7</sup> showed certain unusual features which will be discussed briefly. The carbene C atom is surrounded by three groups [ $\text{Cr}(\text{CO})_5$ ,  $\text{OCH}_3$  and  $\text{C}_6\text{H}_5$ ]. The three bonds lie in a plane and their angles show clearly the  $sp^2$  hybridization of the carbene atom. The bond distance between the O atom of the  $\text{OCH}_3$  group and the carbene C atom is shorter ( $1.33\text{ \AA}$ ) than a normal C—O single bond distance ( $1.43\text{ \AA}$ ) due to some  $p_\pi-p_\pi$  double bond character. The chromium—C<sub>carbene</sub> atom



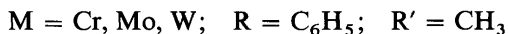
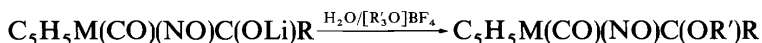
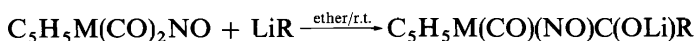
distance is distinctly shorter than that estimated for a Cr—C single bond due to some weaker  $d_{\pi}-p_{\pi}$  backbonding from filled chromium  $d$ -orbitals of appropriate symmetry to the vacant  $p$  orbital of the  $C_{\text{carbene}}$  atom.

We consider that the donor function of the carbene ligand to the  $\text{Cr}(\text{CO})_5$  residue predominates over its acceptor function. This is the reason for the rather high dipole moment of, for example,  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  ( $\mu_{\text{C}_6\text{H}_{12}, 20^\circ\text{C}} = 4.08 \pm 0.1 \text{ D}$ ). The negative end of the dipole is on the  $\text{Cr}(\text{CO})_5$  part of the molecule and the positive end on the carbene ligand, with a rather large distance between them.



Definite proof for the structure of a  $\text{C}_6\text{H}_5\text{Li}$  addition product was afforded by an x-ray investigation of  $[\text{N}(\text{CH}_3)_4][\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{COC}_6\text{H}_5]^\ddagger$ , which was precipitated from an aqueous solution of the  $\text{RLi}$  adduct of  $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$  with  $[\text{N}(\text{CH}_3)_4]\text{Cl}$ . Two  $\text{CO}$  ligands, one  $\pi$ -bonded  $\text{C}_5\text{H}_5$  ring and a benzoyl group are directly bonded to the central  $\text{Mn}$  atom. The presence of the benzoyl group demonstrates unequivocally the addition of the  $\text{C}_6\text{H}_5$  carbanion to the carbon atom of one of the  $\text{CO}$  ligands of  $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ . The  $\text{CO}$  distance of the benzoyl group (1.28 Å) is greater than that in ketones (1.22 Å). Some i.r. measurements show that the negative charge in this complex ion is distributed over all the ligands and is not concentrated on the acyl group. The same is true for all the other analogous  $[\text{N}(\text{CH}_3)_4]^+$  salts of the acylcarbonyl metallates.

Recently we investigated the carbene complex formation of the cyclopentadienyl nitrosyl dicarbonyl complexes of chromium, molybdenum and tungsten<sup>5</sup>. With these compounds there was the question as to whether phenyl lithium would add to a  $\text{CO}$  or  $\text{NO}$  ligand. We found that only  $\text{CO}$  reacts, with the subsequent formation of a methoxyphenyl carbene complex. We believe this to be because the  $\text{C}$  atom of the  $\text{CO}$  group has a higher positive charge than the  $\text{N}$  atom of the  $\text{NO}$  ligand.

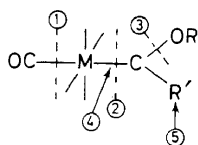


The i.r. spectra in the  $\nu_{\text{NO}}$  and also to some small extent in the  $\nu_{\text{CO}}$  region showed lowered frequencies compared with those of the parent compounds

verifying that charge transfer occurs from the  $\text{C} \begin{matrix} \text{OCH}_3 \\ \text{C}_6\text{H}_5 \end{matrix}$  ligand to the CO and NO ligands. In addition the shielding of the protons of the  $\pi$ -bonded  $\text{C}_5\text{H}_5$  rings was raised, showing the enhanced electron density of the  $\pi$ -cloud of the  $\text{C}_5\text{H}_5$  ring in the carbene complexes. The carbene ligand must therefore be weaker in its backbonding capacity than CO and NO, at least in our new compounds.

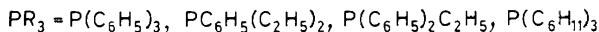
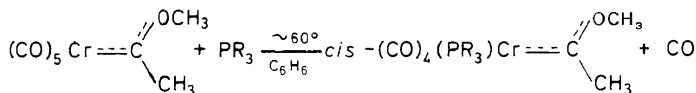
	i.r. spectra ( $\text{cm}^{-1}$ , LiF prism) <i>n</i> -hexane		$^1\text{H-n.m.r.}$ ( $\tau$ values) $\text{C}_5\text{H}_5$ (60 MHz, $\text{CD}_3\text{COCD}_3$ )	
	$\nu_{\text{CO}}$	$\nu_{\text{NO}}$		
$\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{NO}$	2025 vs	1955 vs	1715 vs	4.77 S
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$	2020 vs	1945 vs	1691 vs	4.24 S
$\text{C}_5\text{H}_5\text{W}(\text{CO})_2\text{NO}$	2012 vs	1933 vs	1682 vs	4.09 S
$\text{C}_5\text{H}_5\text{Cr}(\text{CO})(\text{NO})\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$	1978 vs		1675 vs	4.96 S
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})(\text{NO})\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$	1975 vs		1639 vs	4.56 S
$\text{C}_5\text{H}_5\text{W}(\text{CO})(\text{NO})\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$	1964 vs		1600 vs	4.46 S

Hexacoordinated metal carbonyl methoxyorgano-carbene complexes,  $(\text{CO})_5\text{CrC}_R^{\text{OCH}_3}$  ( $R = \text{CH}_3, \text{C}_6\text{H}_5$ ), show, to our present knowledge, at least five interesting types of reaction, which will be dealt with subsequently in some detail.

