

9.6. TYPICAL INTERATOMIC DISTANCES: ORGANOMETALLIC COMPOUNDS AND COMPLEXES

Table 9.6.3.1. *Ligand index (cont.)*

Contact atom	Ligand class	Ligand class identifier
Nitrogen (<i>cont.</i>)	amidinate [RNC(R)NR]	4.11
	Schiff bases	4.12
	phthalocyanines, porphyrins, pyrroles	4.13
	pyrazolate, imidazolate and derivatives	4.14
	pyridine, polypryidyls (bpy, <i>o</i> -phen)	4.15
	pyrazines, pyridazines, pyrimidines	4.16
	other N ₂ ligands (NRNR ₂ , NNR ₂ , NRNR)	4.17
	triazenido (RNNNR)	4.18
	hydrazones and related species (NR ₂ N=CR)	4.19
	oximes	4.20
	<i>N</i> -nitrite (NO ₂)	4.21
	amine (NR ₃)	4.22
	borazines	4.23
	Oxygen	oxo (O)
hydroxy (OH)		5.2
alkoxy, aryloxy, <i>etc.</i> (OR)		5.3
<i>O</i> -ketones (OCR ₂), urea		5.4
carboxylates (O ₂ CR)		5.5
oxalate (O ₂ CCO ₂)		5.6
acetylacetonates [RC(O)CRC(O)CR]		5.7
α , β -diones (<i>e.g.</i> <i>o</i> -quinones)		5.8
carbonate (CO ₃ ²⁻)		5.9
<i>N</i> -oxides (<i>e.g.</i> pyridine <i>N</i> -oxide)		5.10
nitrate (NO ₃ ⁻)		5.11
<i>O</i> -nitrite (NO ₂ ⁻)		5.12
dioxygen, peroxides		5.13
phosphine oxides (OPR ₃)		5.14
phosphate (PO ₄ ³⁻)		5.15
other P—O anions		5.16
<i>O</i> -dialkyl sulfoxides (OSR ₂)		5.17
sulfate (SO ₄ ²⁻)		5.18
other S—O anions (sulfonates, <i>etc.</i>)		5.19
<i>O</i> -SO ₂		5.20
other oxyanions (<i>e.g.</i> ClO ₄ ⁻)		5.21
aqua		5.22
alcohols (ROH)		5.23
ethers (ROR')		5.24
miscellaneous (η^2 -acyl, η^2 -CO ₂ , μ -NCO)	5.25	
Fluorine	fluoride (F)	6.1
	fluoroanions (BF ₄ ⁻ , PF ₆ ⁻)	6.2
Silicon	miscellaneous	7.1
Phosphorus	phosphorus (P)	8.1
	phosphinidenes (PR)	8.2
	phosphides (PR ₂)	8.3
	oligo-phosphorus ligands (P ₃ , PR ₂ PR ₂ , PRPR, <i>etc.</i>)	8.4
	phosphines (PR ₃)	8.5
	diphosphines (<i>e.g.</i> diphos)	8.6
	phosphites [P(OR) ₃]	8.7
	aminophosphines, cyclotriphosphazenylyl, misc. P—N ligands	8.8
Sulfur	sulfides (S)	9.1
	thiolates (SR)	9.2

Table 9.6.3.1. *Ligand index (cont.)*

Contact atom	Ligand class	Ligand class identifier	
Sulfur (<i>cont.</i>)	<i>S</i> -thiocyanate (SCN)	9.3	
	thioketones, thiourea (S=CR ₂)	9.4	
	thiocarboxylates (S ₂ CR ⁻)	9.5	
	thiocarbamates (S ₂ CNR ₂ ⁻)	9.6	
	xanthates (S ₂ COR ⁻), dithio-carbonates	9.7	
	trithiocarbonate (CS ₃ ²⁻), thioxanthates	9.8	
	α , β -dithiones	9.9	
	phosphine sulfides	9.10	
	dithiophosphinates (S ₂ PR ₂ ⁻)	9.11	
	polysulfur ligands (S ₂ , SSR, <i>etc.</i>)	9.12	
	thioethers (SR ₂)	9.13	
	<i>S</i> -SO ₂ , <i>S</i> -SO ₃ , <i>etc.</i>	9.14	
	disulfides (RSSR)	9.15	
	<i>S</i> -dialkyl sulfoxides (R ₂ SO)	9.16	
	miscellaneous (η^2 -CS ₂)	9.17	
	Chlorine	chloride (Cl)	10.1
	Arsenic	arsines (AsR ₃)	11.1
miscellaneous		11.2	
Selenium	miscellaneous	12.1	
Bromine	bromide (Br)	13.1	
Tellurium	miscellaneous	14.1	
Iodine	iodide (I)	15.1	

