

# A SURVEY OF RECENT X-RAY STRUCTURAL STUDIES OF ORGANOMETALLIC COMPOUNDS

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## INTRODUCTION

The application of chemical crystallography in the area of co-ordination chemistry, and especially in organometallic chemistry, has received increased impetus during recent years. Much of this has been made possible by technological developments in other fields, particularly in the development of computers and, to a lesser extent, with diffraction apparatus. That structure analysis can now be undertaken with a reasonable expectation of results within a matter of weeks rather than years, has led to two broad developments in study. On the one hand many more examples of single studies of compounds which exhibit special features occur whilst on the other it is becoming increasingly rewarding to examine groups of related compounds in order to study systematic variations in molecular geometry. This increase in structure determination capability has coincided almost exactly with the great revival of interest in organometallic chemistry subsequent to the discovery of ferrocene. In this paper we shall restrict ourselves to the consideration of some examples of systematic study and examine a few groups of inter-related compounds which have been studied by a variety of different workers. In all the examples chosen, the areas are under continued scrutiny and many of the publications quoted have appeared within the past twelve months. In such a recent field of activity therefore it is possible that current and as yet unpublished results may alter one's view. However certain trends are appearing which we think are more likely to be amplified by such results. It is these trends which are reported in this paper.

## CYCLIC COMPLEXES OF CHROMIUM AND MOLYBDENUM TRICARBONYLS

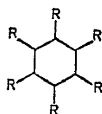
There now exists a number of detailed structure analyses of tricarbonyl-metal complexes of six, seven, and eight-membered rings. In the case of the six and seven-membered species examples exist which involve fused rings. The various compounds include the tricarbonylchromium complexes of benzene<sup>1</sup>, hexamethylbenzene<sup>2</sup>, naphthalene<sup>3</sup>, anthracene<sup>4</sup>, phenanthrene<sup>5, 6</sup>, dihydrophenanthrene<sup>7</sup>, toluidine<sup>8</sup>, 1-aminonaphthalene<sup>9</sup> and the charge-transfer complex<sup>10</sup> between anisole and trinitrobenzene as well as biphenyl<sup>11</sup> (although we shall ignore this and all other structure determinations which are based upon two-dimensional treatment since it is recognised that such determinations while they have led to correct structures, are usually too imprecise for detailed argument and suffer from the fact that errors are frequently underestimated.) For the seven-membered

ring complexes an important, and early, analysis was that of the tricarbonylmolybdenum complex of cycloheptatriene<sup>12</sup>, whilst tricarbonylchromium complexes of 7-*exo*-phenylcycloheptatriene<sup>13</sup> and 1-ethoxy-3-oxo-3a-phenyl-3.3a-dihydroazulene<sup>14</sup> are available for comparison. To these should be added the [10]-annulene complex formed from 1,6-methanocyclodecapentaene<sup>15</sup> and that from tricyclo-[4,3,1,0]-decadiene.<sup>16</sup> Complexes of cyclo-octatriene<sup>17</sup> and tetramethylcyclo-octatetraene<sup>18</sup> complete the picture.

### Chromium-carbon (ring) separations

We examine first the six-membered ring complexes, and inquire if the metal is symmetrically bonded to the ring. We first make a distinction, however, between those complexes which are highly symmetrical, benzene and hexamethylbenzene, and the remainder. In *Table 1* are listed the

*Table 1*



	chromium-carbon distances (Å)						mean values for selected pairs			Ref.
R = H	2.230	2.218	2.216	(2.216)	(2.218)	(2.230)	1,4	2,3	5,6	1
R = Me	2.211	2.253	2.235	2.226	2.241	2.233	2.223	2.217	2.224	2
	average values: benzene				2.221					
					hexamethylbenzene	2.233				

published data for all the individual Cr—C distances in this pair of compounds (of which only half are symmetrically unique for benzene) and we see that no regular variation occurs, and thus there is no evidence for systematic variation in bond length within these symmetrically substituted complexes. The average values, 2.22 and 2.23 Å, are however, significantly longer than those found in dibenzene chromium<sup>19, 20</sup>, 2.14 Å. In the arene tricarbonyl complexes it seems clear that the weaker acceptor qualities of the ligands, when compared with carbon monoxide, results in preferential double bonding to the carbon monoxide but that some double bonding is nevertheless possible when no other outlet is available as in dibenzenechromium.