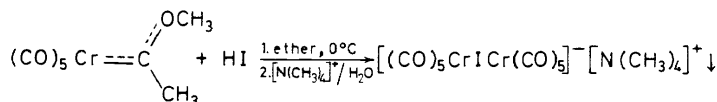


- ① CO substitution
- ② carbene substitution
- ③ 'ester' cleavage
- ④ addition and rearrangement
- ⑤ H substitution

(1) Substitution of CO, with the carbene ligand remaining intact, is possible with  $\text{P}(\text{C}_6\text{H}_5)_3$  and other tertiary phosphines<sup>9,10</sup>.

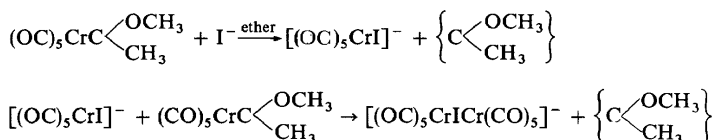


(2) Carbene substitution occurs, for example, when HI reacts with a carbene complex like  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{CH}_3$ . The final product is the iodine-bridged iododecacarbonyldichromium anion<sup>11,12</sup>.



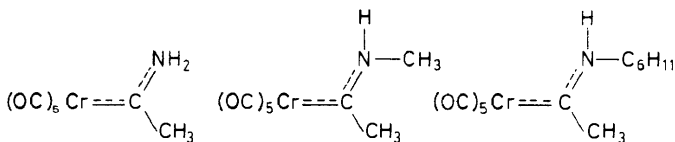
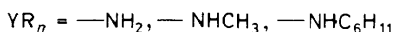
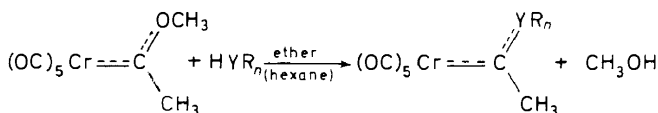
TRANSITION METAL CARBONYL CARBENE COMPLEXES

The first step is the cleavage of the carbene with the formation of the strong nucleophile  $[(OC)_5CrI]^-$ , which attacks a second complex carbene molecule.



The carbene can also be easily liberated by reaction with, say, carbon monoxide under pressure, or pyridine.

(3) The reactions of the carbene complexes with primary and secondary amines seem to us particularly interesting.  $(CO)_5CrC(OCH_3)CH_3$  behaves similarly to an ester, in which the ketonic O atom is substituted for a  $(CO)_5Cr$  group, the latter being presumably still more electronegative than O. (At least, the complex undergoes aminolysis much faster than usual organic esters.) The reactions with ammonia, methylamine, and cyclohexylamine and the resulting aminomethylcarbene complexes are shown with some of their properties<sup>9, 13</sup>.