number of the metal. For a given metal, the first line of an entry in Table 9.6.3.3 gives statistics covering all appropriate occurrences of metal–ligand distances. Further lines give statistics for metal–ligand distances for subdivision based largely on chemical criteria (*e.g.* metal oxidation state or coordination number). Cases where one atom of a ligand bridges two or more metal atoms were included only when the metal atoms were all of the same type and, unless specified, only when the metal–ligand distances were symmetrical (range for distances ≤ 0.1 Å).

In many instances, the number of structures having interatomic distances involving a given metal for a particular ligand is too small (< 4) for statistics to be quoted. In these cases, individual structures, and the distances in them, are given. These structures are identified by their CSD reference code (*e.g.* BOZMIN); short-form literature references, ordered alphabetically by reference code, are in Appendix 2.

Each line of Table 9.6.3.3 contains nine columns of which six record the statistics of the bond-length distribution described above. The content of the remaining three columns: Bond, Substructure, and Note, are described below.

9.6.3.1. *The 'Bond' column*

This specifies the atom pair to which the line refers. Therefore, in the case of triethylphosphine complexes (section 8.5.2), there are 18 lines, in which the bond column contains P—C, followed by 17 entries for Ti—P through to Au—P, indicating statistics for both intraligand and metal–ligand atom pairs.

9.6.3.2. *Definition of 'Substructure'*

This column provides details of any subdivision of particular metal–ligand bonds that has been applied. Thus, for terminal

9. BASIC STRUCTURAL FEATURES

iron-chlorine bonds (in section 10.1.1.1), the second and third lines of the Fe—Cl entry refer to complexes in which the iron atom is four-coordinate and in oxidation state II and III, respectively. In some cases, subdivision has been carried out

on the basis of ligand substituents in those cases where a well defined subdistribution was observed. For clarity, in a number of cases the ligand structure and numbering scheme are illustrated in Fig. 9.6.3.1. The reader will be aware that formal oxidation