When the ligand is unsymmetrically substituted, however, as evidenced in *Table 2*, there exists such a geometry that two Cr—C distances are greater than the remaining four. These four shorter values vary little from their mean, 2.21 Å, a distance close to the symmetric value; likewise the longer show only small variation from 2.30 Å. This pattern, though shown most

Table 2



		chromium-carbon distances (Å)						mean values for selected pairs				Ref.
		1	2	3	4	5	6	1,4	2,3	5,6	(5,6)- (1,4)	
naphthalene anthracene phenanthrene dihydrophenanthrene		2.214	2.213	2.191	2.186	2.306	2.337	2.200	2.202	2.321	+0.120	4
		2.219	2.217	2.221	2.215	2.340	2.324	2.217	2.219	2.332	+0.119	5
		2.212	2.210	2.206	2.208	2.289	2.289	2.210	2.208	2.289	+0.080	6
		2.209	2.208	2.207	2.200	2.248	2.232	2.205	2.208	2.240	+0.034	7
		average values: Cr-C(1,4)						(2.314 excluding dihydrophenanthrene)				
		Cr-C(5,6)										
<i>o</i> -toluidine R <sub>1</sub> = NH <sub>2</sub> , R <sub>2</sub> = Me 1-aminonaphthalene		2.23	2.23	2.23	2.20	2.26	2.37	2.22	2.23	2.32	+0.10	8
		2.19	2.23	2.24	2.22	2.30	2.30	2.21	2.23	2.30	+0.07	9

Table 3



*Deviations of atoms from least-squares plane (Å)*

	1	2	3	4	5	6	Cr	dihedral angle (°)
benzene	+0.008	-0.004	-0.004	+0.008	-0.004	-0.004	+1.724	8.6
hexamethylbenzene	-0.013	+0.008	-0.002	+0.001	-0.007	+0.013	+1.726	7.1
naphthalene	+0.042	-0.008	-0.035	+0.039	-0.006	-0.032	+1.745	3.5
anthracene	+0.053	-0.023	-0.028	+0.048	-0.017	-0.033	+1.753	0.9
phenanthrene	+0.025	-0.008	-0.017	+0.025	-0.017	-0.007	+1.733	
dihydrophenanthrene	+0.002	+0.002	-0.008	+0.011	+0.001	-0.007	+1.717	
o-toluidine†	+0.035	+0.012	-0.029	+0.000	+0.043	-0.061	+1.768	2.7
1-aminonaphthalene	+0.029	-0.014	-0.018	+0.034	-0.019	-0.013	+1.732	4.3

† The carbon of the methyl groups is -0.129 Å and the N of the amino group is +0.024 Å displaced from the least-squares plane. (R<sub>1</sub>=NH<sub>2</sub>, R<sub>2</sub>=Me).

convincingly in the complexes where the two adjacent carbons of the six-ring are substituted by a further ring, is also reproduced in the single example of a benzene ring with non-cyclic *ortho* substituents.

The geometric properties of a regular planar hexagon, however, do not permit a point to be situated such that it be equidistant from four corners without it being placed similarly with respect to the other two. This effect, then, is not to be ascribed to the metal atom moving a little to one side, away from the substituent groups of the ring, but rather to distortion from planar, hexagonal symmetry of the ring. We therefore seek systematic distortions in these systems which yield this observed effect. It is frequently reported that the ligands are planar, within experimental error, and with mean C—C distances which do not vary much from the free ligand, where that has also been determined. In *Table 3* we list the deviations from the 'best' least-squares planes defined by the six carbon atoms of the ring.