$$\nu_{CO}: 2063m, 1979w \\ 1945s \text{ cm}^{-1}$$

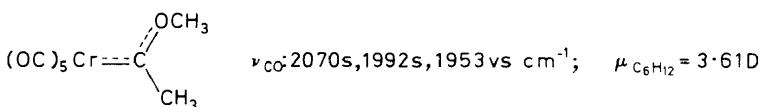
$$\mu_{C_6H_{12}} = 5.64 D$$

$$\nu_{CO}: 2058m, 1972w \\ 1940s \text{ cm}^{-1}$$

$$\mu_{C_6H_{12}} = 6.15 D$$

$$\nu_{CO}: 2061m, 1970w \\ 1938s \text{ cm}^{-1}$$

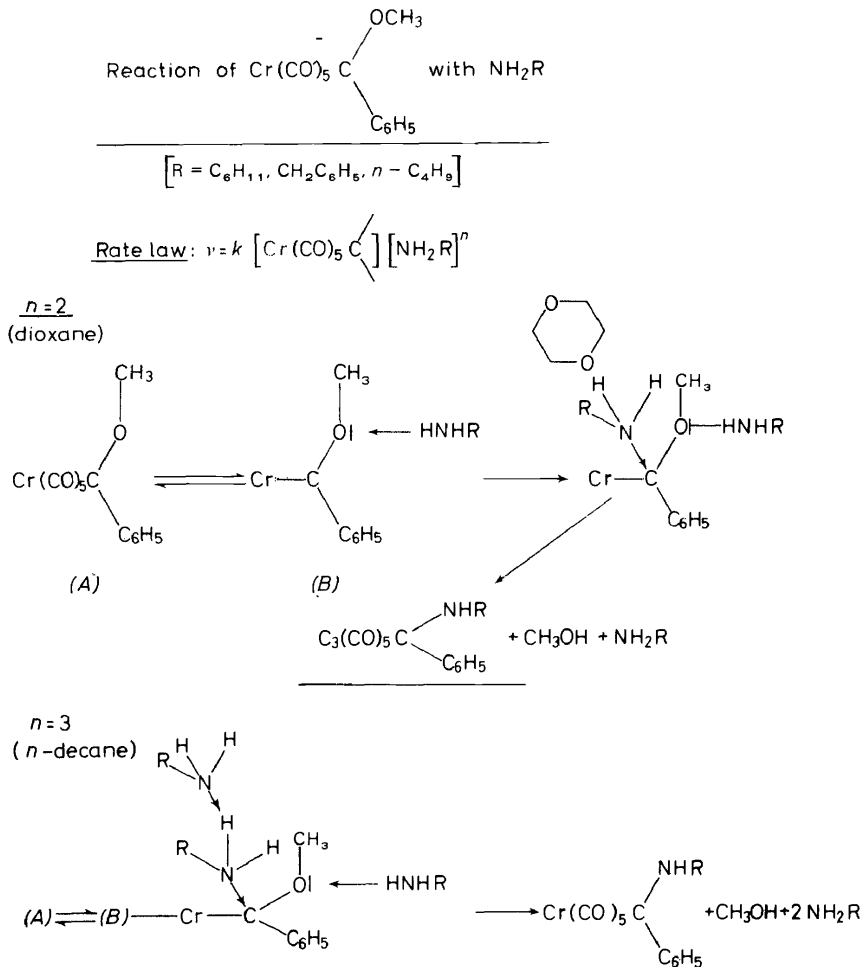
$$\mu_{C_6H_{12}} = 7.17 D$$



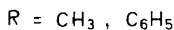
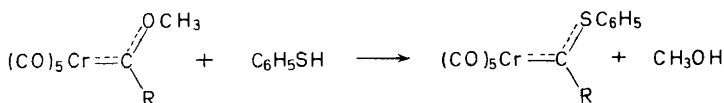
If one compares the i.r. spectra (obtained under the same conditions in nujol mulls) in the  $\nu_{CO}$  region of, for example  $(CO)_5CrC(OCH_3)CH_3$  and  $(CO)_5CrC(NHCH_3)CH_3$ , one observes a lowering of the  $\nu_{CO}$  frequencies in the aminocarbene complex. This confirms, as does the higher dipole moment of  $(CO)_5CrC(NHCH_3)CH_3$ , the poorer  $\pi$ -acceptor strength of the aminocarbene complex. This is a consequence of the stronger donor function of N instead of O in the carbene ligand. This is in excellent agreement with

our idea of the bonding and the location of the positive and negative centres in the molecules.

The aminolysis of  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  was studied in more detail kinetically and showed a complicated reaction type. The rate law proved to be third or fourth order depending on the donor nature of the solvents used<sup>14</sup>.

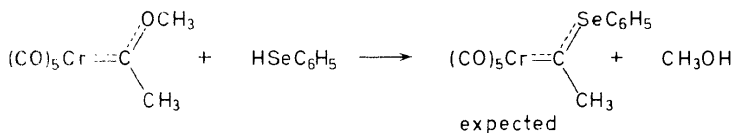


Thiophenol reacts in a similar way to amines. S atoms can therefore also be used as heteroatoms to stabilize the carbene ligand<sup>13, 15</sup>.



TRANSITION METAL CARBONYL CARBENE COMPLEXES

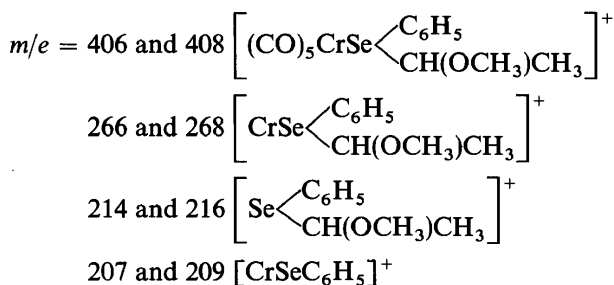
(4) A remarkable addition and rearrangement reaction of the carbene complexes  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{CH}_3$  and  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  was found in their reaction with selenophenol. There is definite proof for the formation of a selenoether complex<sup>16</sup>.



found:  $\text{SeCrC}_{14}\text{H}_{12}\text{O}_6$

mass spectrum

(ATLAS CH4, 50 eV)



<sup>1</sup>H-n.m.r. spectrum

(in  $\text{CDCl}_3$ )

$\tau = 8.40$  ( $\text{CH}_3$ ) [3]

$\tau = 6.45$  ( $\text{OCH}_3$ ) [3]

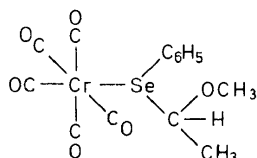
$\tau = 4.80$  ( $\text{CH}$ ) [1]

$\tau = 2.37$  ( $\text{C}_6\text{H}_5$ ) [5]

The i.r. spectrum  
(hexane,  $\text{cm}^{-1}$ )

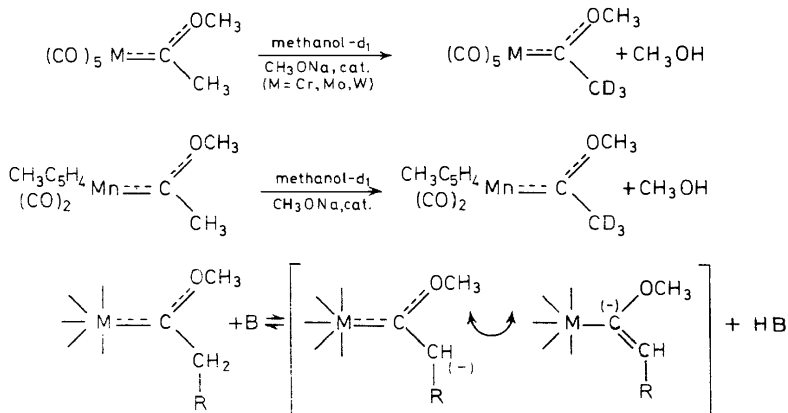
$\nu_{\text{CO}}$ : 2070s, 1990s, 1948 vs. 1934s  $\text{cm}^{-1}$

