PERSPECTIVES IN
STRUCTURAL CHEMISTRY

VOLUME I

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STRUCTURAL CHEMISTRY
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Preface

The appearance of yet another series of review books would seem to require some justification, for we are all uncomfortably aware nowadays that we have far too much to read already. Nevertheless, new reviews keep on coming out, and it can be assumed that at least the authors and editors of these publications see some merit in them. Most authors and editors are, after all, busy people with lots of other things to do besides writing or editing review articles, which, as they well know, are unlikely to bring them either fame or riches. They must believe that such review articles will meet some need.

For some time we have felt there is room for a publication that would provide regular reviews of the ever increasing torrent of papers in the field of structural chemistry, structural chemistry being understood as that branch dealing with the metrical aspects of molecular structure. We were by no means sure, however, that this feeling was shared by other scientists in the field, whose support and collaboration would be necessary if the new publication was to prosper. Only after we had made an informal poll of a group of active structural chemists scattered throughout the world were we confident enough to go ahead with plans for the projected publication, for our poll revealed a high degree of support for the idea of a new review, particularly for one in which the chemical implications of structural studies, rather than the technical aspects, would be emphasized.

One of the most important tasks in structural chemistry today is, we believe, that of making critical assessments of the mass of already published material in the search for unifying ideas. To mention only two examples: we know almost nothing about the weak interactions that control preferred packing arrangements of molecules in crystals, and we are only beginning to understand the conformational complexities of organic molecules, although a vast amount of information on these and other untouched matters is stored away in the literature. Much of this potentially valuable structural information implicit in the results of diffraction analyses is often passed over by the authors themselves (who are presumably happy enough to have completed the analysis successfully) and has to be actively sought and recovered from the authors' description of their results.

Our objective here is to create a forum for such constructive reviews in which the attempt is made to weave the results of individual structure determinations into some kind of cohesive pattern. At present there is no really suitable journal for articles of this kind, which would not necessarily contain any new facts but rather re-interpretations of old ones. One difficulty in our way will be to find a sufficient number of knowledgeable, suitably qualified, and willing authors. We believe that a necessary condition for an authoritative review article is that the reviewer be intimately familiar both with the subject matter and with the techniques employed to supply the relevant information. For this reason we find many of the occasional review articles on given topics in structural chemistry, dispersed as they are throughout the literature, to be unsatisfactory. Too often the reviewer has only a very superficial acquaintance with the technical details of the methods employed to obtain the results under discussion and can merely report "the structure of compound A was determined by scientist B, the accuracy claimed being C". This is not to say that authoritative, critical reviews of the structural literature cannot be found; an excellent source for such reviews is Structure Reports, published by the International Union of Crystallography. Each volume covers the structural literature of a single year in comprehensive fashion, albeit some seven to ten years after the original material was published. However, in these reviews, excellent as they are, little attempt is made to relate the structural implications of the work to other structural studies, and no attempt whatsoever is made to relate them to chemistry in a wider sense.

We are aware that neither we nor our authors can know in advance whether the attempt to survey a given region of structural chemistry will actually lead to the recognition of cohesive patterns or unifying ideas. It will often be the case that we do not even know the right questions to ask. We have to expect that some of these attempts may end up by merely establishing that the structural results are various and that no coherent pattern can be distinguished; or that they may even add to an already confusing picture, by bringing into the open facets that have been ignored or forgotten. Sometimes, it is to be anticipated, what is intended as a review of a supposedly well-defined field may develop into a digression of an open-ended character. Thus we see that our objective in these reviews is something of an unattainable ideal, but we shall consider the venture to be very worthwhile if this ideal is even approached.

To this end, we call on specialists in structural chemistry to provide constructive, critical, chemically oriented reviews of a given area of their field. Since diffraction methods have supplied most of the information relevant to structural chemistry, most of our reviewers will be expert in diffraction matters although we shall not ignore the important contributions made by spectroscopic methods, particularly in establishing the fine detail of the structures of small molecules. But, although we take the technical expertise of our reviewers for granted, we are not asking them to write exclusively for the specialist reader. On the contrary, we encourage them to concentrate on describing the structural inter-relations and their chemical implications, avoiding, as far as possible, over-involvement with methodology and technical detail. We feel that this approach is especially valuable in these days when, primarily as a result of the development of computers and improved apparatus, the volume and influence of diffraction studies has reached levels of importance that were almost completely unexpected twenty years ago. Thus we hope that these reviews will prove useful to the non-specialist in diffraction techniques, who is interested only in the results and their implications. We hope that they may also provide the seeds of understanding to the theoretical chemist, who, sooner or later, will be able to make sense of it all and explain it for us.