We note that although the variations are small, and indeed frequently within a few standard deviations, nevertheless the same type of deviation occurs in every member *i.e.* the 1,4 carbons lie on one side of the plane and the 2,3,5,6 carbons on the other†. Further the 1,4 carbons are always on that side adjacent to the metal atom. The ligand is thus folded slightly, across the 1,4 direction and this arrangement permits the metal to be equidistant from four atoms and to be somewhat further from the remaining two. The dihedral angles involved in these systems are listed in *Table 3* and it will be seen that in all cases the magnitude of the fold is small, on average some  $4\frac{1}{2}^\circ$ . We shall later consider the same deformation in comparison with the seven and eight-ring complexes where the effect becomes increasingly more marked.

A similar collection of metal-carbon distances for the seven-membered ring complexes are listed in *Table 4*. In each of the three analyses of cycloheptatriene complexes, the authors note that six of the seven carbons are approximately coplanar and that the seventh (methylene) carbon is tilted out of the plane so that the metal-carbon distance involved with this last atom is much larger than the other six. The other six metal-carbon distances can be divided into two groups, once again four around 2.20 Å and two approximately 2.30 Å for the chromium complexes. The same variation holds for the molybdenum complex where the difference in molybdenum-carbon lengths is 0.12 Å, and comparison of the molybdenum and chromium values suggests an increase for the radius of molybdenum over chromium of 0.13–0.15 Å on the supposition that bonding is similar in these complexes. This value is in strikingly good agreement with the zero-valent radii proposed by Cotton and Richardson, 1.62 and 1.48 Å for molybdenum and chromium respectively<sup>21, 22</sup>. In *Table 4* are also listed the values for two complexes in which the 1,6 atoms are linked either by a conjugated four-carbon diene or a saturated three-carbon chain respectively. These

† The values for *o*-toluidine require some additional comment since the displacements at C(5) and C(6) show irregularity. The methyl and amino substituents are attached to these atoms respectively and both substituents are displaced from the least-squares plane, and in the opposite sense to the deviations of the ring carbon atoms themselves. This steric problem, due to the hydrogens of the substituent groups, is not present in any of the other *o*-substituted complexes.

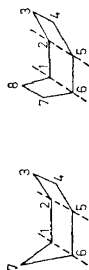
Table 4



## Metal-carbon distances (Å)

	2	3	4	5	6	7	8	Ref.
cycloheptatriene	2.368	2.314	2.311	2.328	2.433	2.958		12
	<i>average values:</i>							
			Mo-C(2,5)		2.33			
			Mo-C(1,6)		2.45			
7-exo-phenyl-cycloheptatriene	2.204	2.203	2.207	2.205	2.310	2.877		13
1-ethoxy-3-oxo-3a-phenyl-3.3a-dihydro-azulene	2.21	2.19	2.20	2.20	2.31	2.81		14
	2.22	2.23	2.19	2.15	2.27	2.88		14
	<i>average values:</i>							
			Cr-C(2,5)		2.20			
			Cr-C(1,6)		2.30			
1.6-methanocyclodecapentaene	2.22	2.19	2.20	2.19	2.57	3.25		5
tricyclo[4,3,1,0,1,9]-decadiene-2,4	2.16	2.18	(2.18)	(2.16)	2.50	3.46		16
	<i>average values:</i>							
			Cr-C(2,5)		2.19			
			Cr-C(1,6)		2.54			
cyclo-octatriene	2.12	2.24	2.28	2.38	2.38	3.22	3.16	17
1,3,5,7-tetramethyl-cyclo-octatetraene	2.207	2.248	2.226	2.195	2.289	3.150	3.159	18
	<i>average values:</i>							
			Cr-C(2,5)		2.25,			
			Cr-C(1,6)		2.37,			