structure

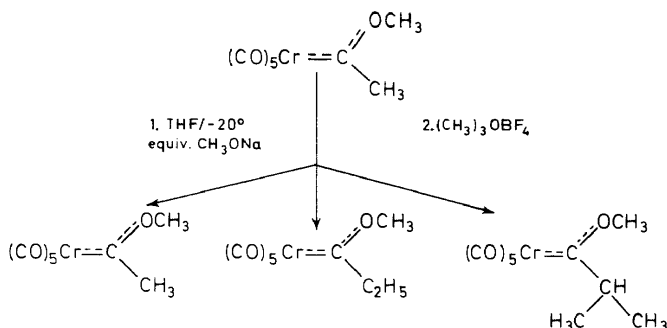


(5) Most surprisingly the H atoms of the  $\text{C}_{\text{carbene}}$ -bonded  $\text{CH}_3$  group in the methoxymethylcarbene ligand show an enhanced acidic character, attributable to the electron donor behaviour of the carbene ligand as a

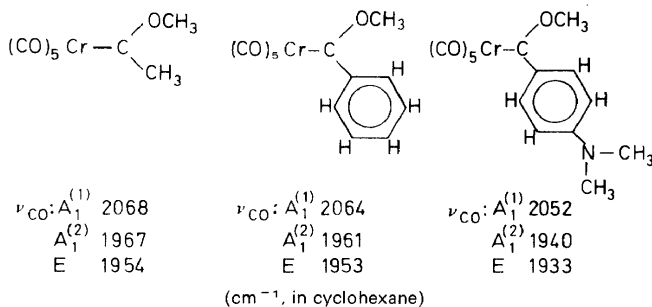
whole into the  $\text{Cr}(\text{CO})_5$  part of the molecule<sup>17</sup>. An immediate very fast deuteration catalysed by  $\text{CH}_3\text{ONa}$  occurred in  $\text{CH}_3\text{OD}$  solution. A similar result was found for  $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_2\text{C}(\text{OCH}_3)\text{CH}_3$ . The transition state is presumably formed by the abstraction of a proton by the base.



This reaction can be used to build up an ethyl or an isopropyl group from the  $\text{CH}_3$  group.



This observation of the enhanced acidity of the  $\text{CH}_3$  group bonded to the carbene carbon atom convinced us that there was some displacement of electron density from this part of the molecule also on to the carbene C atom and further on to the  $\text{Cr}(\text{CO})_5$  group. Evidence of electron withdrawal from

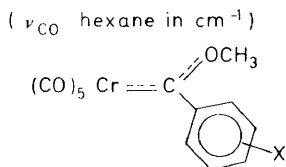




## TRANSITION METAL CARBONYL CARBENE COMPLEXES

groups bonded to  $C_{\text{carbene}}$  was provided by a comparison of the  $\nu_{\text{CO}}$  stretching frequencies in  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{CH}_3$ ,  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  and the specially prepared  $(\text{CO})_5\text{CrC}(\text{OCH}_3)[p\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2]^{18}$ .

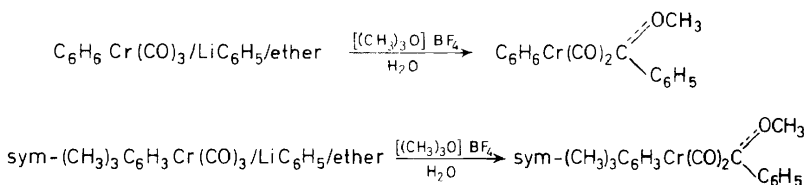
The lowering of the  $\nu_{\text{CO}}$  frequencies for the latter compound is attributable to a transfer of electron density to the metal promoted by the electron-releasing  $p\text{-N}(\text{CH}_3)_2$  substituent of the phenyl ring. In consequence of this first result more  $p$ - and  $m$ -substituted phenylmethoxycarbene pentacarbonyl chromium complexes were prepared and their  $\nu_{\text{CO}}$  frequencies compared.



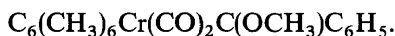
X	$A_1^{(1)}$	$A_1^{(2)}$	$E$	Hammett $\sigma$ -constant
$p\text{-N} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$	2052	1940	1933	-0.600
$p\text{-OCH}_3$	2058	1952	1941	-0.268
$p\text{-CH}_3$	2061	1954	1942	-0.170
$p\text{-H}$	2064	1961	1953	0
$p\text{-Cl}$	2064	1966	1953	+0.227
$p\text{-Br}$	2064	1964	1952	+0.232
$m\text{-N} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$	2060	1946	1946	-0.211
$m\text{-OCH}_3$	2065	1964	1952	+0.280
$m\text{-Cl}$	2065	1967	1953	+0.373

For  $p$ -substituents with negative Hammett  $\sigma$ -constants an almost linear relationship was observed between the  $\sigma$ -constants and the lowering of the  $\nu_{\text{CO}}$  frequencies. Both inductive and mesomeric effects participate in this charge transfer. This means, for example, that the perpendicular position of the phenyl ring to the carbene plane, found in the X-ray investigation of  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$ , may not be maintained in these compounds, at least in solution where rotation of the  $\text{C}_6\text{H}_4\text{R}$  rings is to be assumed. On the other hand no withdrawal of electron density was observed for  $p$ -substituents with positive Hammett  $\sigma$ -constants. Charge compensation in these compounds probably occurs via the  $\text{OCH}_3$  group, the electronegativity of terminal CO ligands being too strong for a weakening of their  $\text{C} \equiv \text{O}$  bonding.  $m$ -Substituents, which can influence the electron density in the ring only by an inductive effect, showed for substituents with negative Hammett  $\sigma$ -constants, e.g.  $\text{N}(\text{CH}_3)_2$ , the same effect as was found for the  $p$ -substituents but less pronounced. Substituents with positive constants again caused no withdrawal of electron density from the CO ligands. There is some indication from i.r. measurements that the  $\text{OCH}_3$  group balances the loss of electron density via the  $C_{\text{carbene}}$  atom.