We shall try to keep a reasonable balance among inorganic, organic, physical, and biological chemistry, although this balance is unlikely to be achieved in every volume—we cannot pretend that it has been achieved in this first volume! We shall not attempt to cover specialized topics in crystallography, topics in chemical bonding theory, or introductory articles.

This series was born, at least conceptually, during a very pleasant visit to Bratislava in September, 1964. We should like to express our thanks to Dr. F. Hanic and to the Slovakian Academy of Science for their hospitality on that occasion.

J. D. Dunitz
November 1966 J. A. Ibers

Contents

π-Complexes of Transition Metals with Aromatic Systems

P. J. WHEATLEY,* Monsanto Research S.A.,
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I. SCOPE

This Review is concerned primarily with X-ray structural determinations of π-complexes of transition metals, the aim being to discover

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to what extent the molecular dimensions that have been obtained can be used to throw light on the nature of the bonding in these molecules. In order to keep within reasonable bounds, it has proved necessary to be selective.

The *transition elements* are defined in the narrowest sense, and lie in the series Sc–Ni, Y–Pd, and Lu–Pt inclusive, that is, the elements with atomic numbers 21 through 28, 39 through 46, and 71 through 78. Not all of these elements are represented. π-Complexes of Be,[1] Mg,[1,2] Cu,[3–8] Ag,[5,9–11] In,[12,13] Tl,[13,14] and U[15] are discussed only insofar as the results are relevant to the main theme.

The *aromatic systems* are defined in the chemical sense to mean molecules or molecular fragments that may be shown (or may reasonably be believed) to undergo substitution reactions and that do not, therefore, possess olefinic properties. This definition also implies cyclic delocalization of π-electrons and, in practice, largely reduces to a consideration of four-, five-, six-, and seven-membered homocyclic rings. There is one structural determination of a π-complex containing a π-bonded heterocycle, and four further examples in which the reaction of a metal carbonyl with an acetylene or an olefin yields a polynuclear π-complex in which a ferracyclopentadienyl or osmacyclopentadienyl ring is π-bonded to another iron or osmium atom. These five molecules will be considered. On the other hand, the large body of compounds that contain, for instance, π-bonds to isolated double bonds, or to allyl or butadiene residues, in which linear delocalization undoubtedly occurs, will not be discussed in detail.[16–55]

The literature has been searched up to the end of 1965.

II. NOMENCLATURE

Since no definite nomenclature rules appear to have become established that cover the whole field of organometallic compounds, a partly pragmatic approach has been adopted (cf. Coates[56] and Wilkinson and Cotton[57]). In formulae, the aromatic part of the molecule is placed first, then the metal, and lastly the other groups.

When bond lengths are referred to, the following abbreviations are used for substituted or unsubstituted π-bonded aromatic ring systems:

Cb	Cyclobutadiene
Cp	Cyclopentadienyl
Ch	Cycloheptatrienyl

In addition, the following abbreviations will be employed when no confusion is likely:

M	Transition metal
ED	Results obtained from an electron-diffraction investigation
MW	Results obtained from a study of the microwave spectrum
M–C(Ring)	Distance from the transition metal to a carbon atom in an aromatic ring
M–Ring	Perpendicular distance from the transition metal to the least-squares plane through the atoms of the aromatic ring

III. RESULTS

The available experimental results are presented in Tables 1–7. It has occasionally been necessary to calculate molecular quantities not listed in the original papers. In the course of these calculations, which were carried out on an Elliott 803B computer with the programming system of Daly, Stephens, and Wheatley,[58] some quantities that were listed have of necessity been recalculated. These values are shown in heavy type in the Tables. They were obtained from the original cell dimensions and coordinates (corrected, when necessary, for obvious printing mistakes), the resulting coordinates in Å being carried to four decimal places, and from five-figure trigonometric functions. In general, the agreement with the original results is good, but differences of up to 0.1 Å do occur.