Table 5



	<i>Deviations of atoms from least-squares plane (Å)</i>							<i>dihedral angle (°)</i>
	2	3	4	5	6	1	Cr or Mo	
cycloheptatriene	+0.043	-0.033	-0.015	+0.045	-0.024	-0.014	+1.763	6.3
7-exo-phenylcycloheptatriene	+0.050	-0.020	-0.024	+0.031	-0.005	-0.032	+1.593	5.7
1-ethoxy-3-oxo-3a-phenyl-3,3a-dihydroazulene	+0.05	-0.01	-0.04	+0.04	-0.01	-0.03	+1.58	6.6
1,6-methanocyclodecapentaene	+0.149	-0.075	-0.096	+0.161	-0.069	-0.069	+1.730	21.6
tricyclo[4.3.1.0 <sup>1,6</sup> ]decadiene-2,4	+0.154	-0.082	-0.072	+0.154	-0.082	-0.072	+1.743	21.4
cyclooctatriene	+0.143	-0.087	-0.036	+0.071	-0.012	-0.079	+1.509	15.0
tetramethylcyclooctatetraene	+0.119	-0.045	-0.077	+0.095	-0.027	-0.065	+1.511	15.5

complexes continue to show four distances around 2.20 Å but the two longer distances have increased to 2.54 Å.

All these seven-membered ring compounds show folds which are similar, geometrically, to the six-membered rings *i.e.* across the 2,5 positions. In *Table 5* are listed the deviations from the least-squares planes defined by carbons 1–6. In all cases atoms 2 and 5 occur on the metal side of the least-square plane with the remaining carbons, and the methylene carbon, on the other. The dihedral angles between the pairs of planes which make up the fold are, for the cycloheptatriene complexes, in the range 5.7–6.6°, a little greater than in the six-ring complexes. Simultaneously, because of the greater ring size associated with the expansion of the 1–6 separation from 1.4 to 2.2 Å, the metal-plane distance is reduced from the value of 1.74 Å in the six-ring complexes to 1.59 Å in these cycloheptatrienes.

It is clear, however, that the 1,6-methanocyclodecapentaene and tricyclo[4,3,1,0]-decadiene complexes belong to a different category. Here the ring is much more severely folded and the chromium-carbon distance differences more marked. Further, whereas the cycloheptatrienes continue to show marked alteration in carbon-carbon bond length, this pair of complexes shows no such variations in accord with the aromaticity of the free ligands<sup>23</sup>. Indeed whereas the cycloheptatriene complexes show a pronounced change in ligand shape as a result of complex formation<sup>15</sup>, there is relatively little change in the case of 1,6-methanocyclodecapentaene (and presumably also in the decadiene) although the initial shapes of the seven-rings in cyclo-heptatriene and the bridged 10[annulene] are not very different.

*Tables 4* and *5* also contain the equivalent information pertaining to the eight-ring complexes. It seems here that there may be greater variation in metal-carbon distances than in the six and seven-ring systems. Nevertheless the pattern of four short distances around 2.22 Å and two longer ones about 2.36 Å is clearly present. The fold of the ligand is even more marked and amounts to some 15°. Since the 1,6 separation has now increased to approximately 2.9 Å, the chromium—plane distance reduces still further to 1.51 Å. This parameter thus roughly decreases by 0.1 Å per carbon atom between the six and eight-membered rings.

### Shape and orientation of the tricarbonylmetal group and metal-CO distances

Although it is not uncommon to regard the carbon monoxide ligands as occupying three *cis* octahedral positions with idealised  $C_{3v}$  symmetry, in fact, as has been pointed out in the individual cases by the investigators, such idealized symmetry is never attained. *Table 6* contains the angular information for the various complexes. The average angle subtended at the metal is *less* than 90°, although in some complexes one angle may be significantly greater than 90°. The two angles with close values are usually the larger ones. Only broad generalisations can be made from the published data. It seems that as we go from six-ring to eight-ring the spread in angular values increases. This could be a consequence of the increased departure from near hexagonal symmetry as additional carbon atoms are inserted. In agreement with this generalisation, we note that the deviations are least