Finally, to study the  $sp^2$  hybridized  $C_{\text{carbene}}$  atom from the remaining third covalent bond we looked for substituted chromium hexacarbonyl derivatives with arene ligands. The electrophilic character of an arene  $\text{Cr}(\text{CO})_2$  fragment should be lower than that of  $\text{Cr}(\text{CO})_5$ .



The preparation gave the expected much more labile complexes  $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$  and  $\text{sym}-(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_2\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$  in very low yields<sup>5</sup>. It was not possible to obtain



Comparisons of the  $\nu_{\text{CO}}$ ,  $\nu_{\text{C}_{\text{carbene}}-\text{O}}$ ,  $\nu_{\text{H}_3\text{C}-\text{O}}$ ,  $\nu_{\text{C}_{\text{carbene}}-\text{C}_6\text{H}_5}$  frequencies demonstrated the lowered donation of electron density to the transition metal, which is obviously no longer so poor in electron density as when in combination with five CO ligands.

These observations and the higher lability of these carbene complexes are in accord with some weakening of the  $\text{C}_{\text{carbene}}-\text{Cr}$  dative bond.

#### i.r. spectra ( $\text{cm}^{-1}$ )

	$\nu_{\text{C}_{\text{carbene}}-\text{O}}$	$\nu_{\text{H}_3\text{C}-\text{O}}$	$\nu_{\text{C}_{\text{carbene}}-\text{C}_6\text{H}_5}$
	(nujol mull, NaCl prism)		
$(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$	1224	982	874
$\text{C}_6\text{H}_6\text{Cr}(\text{CO})_2\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$	1170	980	864
$\text{sym}-(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_2\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5$	1164	974	851

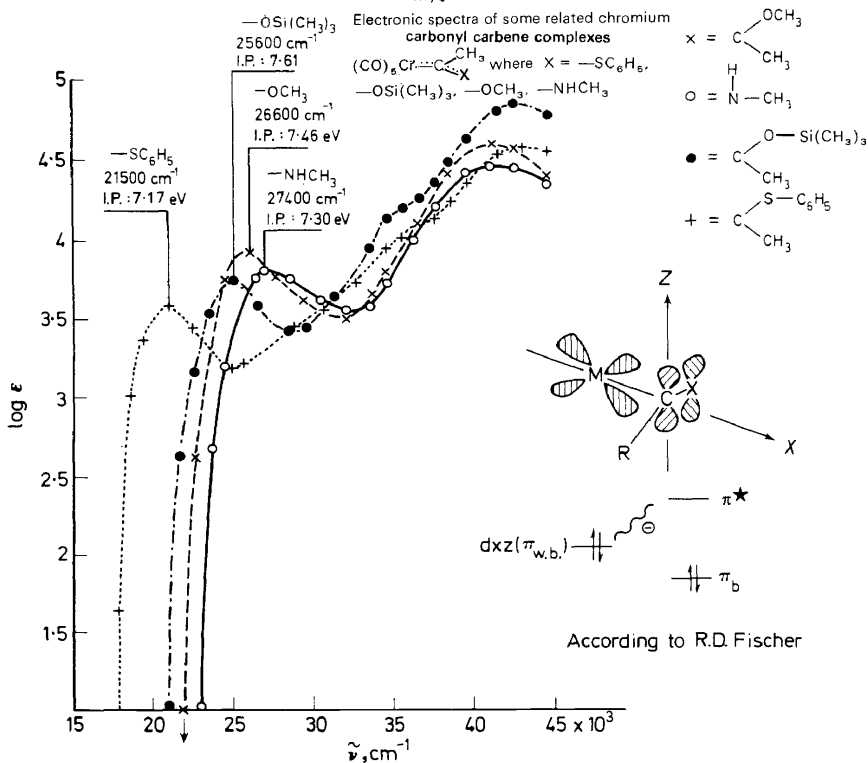
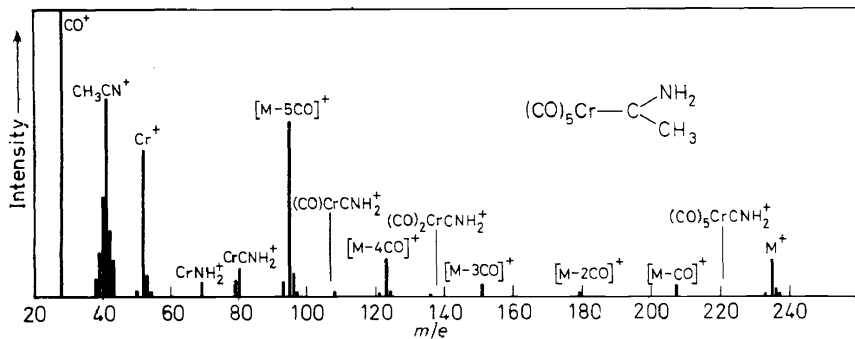
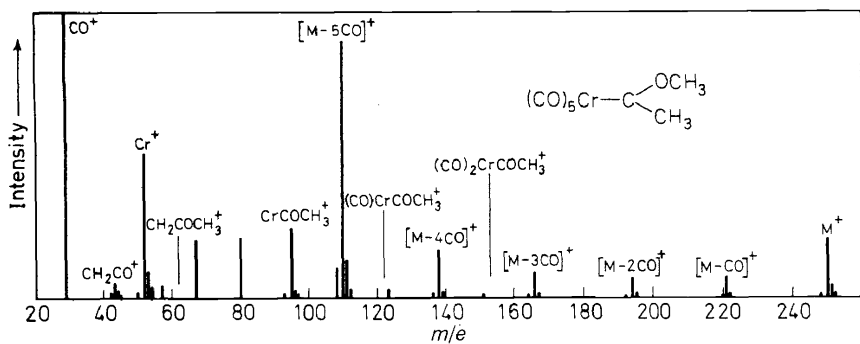
The rather high intensity of the  $\text{CrC}(\text{OCH}_3)\text{CH}_3^+$  and  $\text{CrC}(\text{NH}_2)\text{CH}_3^+$  fragments in the mass spectra of just two representative carbene complexes confirm independently the preferred donor bonding of the carbenes to the transition metal, which will be stronger for  $\text{Cr}^+$  than for  $\text{Cr}^0$ <sup>19</sup>.