Values in square brackets are considered to be unreliable for one of a variety of reasons: they may be the results of limited two-dimensional X-ray analyses; they may suffer from molecular disorder

Table 1. Distances (in Å) in π-complexes of four-membered homocyclic rings.

Compound	C(Cb)–C(Cb)	Range
$(\pi\text{-Ph}_4\text{C}_4)\text{Fe(CO)}_3$	**1.459**	**1.444–1.469**
$(\pi\text{-Me}_4\text{C}_4)\text{NiCl}_2\cdot\frac{1}{2}\text{C}_6\text{H}_6$	1.431	1.399–1.455

Compound	M–C(Cb)	Range	M–Cb	Refs.
$(\pi\text{-Ph}_4\text{C}_4)\text{Fe(CO)}_3$	**2.067**	**2.053–2.091**	**1.790**	60, 61
$(\pi\text{-Me}_4\text{C}_4)\text{NiCl}_2\cdot\frac{1}{2}\text{C}_6\text{H}_6$	2.022	1.997–2.047	1.749	62

Table 2. Distances (in Å) in π-complexes of five-membered homocyclic rings, the complexes having 'effective' axial symmetry.

Compound	C(Cp)–C(Cp)	Range	M–C(Cp)	Range	M–Cp	Refs.
$(\pi\text{-}C_5H_5)TiCl_3$	—	—	—	—	[2.08]	63
$(\pi\text{-}C_5H_5)_2V^a$	—	—	[2.30]	—	[1.96]	2
$(\pi\text{-}C_5H_5)(\pi\text{-}C_7H_7)V$	1.424	—	2.23	—	1.90	64
$(\pi\text{-}C_5H_5)_2Cr^a$	—	—	[2.22]	—	[1.86]	2, 65
$(\pi\text{-}C_5H_5)_2Mn$	—	—	—	—	—	2, 66, 67
$(\pi\text{-}C_5H_5)Mn(CO)_3$	1.394	1.350–1.433	2.151	2.127–2.176	1.80	14, 68
	1.404	1.352–1.433	2.045	2.010–2.070	1.66	
$(\pi\text{-}C_5H_5)_2Fe$	1.43 (ED)	—	2.03 (ED)	—	—	2, 69–74
	1.44 (ED)	—	2.06 (ED)	—	—	
$(\pi\text{-}C_5H_5)_2Co^a$	—	—	[2.13]	—	[1.76]	2, 75
$(\pi\text{-}C_5H_5)_2CoClO_4$	—	—	[2.1]	—	—	76
$(\pi\text{-}C_5H_5)NiNO$	[1.40 (ass.)]	—	2.107 (MW)	—	1.72^b	77
$(\pi\text{-}C_5H_5)_2Ni^a$	—	—	2.18 (ED)	—	—	2, 75, 78, 79
	—	—	[2.20]	—	[1.84]	
$(\pi\text{-}C_5H_5)Nb(CO)_4$	—	—	—	—	—	80
$(\pi\text{-}C_5H_5)_2Ru$	1.434	1.378–1.455	2.208	2.193–2.223	1.841	81, 82
$(\pi\text{-}C_5H_5)_2Os^c$	—	—	[2.22]	—	[1.86]	82

[a] Isostructural with $(\pi\text{-}C_5H_5)_2Fe$.

[b] Calculated assuming C(Cp)–C(Cp) = 1.43 Å.

[c] Isostructural with $(\pi\text{-}C_5H_5)_2Ru$.

Table 3. Distances (in Å) in π-complexes of five-membered homocyclic rings, the complexes lacking 'effective' axial symmetry.