Table 6

<i>C—Cr—C angles</i>					
benzene	89.4	89.4	86.7		
hexamethylbenzene	90.1	89.2	88.6		
<i>o</i> -toluidine	90	89	86		
anisole-trinitrobenzene	92	89	87		
naphthalene	90.7	90.1	87.0		
1-aminoaphthalene	91	89	86		
anthracene	90.7	89.0	87.4		
phenanthrene	90.6	89.9	87.1		
dihydrophenanthrene	89.8	89.2	87.8	<i>Av.</i>	<i>range.</i>
	90.5	89.3	87.1	89.0	3.4
cycloheptatriene (Mo)	80.0	88.2	83.5		
7- <i>exo</i> -phenylcycloheptatriene	91.2	89.2	86.3		
1-ethoxy-3-oxo-3a-phenyl-3.3a-dihydroazulene	91	89	82		
1,6-methanocyclopentadiene	88.0	87.6	86.0		
tricyclo[4,3,1,0]-decadiene	88.1	86.6	86.6		
	89.6	88.1	85.2	87.6	4.4
cyclo-octatriene	95.4	91.0	78.8		
tetramethylcyclo-octatetraene	94.3	91.0	81.4		
	94.8	91.0	80.1	88.6	14.7

in the seven-ring compounds for the decadiene complex which shows the shortest 1,6 separation.

The reported Cr—C<sub>sp</sub> distances show variations between 1.76 and 1.88 Å, mean 1.83 Å, *i.e.* they are always shorter than the value reported for hexacarbonylchromium itself, 1.916(3) Å<sup>24</sup>, which itself requires an explanation for shortening by invoking partial double-bond character<sup>24, 25</sup>. The further shortening is in general agreement with the view that the organic ligands are poor acceptors.

The variations from the mean value, and in particular those for which the shorter values have been reported, have sometimes been further ascribed to specific electronic effects within the molecules concerned. We list in Table 7 all the Cr—C<sub>sp</sub> and C—O distances for the complexes discussed. The quantities are listed in decreasing order of Cr—C distance and the C—O distances are given in the same order so that they can be associated with the Cr—C values. We list the average Cr—C and C—O values for each group together with their sum. It will be seen that a shorter Cr—C distance is associated with a longer C—O distance and that their sum is remarkably constant for any one group, six-, seven-, or eight-membered ring. This suggests that, unless the constancy be a chance phenomenon, either the carbon atoms are more difficult to place than the oxygen atoms, or that the changes in bond-length *vs.* bond-order for the Cr—C and C—O bonds with the appropriate bond orders involved just compensate. This latter suggestion does not seem to be in keeping with published bond-length *vs.* bond-order curves<sup>22</sup>. It suggests that great care should be exercised in interpreting any single observational value.

Table 7

	bond lengths (Å)							
	Cr—C	C—O	Cr—C	C—O	Cr—C	C—O	Cr—C	C—O
benzene	1.842	1.150	1.842	1.150	1.841	1.135	1.842	1.145
hexamethylbenzene	1.831	1.153	1.823	1.137	1.789	1.200	1.814	1.163
anisole	1.82	1.17	1.78	1.18	1.77	1.23	1.79	1.19
<i>o</i> -toluidine	1.80	1.16	1.78	1.20	1.76	1.18	1.78	1.18
naphthalene	1.830	1.137	1.818	1.167	1.815	1.147	1.812	1.150
1-aminonaphthalene	1.830	1.11	1.77	1.19	1.68	1.26	1.76	1.19
anthracene	1.834	1.163	1.826	1.142	1.812	1.184	1.825	1.163
phenanthrene	1.857	1.136	1.844	1.145	1.828	1.165	1.843	1.149
dihydrophenanthrene	1.843	1.140	1.834	1.142	1.821	1.148	1.833	1.143
<i>av.</i>	1.832	1.147	1.813	1.161	1.791	1.183	1.812	1.164
<i>sums.</i>	2.979		2.974		2.974		2.976	
7- <i>exo</i> -phenylcycloheptatriene	1.821	1.158	1.820	1.178	1.798	1.189	1.813	1.175
1,6-methanocyclodecapentaene	1.83	1.16	1.83	1.16	1.80	1.16	1.82	1.16
tricyclo[4,3,1,0]-decadiene	1.82	1.16	1.82	1.16	1.79	1.17	1.81	1.16
1-ethoxy-3- <i>oxo</i> -3a-phenyl-1,3a-dihydroazulene	1.88	1.12	1.87	1.11	1.76	1.21	1.84	1.15
	1.86	1.09	1.80	1.16	1.78	1.20	1.81	1.15
<i>av.</i>	1.842	1.138	1.828	1.154	1.786	1.186	1.819	1.159
<i>sums.</i>	2.980		2.982		2.972		2.978	
cyclooctatriene	1.87	1.17	1.87	1.21	1.83	1.20	1.86	1.19
tetramethylcyclooctatetraene	1.855	1.148	1.852	1.163	1.839	1.160	1.848	1.157
<i>av.</i>	1.862	1.159	1.861	1.186	1.825	1.180	1.852	1.175
<i>sums.</i>	3.021		3.047		3.015		3.027	