The remarkable variation in colour of the complexes (from almost colourless to red) encouraged us to have a brief look at the electronic spectra. The first absorption band (most probably due to a  $\pi-\pi^*$  transition) undergoes a noticeable bathochromic shift when the heteroatom of the stabilizing group X is changed in the order N, O, S. The corresponding ionization potentials of the gaseous molecules tend to increase in the same direction, suggesting some increase in bonding character of the carbene ligand for the initially non-bonding metal electrons.

If the relative stabilities of the complexes are also taken into account it appears that the most important factor is an effective  $\text{X} \rightarrow \text{C}$  bond, and that any  $\text{M} \rightarrow \text{C}$  backbonding is less important in determining the stability.

Changing from coordination number six to coordination number five we also investigated the addition of RLi reagents to iron pentacarbonyl.

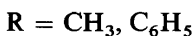
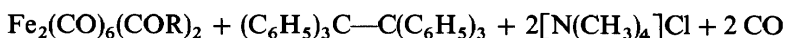
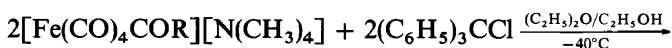
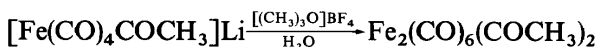
# TRANSITION METAL CARBONYL CARBENE COMPLEXES



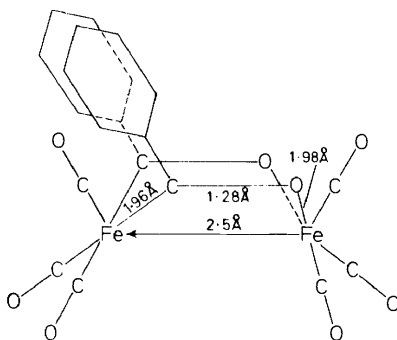
Only at low temperatures were we able to isolate the expected  $\text{CH}_3\text{Li}$  and  $\text{C}_6\text{H}_5\text{Li}$  adducts, which were subsequently transformed into the tetramethyl ammonium salts<sup>20</sup>.



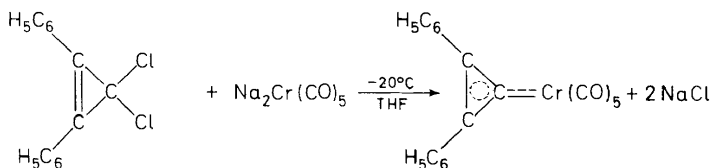
Reaction of these acyltetracarbonyl metallates of iron with  $[(\text{CH}_3)_3\text{O}]\text{BF}_4$  in an attempt to prepare  $(\text{CO})_4\text{FeC}(\text{OCH}_3)\text{CH}_3$  and  $(\text{CO})_4\text{FeC}(\text{OCH}_3)\text{C}_6\text{H}_5$ , gave totally unexpected dimers of the composition  $[\text{Fe}(\text{CO})_3(\text{COCH}_3)]_2$  and  $[\text{Fe}(\text{CO})_3(\text{COC}_6\text{H}_5)]_2$ . Subsequently the yields were improved by using trityl chloride instead of  $[(\text{CH}_3)_3\text{O}]\text{BF}_4$ .



Some x-ray investigations have shown that  $[\text{Fe}(\text{CO})_3\text{COC}_6\text{H}_5]_2$  is an asymmetric dimer of a new type with two bridging  $\text{OCC}_6\text{H}_5$  groups<sup>21</sup>.



Specially important is the first totally hydrocarbon carbene carbonyl complex of chromium, namely 2,3-diphenylcyclopropenyldiene pentacarbonyl chromium<sup>22</sup>, since there is no longer any heteroatom present. Stabilization is afforded by the ring system containing  $2\pi$ -electrons.

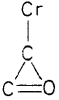


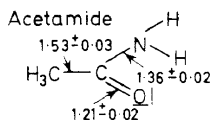
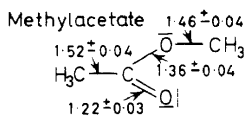
A survey of the x-ray results so far obtained for carbonyl carbene complexes demonstrates some of the general features of this new class of compounds. The  $\text{Cr}-\text{C}_{\text{carbene}}$  distances vary considerably—values range