Compound	C(Cp)–C(Cp)	Range	M–C(Cp)	Range	M–Cp	Refs.
$(\pi\text{-}C_6H_5)_2TiCl_2Al(C_2H_5)_2$	—	—	[2.3]	—	—	83
$[(\pi\text{-}C_5H_5)TiCl_2]_2O$	**[1.40]**	**[1.36–1.45]**	**[2.26]**	**[2.25–2.27]**	**[1.92]**	63, 84
$[(\pi\text{-}CH_3C_5H_4)Mn(CO)_2]_2C_6H_4[As(CH_3)_2]_2$	—	—	2.15	—	—	85
$(\pi\text{-}C_5H_5)(\pi\text{-}B_9C_2H_{11})Fe$	**1.356**	**1.328–1.377**	**2.072**	**2.038–2.103**	**1.721**	86
$(\pi\text{-}C_9H_7)_2Fe$	[1.43]	[1.39–1.47]	[2.09]	[2.02–2.13]	[1.72]	87
$(\pi\text{-}C_6H_5COC_5H_4)_2Fe$	[1.41]	—	[2.05]	—	[1.66]	88, 89
$(\pi\text{-}C_5H_4SO_2Cl)_2Fe^a$	**1.378**	**1.286–1.467**	**2.029**	**1.982–2.134**	**1.657**	90
$[(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4)Fe]_2$	1.402	1.35–1.46	2.035	1.97–2.07	1.662	91–93
$[(\pi\text{-}C_2H_5C_5H_4)(\pi\text{-}C_5H_4)Fe]_2$	—	—	—	—	—	94
$[(\pi\text{-}C_5H_4Cl)(\pi\text{-}C_5H_4)Fe]_2$	—	—	—	—	—	95
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	**1.408**	**1.362–1.439**	**2.109**	**2.040–2.158**	**1.735**	96
$(\pi\text{-}C_5H_4CH_2)Fe(CO)_2Fe(CO)_4$	**1.431**	**1.416–1.451**	**2.069**	**2.020–2.123**	**1.672**	97
$[(\pi\text{-}C_5H_5)Fe(CO)]_2(CO)(C_6H_5NC)$	—	—	—	—	—	98
$(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4COC_5H_4\text{-}\pi)Ru(\pi\text{-}C_5H_5)$	—	—	—	—	—	99
$[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4\text{–}C_5H_4\text{-}\pi)]_2Fe$	—	—	—	—	—	100
$(\pi\text{-}C_5H_5)[\pi\text{-}(CH_3)_4C_5O]Co$	1.43	—	2.07	—	1.67	101
$(\pi\text{-}C_5H_5)Co(C_6H_5COC_5H_5)$	—	—	2.05	—	—	102
$(\pi\text{-}C_5H_5)Co(C_6H_5\text{–}C_5H_5)$	1.458	1.416–1.495	2.080	2.054–2.146	1.67	103, 104

[a] These figures have been calculated with the 'uncorrected' coordinates, which appear to be in many ways preferable to the 'corrected' ones.

Table 3—*contd.*

Compound	C(Cp)–C(Cp)	Range	M–C(Cp)	Range	M–Cp	Refs.
$(\pi\text{-}C_5H_5)Co[(CF_3)_4C_5O]$	1.436	1.376–1.491	2.075	2.044–2.113	1.68	105
$[(\pi\text{-}C_5H_5)CoC_5H_5]_2C_5H_4$	—	—	—	—	—	106
$(\pi\text{-}C_5H_5)NiC_5H_5C_2(COOCH_3)_2$	1.421	1.375–1.491	2.130	2.091–2.191	1.75	107
$(\pi\text{-}C_5H_5)Ni[C_5H_5C_4(CH_3)_4]$	1.406	1.394–1.416	2.132	2.098–2.168	1.764	108
$[(\pi\text{-}C_5H_5)Ni]_3(CO)_2$	**[1.41]**	—	**[2.15]**	**[2.14–2.17]**	**[1.78]**	109
$(\pi\text{-}C_5H_5)_2MoH_2$	**1.425**	**1.340–1.495**	**2.289**	**2.217–2.365**	**1.939**	110, 111
$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$	1.416	1.370–1.442	2.345	2.302–2.378	—	112, 113
$(\pi\text{-}C_5H_5)Mo(CO)_3C_2H_5$	1.43	—	2.38	—	2.04	114
$[(\pi\text{-}C_5H_5)Mo(CO)_2]_2(H)[P(CH_3)_2]$	1.391	1.323–1.453	2.329	2.265–2.389	2.00	115
$(\pi\text{-}C_9H_7)_2Ru$	—	—	—	—	—	116
$(\pi\text{-}CH_3COC_5H_4)_2Ru$	[1.41]	—	[< 2.18]	—	—	117
$(\pi\text{-}C_6H_5COC_5H_4)_2Ru$	—	—	—	—	—	118
$(\pi\text{-}C_5H_5)Rh(C_2H_4)_2$	—	—	—	—	—	119
$(\pi\text{-}C_5H_5)Rh[C_6(CF_3)_6]$	—	—	—	—	1.83	120
$(\pi\text{-}C_5H_5)Rh(C_2F_5)(CO)I$	**1.453**	**1.409–1.502**	**2.246**	**2.216–2.264**	**1.875**	121, 122
$[(\pi\text{-}C_5H_5)W(CO)_3]_2$[b]	—	—	—	—	—	112, 113
$(\pi\text{-}C_5H_5)Re(CH_3C_5H_5)(CH_3)_2$	—	—	—	—	—	123