**Changes in ligand dimensions on complexing**

In the cases of benzene, naphthalene, anthracene, phenanthrene and 1,6-methanocyclodecapentaene the dimensions of the complexed ligands have been compared with those of the uncomplexed ones. In the cycloheptatriene series comparison can be made with the ring contained in a derivative of thujic acid.

Perhaps the most striking observation is that the bonding linear quantities involved in these compounds are not very greatly altered as a result of a complex formation. In the case of the aromatic ligands, where alternation of bond length occurs in the free hydrocarbon that alternation is decreased in the complex. At the same time, the average bond length in the complexed ring is increased from its value in the free hydrocarbon. Such increases are rather small *e.g.* the average carbon-carbon distances in the three rings in anthracene increase from 1.410 through 1.414 to 1.418 Å in the complex compared with 1.409 Å in the free anthracene molecule.

The greatest changes observed occur in the overall shape of such molecules as the cycloheptatriene, cyclo-octatriene and cyclo-octatetraene as has been already mentioned. It is not yet clear why the cyclodecapentaene and tricyclodecadiene complexes do not undergo precisely similar conformational changes unless it be due to the difference in orientation of the tricarbonyl groups in the two groups of complex. Further studies are called for before this problem can be settled.

In the substituted hydrocarbons the average exocyclic bond length in the complexed form is increased from its value in the free hydrocarbon and this increase is usually greater than the corresponding increase in the ring lengths.

As a result of these detailed examinations of the published structures of these complexes it seems reasonable to consider the bonding between a tricarbonylmetal group, either chromium or molybdenum, and a hydrocarbon ligand as one in which the metal, whilst requiring, as far as possible, six electrons nevertheless makes stronger bonds involving four of these electrons. The structures can then be regarded as 4 + 2 electron structures.

**CARBENE COMPLEXES OF TRANSITION METALS**

Although carbene complexes have been postulated as intermediates in a number of synthetic reactions involving metal catalysts, the number of isolatable complexes which have been studied by diffraction analysis remains relatively small. It is also unfortunate that, so far, no complex has yet been isolated from a reaction in which liberated carbene, or substituted carbene, is trapped unequivocally by the metal. However it has proved to be possible to prepare a large number of these complexes indirectly by nucleophilic attack on metal carbonyls, both pure and substituted, and it is the products of these reactions that have been investigated<sup>26</sup>. The compounds studied include [methoxy(phenyl)carbene]-pentacarbonylchromium<sup>27, 28</sup> together with its tungsten analogue<sup>27</sup>, although with the latter the large scattering power of tungsten limits the accuracy of the determination and we shall not consider the values obtained further, [methoxy(methyl)carbene]triphenylphosphine)tetracarbonylchromium<sup>29,30</sup>, [methylamino(methyl)car-

bene]pentacarbonylchromium<sup>31</sup> and [diethylamino(methyl)carbene]-pentacarbonylchromium<sup>32</sup>. All these compounds contain the common feature of the presence of three co-ordinate carbon with features which would be expected from a carbene complex.