## TRANSITION METAL CARBONYL CARBENE COMPLEXES

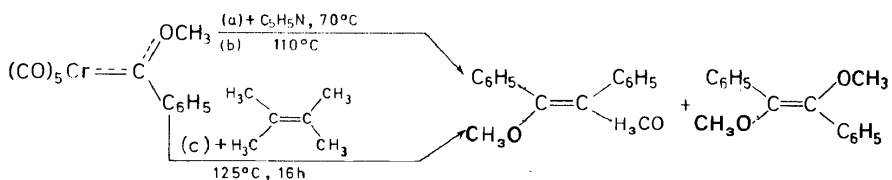
from 2.04 Å to 2.15 Å depending upon the donor strength of the heteroatom. The fairly short  $C_{\text{carbene}}-\text{O}$  and  $C_{\text{carbene}}-\text{N}$  bond lengths are indicative of some double bond character, and enable an analogy to be drawn between the carbene complexes and esters and acidamides. That the metal- $C_{\text{CO}}$  distances are much shorter than the metal- $C_{\text{carbene}}$  distances, shows the stronger double bond character of the metal-CO bond. In the case of the cyclopropenyldiene complex the carbene character of the complex is clearly to be seen from the  $\text{Cr}-C_{\text{carbene}}$  distance of 2.05 Å and the weakly superimposed cyclopropene structure.

Bond distances (Å)

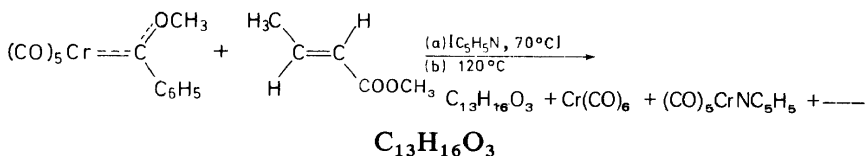
	$\text{Cr}-C_{\text{CARB}}$	$C_{\text{CARB}}-\text{C}$	$C_{\text{CARB}}-\text{O}(\text{N})$	$\text{Cr}-C_{\text{CO}}$	$\text{C}\equiv\text{O}$	
$(\text{CO})_5\text{Cr}-\text{C} \begin{matrix} \text{C}_6\text{H}_5^7 \\ \text{OCH}_3 \end{matrix}$	2.04	1.47	1.33	1.88	1.14	
$\phi_3\text{P}(\text{CO})_4\text{Cr}-\text{C} \begin{matrix} \text{CH}_3^{23} \\ \text{OCH}_3 \end{matrix}$	2.04	1.54	1.33	1.84	1.18	
$(\text{CO})_5\text{Cr}-\text{C} \begin{matrix} \text{NHCH}_3^{24} \\ \text{CH}_3 \end{matrix}$	2.09	1.51	1.33			
$(\text{CO})_5\text{Cr}-\text{C} \begin{matrix} \text{N}(\text{C}_2\text{H}_5)_2^{25} \\ \text{CH}_3 \end{matrix}$	2.15	1.50	1.30	1.90	1.14	
$(\text{CO})_5\text{Cr}-\text{C} \begin{matrix} \text{CH}_2 \\ \text{C}-\text{O}-\text{CH}_3 \\ \text{N}-\text{H} \\ \text{C}_6\text{H}_{11} \end{matrix}$	2.15	1.51	1.32	1.88	1.14	
$(\text{CO})\text{Cr}=\text{C} \begin{matrix} \text{C}-\text{C}_6\text{H}_5^{27} \\ \text{C} \\ \text{C}-\text{C}_6\text{H}_5 \end{matrix}$	2.05	1.40 1.39		1.90	1.13	1.35



The carbene complexes offer stabilized carbenes which can be cleaved easily by other ligands, e.g. CO, pyridine. They offer therefore also a useful tool for research into the organic chemistry of these fascinating species. We have found some interesting results in this respect. Thermolysis or treatment of  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{C}_6\text{H}_5$  by various reagents yielded dimerized *cis*- and *trans*- $\alpha,\alpha$ -dimethoxystilbene<sup>28</sup>. No cyclo-addition of the carbene to tetramethylethylene was observed.

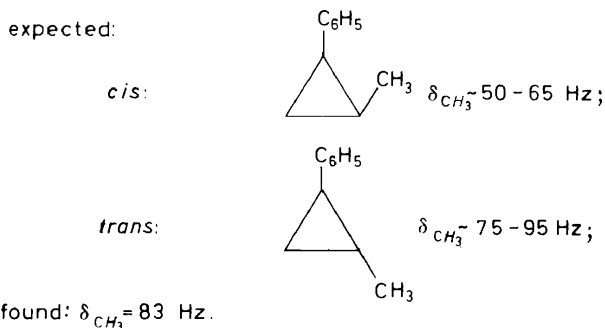


A cyclopropane derivative of methoxyphenylcarbene was, however, formed with the methylester of crotonic acid. According to our present understanding a polarized  $\text{C}^+=\text{C}^-$  bond is needed in the scavenger molecule.

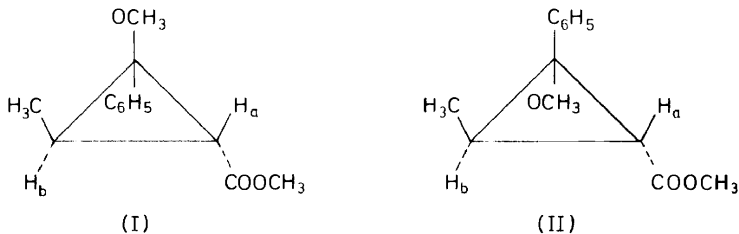


$^1\text{H}$ -n.m.r. spectra ( $\text{CCl}_4$ ):  $\tau$ -values w.r.t. internal TMS standard

2.72 (5 S) $\text{C}_6\text{H}_5$ ;	6.61 (3 S) $\text{COOCH}_3$ ;	6.90 (3 S) $\text{OCH}_3$ ;
7.92 (1 M) $\text{H}_b$ ;	8.22 (1 D) $\text{H}_a$ ;	8.62 (3 D) $\text{CH}_3$ ;
expected: $J_{\text{trans}-\text{H}_a, \text{H}_b} \sim 5-7 \text{ Hz}$ ; $J_{\text{cis}-\text{H}_a, \text{H}_b} \sim 9-11 \text{ Hz}$		
found: $J_{\text{H}_a, \text{H}_b} = 7 \text{ Hz}$		