[b] Isostructural with $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

Table 4. Distances (in Å) in π-complexes of two five-membered rings joined by an aliphatic chain.

Compound	C(Cp)–C(Cp)	Range	M–C(Cp)	Range	M–Cp	Refs.
$(\pi\text{-}C_5H_4)Me_4C_2(\pi\text{-}C_5H_4)Fe$	1.435	1.401–1.464	2.042	1.965–2.099	1.635	124
$(\pi\text{-}C_5H_4)[CH_2]_2CO(\pi\text{-}C_5H_4)Fe$	1.424	1.408–1.446	2.039	2.007–2.072	1.640	125

Table 5. Distances (in Å) in π-complexes of five-membered heterocyclic rings.

Compound	M–C(Ring)	Range	M–Ring	Refs.
$(\pi\text{-}C_4H_4S)Cr(CO)_3$	**2.210**	**2.195–2.234**	**1.894**	126
$[\pi\text{-}(CH_3)_2C_4(OH)_2Fe(CO)_3]Fe(CO)_3$	**2.131**	**2.111–2.152**	**1.721**	127, 128
$[\pi\text{-}C_6H_5C_4H(C_4H_4)Fe(CO)_3]Fe(CO)_3$	2.150	2.09–2.21	—	129
$[\pi,\pi\text{-}(C_6H_5)_4C_4Fe(CO)_3][Fe(CO)_3]_2$	**2.150**	**2.091–2.202**	**1.683**	130
$[\pi\text{-}(CH_3)_2C_4H_2Os(CO)_3]Os(CO)_3$	—	—	—	131

Table 6. Distances (in Å) in π-complexes of six-membered homocyclic rings.

Compound	$C(C_6H_6)$–$C(C_6H_6)$	Range	M–$C(C_6H_6)$	Range	M–(C_6H_6)	Refs.
$(\pi\text{-}C_6H_6)_2Cr$	1.416	1.415–1.416	2.142	2.140–2.143	1.607	132–138
$(\pi\text{-}C_6H_6)Cr(CO)_3$	1.401	1.371–1.421	2.221	2.216–2.230	1.724	14, 139–142
$[\pi\text{-}C_6(CH_3)_6]Cr(CO)_3$	1.417	1.370–1.461	2.233	2.211–2.253	1.726	143
$(\pi\text{-}C_{14}H_{10})Cr(CO)_3$[a]	**1.433**	**1.363–1.556**	**2.217**	**2.146–2.364**	**1.688**	144
$(\pi\text{-}C_{14}H_{10})Cr(CO)_3$[b]	1.429	1.396–1.456	2.263	2.21–2.34	—	145
$(\pi\text{-}CH_3C_6H_5)_2CrI$	[**1.42**]	[1.42]	[**2.08**]	[**2.08–2.09**]	[**1.53**]	146, 147
$(\pi\text{-}C_6H_5\text{–}C_6H_5\text{-}\pi)[Cr(CO)_3]_2$	[**1.41**]	[**1.37–1.44**]	[**2.27**]	[**2.20–2.34**]	[**1.77**]	148, 149
$(\pi\text{-}C_6H_6)_2Mo$[c]	—	—	—	—	—	150
$[(\pi\text{-}C_6H_6)PdAl_2Cl_7]_2$	[1.41]	—	[2.34]	—	—	151
$(\pi\text{-}C_6H_6)_2W$[c]	—	—	—	—	—	150

[a] Phenanthrene derivative.

[b] Anthracene derivative.

[c] Isostructural (as far as the heavy atoms are concerned) with $[(\pi\text{-}C_5H_5)]_2Ru$.