Carbene complexes were considered to be stable possibilities by comparison with carbonyl compounds. Singlet carbene,  $CX_2$ , contains six electrons in  $sp^2$ -hybridised orbitals thus utilising only two of the  $p$ -orbitals. The third atomic orbital remains empty. Complexes are then formed by the usual  $\sigma$ -donation and  $\pi$ -back donation mechanism from the lone-pair in one  $sp^2$ -hybridised orbital and into the empty  $p_z$  atomic orbital. Stable complexes should thus exhibit partial double-bond character in the metal-carbon bond, as in carbon monoxide complexes, but this double-bond character would be expected to be less than for the latter since there are fewer acceptor orbitals available for the back-donation process. This variation in bond order should be reflected in the metal-carbon(carbene) distance. Indeed this parameter should be rather more sensitive to the change in bond-order when compared to the corresponding carbonyls since the slope of the bond-length *vs.* bond order curve increases rapidly as the bond-order approaches unity<sup>21, 22</sup>. At the same time there should be other bond-length variations, *e.g.* between the metal and other ligands especially carbonyl groups which may be present in the molecule due to increased back-donation to these ligands. Such variations will, however, be much smaller because of the increased number of ligands.

The situation will be modified when one, or both, of the substituent atoms on the carbene contains lone pairs, for then there arises the possibility of competitive donation between this heteroatom and the metal atom into the empty  $p_z$  orbital. This competition would result in partial, but reduced, double-bond character in both the metal-carbene and heteroatom-carbene bonds. In particular this situation will arise where the heteroatom is oxygen which has originated from the carbon monoxide group originally subjected to the nucleophilic attack. Because of the sensitivity of the variation of bond length with bond order, changes of the heteroatom and even of the substituents on the heteroatom might be expected to cause variations in the metal-carbon separation.

The first structure to be determined in detail, that of [methoxy(phenyl)-carbene]pentacarbonylchromium, established the principal molecular geometric features *e.g.* the coplanarity of the carbene carbon atom with its substituents and the metal atom and the non-alignment of this plane with the principal planes of the octahedral co-ordination polyhedron of the metal. The Cr—C(carbene) distance, 2.04(3) Å, is both significantly longer than the Cr—C(carbonyl) distances in the same molecule (average 1.89 Å) and those in hexacarbonylchromium itself, 1.92 Å<sup>24</sup>. Clearly these values are compatible with less double-bond character of the Cr—C(carbene) bond and greater double-bonding in the remaining Cr—C(O) links. Replacement of an equatorial carbonyl group by triphenylphosphine does not convincingly shorten the Cr—C length, now 2.00(2) Å, although such a variation would be readily explicable as would the likewise insignificant shortening of the remaining C—C(O) distances to 1.87 Å. The major geometric change, as recorded in *Figure 1*, is the rotation of the methoxy

group through  $180^\circ$  from the *cis* position relative to the metal into the *trans* position. The length of the C(carbene)-O(methoxy) bond remains constant,  $1.33(2)$  and  $1.32(2)$  Å, values which indicate appreciable double-bond character.

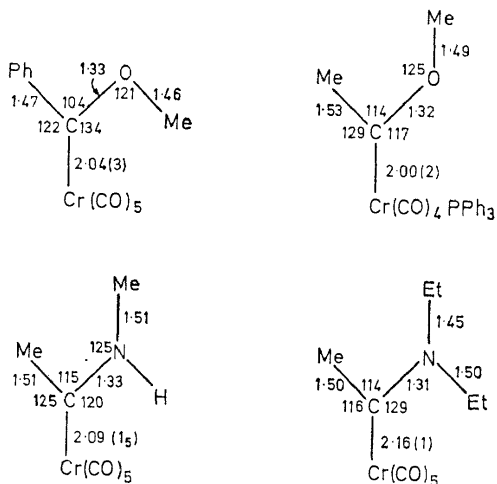


Figure 1. Geometry of carbene-chromium complexes.