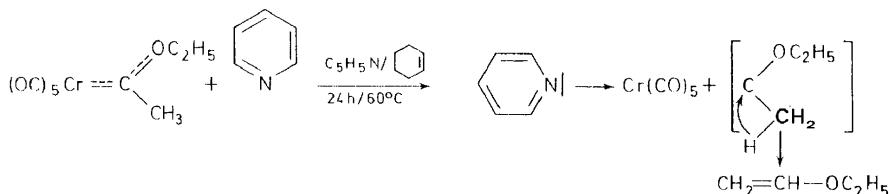


The resulting 1-methoxy-1-phenyl-2-carbomethoxy-3-methyl-cyclopropane<sup>29</sup> was a mixture of the two isomers expected from a stereospecific addition of the carbene to the double bond. The isomer I was isolated in a pure form, as shown by its  $^1\text{H}$ -n.m.r. spectrum, whereas the other isomer with the structure II was identified by its n.m.r. spectrum in the mixture, but could not be isolated.

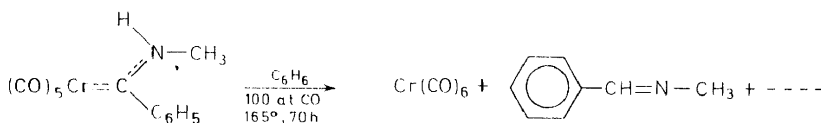


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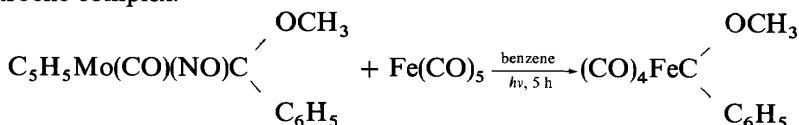
In contrast ethoxymethylcarbene liberated from  $(\text{CO})_5\text{Cr}(\text{OC}_2\text{H}_5)\text{CH}_3$  by reaction with pyridine rearranges to give vinyl ether<sup>30</sup>.



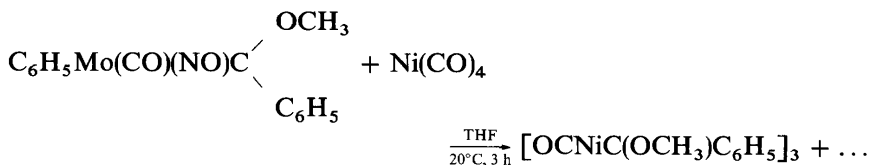
Finally, we found that methylaminophenylcarbene cleaved from  $(\text{CO})_5\text{Cr}(\text{HNCH}_3)\text{C}_6\text{H}_5$  by CO under high pressure rearranges to give benzylidene methylamine<sup>15, 31</sup>.



In all these reactions we can never say whether we are really dealing with free carbenes or with carbenoid metal complexes. In this connection we were particularly interested in one special type of reaction: the transfer of a carbene ligand from one metal to another. We had success in these reactions with the rather labile cyclopentadienyl molybdenum carbonyl nitrosyl methoxyphenylcarbene complex. When we irradiated a mixture of this complex and  $\text{Fe}(\text{CO})_5$  in benzene solution, iron tetracarbonyl methoxyphenylcarbene was formed by a transfer reaction of the carbene from molybdenum to iron<sup>32</sup>. There is once again, however, no proof for the migration of a free carbene, since it is possible that a free  $\text{Fe}(\text{CO})_4$  fragment may react with the starting carbene complex.



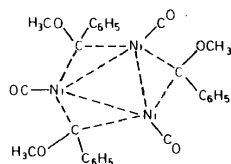
Reaction of the same molybdenum complex with nickel tetracarbonyl in tetrahydrofuran yielded, without irradiation, an extremely labile violet complex, which we believe<sup>32</sup> to be a trimer,  $[\text{OCNiC}(\text{OCH}_3)\text{C}_6\text{H}_5]_3$ .



I would like to mention especially that although some very interesting unstable carbene complexes are formulated in the literature by R. Pettit<sup>33</sup>, M. L. H. Green<sup>34, 35</sup> and others, I thought I should restrict my lecture to the well defined stable transition metal carbonyl carbene complexes in order to

<sup>1</sup>H-n.m.r.-spectrum

	$\tau_{(\text{OCH}_3)}$	$\tau_{(\text{C}_6\text{H}_5)}$
$\text{D}_3\text{C}-\text{C}(\text{O})-\text{CD}_3$ :	5.29; 5.34; 5.43	2.63; 1.75
<i>n</i> -Hexane:	5.42; 5.47; 5.60	2.78; 1.68
Intensity:	3	5
Structure:	3 singlets	multiplets

 $\nu_{\text{CO}}$  (*n*-hexane) 2010  $\text{cm}^{-1}$ 

learn about the behaviour and properties of this new class of organometallic compounds.

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	Dipl. chem. K. H. Dötz	Dipl. chem. M. Leupold
Lic. S. Fontana	Dipl. chem. B. Heckl	Dipl. chem. E. Louis
	Dipl. chem. V. Kiener	Dipl. chem. E. Offhaus

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*For i.r. and <sup>1</sup>H-n.m.r. measurement*

Dr C. G. Kreiter      Dr E. Moser

*For kinetic investigations*

Prof. Dr H. Werner

*For mass spectrometric investigations*

Dr J. Müller

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