Although the metal-carbene distances are much longer than in the carbonyls, they are, however, shorter than the single bond value predicted on the basis of a radius for chromium in the zerovalent state of  $1.48$  Å<sup>21</sup>, and a radius of  $0.73$  Å for  $sp^2$ -hybridized carbon. This is in keeping with the view that back donation, though reduced, still occurs. Nitrogen is a better donor than oxygen and aminocarbene complexes<sup>33</sup> should extend the comparison. The effect first demonstrated in [methylamino(methyl)carbene]pentacarbonylchromium whereby the Cr—C(carbene) distance appears to be marginally increased is demonstrated most convincingly in [diethylamino(methyl)carbene]pentacarbonylchromium where the observed value,  $2.16(1)$  Å, is the longest yet reported in keeping with the donor capability of the diethylamino group. Such a bond can now have but little double-bond character associated with it. The insensitivity of the remaining Cr—C(O) values is demonstrated by their average length in this compound,  $1.89$  Å.

All of the above results have been obtained from observations on neutral complexes. The structure of one salt has been briefly reported<sup>34</sup>. The values shown in Figure 2 parallel the more extensive observations quoted for the chromium series.

The angle subtended at the carbene carbon atom by its substituents is of interest. The spectroscopic value of  $102^\circ$  for methylene itself<sup>35</sup> is found only in [methoxy(phenyl)carbene]pentacarbonylchromium. The others

show an increased value of 114–115°. It should be noted that [methoxy-(phenyl)carbene]pentacarbonylchromium is the only complex in which the substituent on the heteroatom occupies the position *cis* to the metal atom when the *trans* position is vacant. Although the accommodation of a methyl, and even an ethyl, group is not sterically impossible in the *cis* position, the rotation through 180° may be associated with the change of angle.

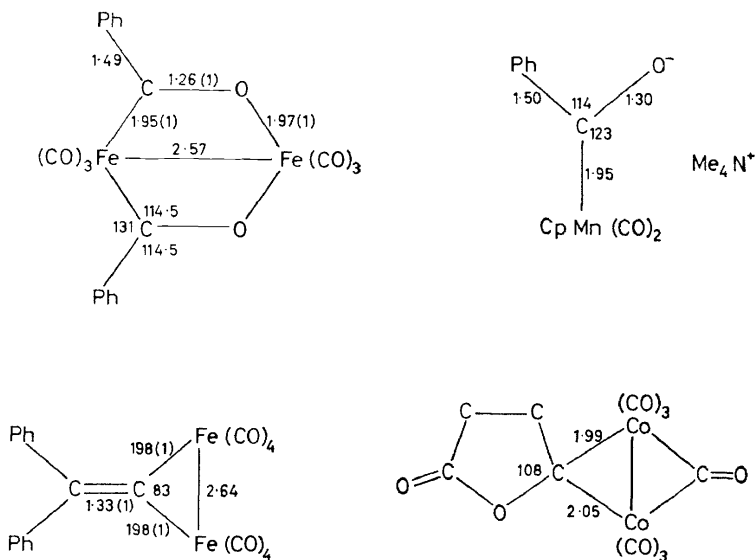


Figure 2. Possible carbene complexes

Whereas all the complexes discussed so far have been monomeric, a most unexpected dimeric complex arose from the now usual work-up procedure of the primary addition product of phenyl-lithium to pentacarbonyliron<sup>36, 37</sup>. In the dimer, two tricarbonyliron units are bridged by Ph—C—O residues so as to make a six-membered boat (*Figure 2*) with Fe—Fe 2.57 Å. and Fe—C 1.95 Å. Of particular interest with regard to the mechanism of the reaction is the observation that both carbene fragments are attached to the same iron atom, the second iron atom linking to both oxygen atoms. The extreme variability of distances which involve iron makes a meaningful analysis difficult but the Fe—C(carbene) bonds would appear to have but little double-bond character.

Finally we may try to follow the analogy with carbon monoxide one stage further. As well as bonding in the terminal, linear manner, carbon monoxide also forms bridges between two and three metal atoms. Whilst the definitive description of a bridging carbene complex may ever elude us, since alternative valency descriptions appear to be always possible, two examples have been recorded which can be described in terms of bridging carbenes<sup>38, 39</sup>. These are included in *Figure 2*.

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