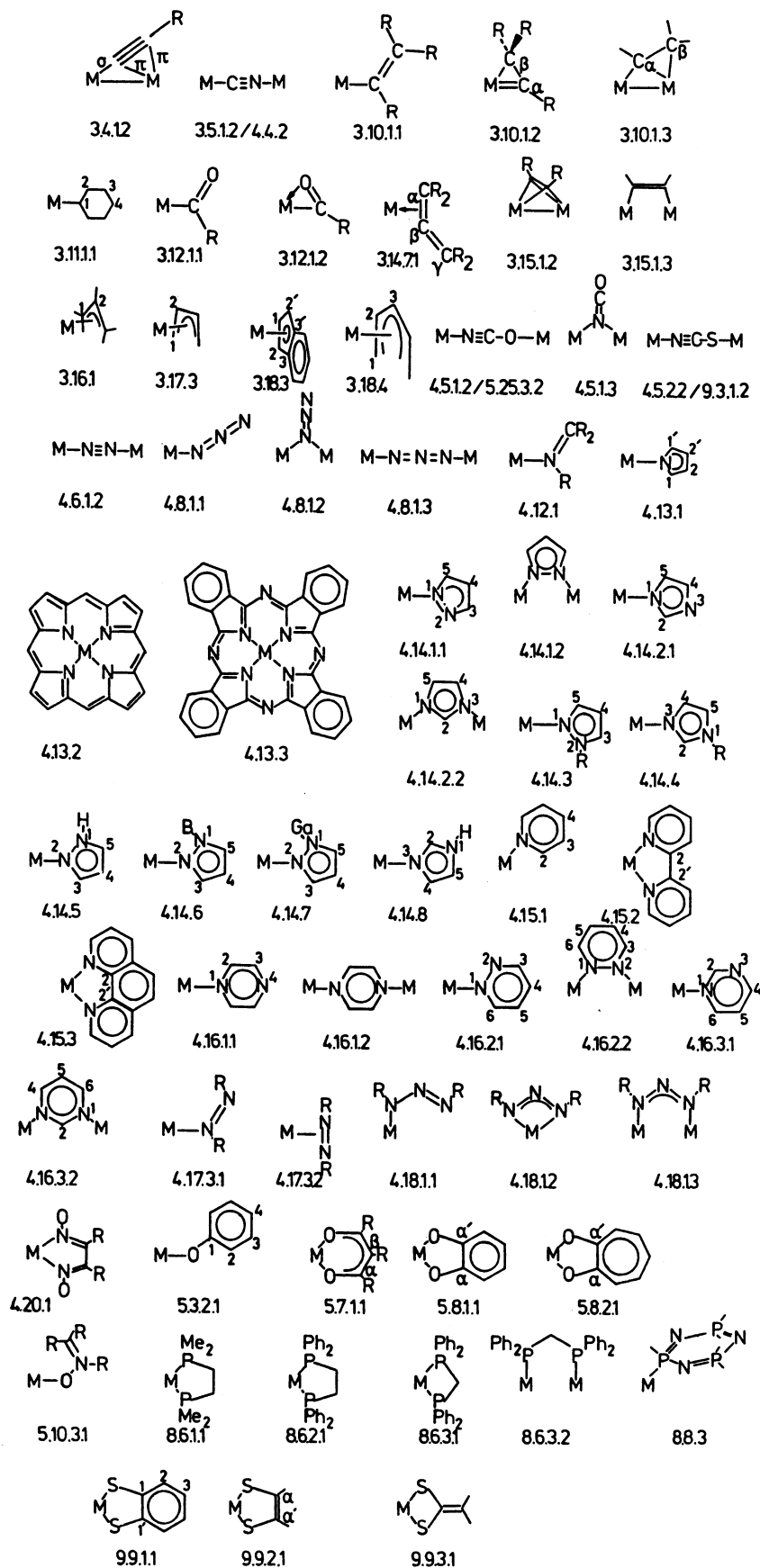


Fig. 9.6.3.1. Diagrams of ligands in Table 9.6.3.3, showing table entry number and ligand atom labelling.

9.6. TYPICAL INTERATOMIC DISTANCES: ORGANOMETALLIC COMPOUNDS AND COMPLEXES

Table 9.6.3.2. Numbers of entries in Table 9.6.3.3

Numbers of entries for which < 4 examples are known are given first, followed by numbers of entries for which statistics are quoted (*i.e.* those with > 4 examples).

		Ligand atoms														
		H	B	C	N	O	F	Si	P	S	Cl	As	Se	Br	Te	I
Ligand class	Metal *†	5	4	66	71	79	4	1	32	49	3	2	1	3	1	3
Sc ¹			1, 0	0, 1		0, 4										
Ti ^{2,3}			2, 0	6, 8	14, 5	4, 15	1, 0		1, 2	4, 3	1, 2	1, 0		1, 0		
V ^{4,5,6}			2, 0	8, 8	6, 5	10, 10	0, 1		3, 3	2, 6	0, 2	1, 0				1, 0
Cr ⁷	1, 0	1, 2	9, 15	12, 13	5, 19	0, 1		1, 0	9, 5	1, 7	1, 1	0, 2	1, 0	2, 0	1, 0	1, 0
Mn		0, 3	15, 12	14, 13	14, 10	1, 0		1, 0	5, 6	7, 4	0, 2	0, 2	1, 0	1, 1	0, 1	1, 1
Fe	0, 2	1, 2	10, 33	13, 19	14, 12		0, 1		6, 13	7, 16	0, 2	0, 2	0, 1	2, 0	0, 1	1, 1
Co ⁸	2, 0	0, 4	11, 27	5, 28	18, 22				6, 10	7, 11	1, 2	0, 2		0, 1		0, 1
Ni ^{9,10}	0, 1	2, 1	7, 20	9, 23	9, 18	1, 0			6, 8	12, 13	0, 2	1, 1	0, 1	0, 2		1, 1
Cu ^{11,12}	1, 0	3, 0	1, 11	7, 35	18, 31	3, 0			3, 3	7, 12	0, 3	0, 1	1, 0	0, 3		0, 3
Zn	1, 0	2, 0	3, 2	7, 16	14, 10					7, 3	0, 2			0, 1		0, 1
Y ¹		1, 0	0, 1		2, 6						0, 1					
Zr ¹³		1, 0	6, 8	10, 1	5, 7	0, 1		1, 1	4, 0	0, 2		1, 0				1, 0
Nb ¹⁴			4, 6	3, 5	2, 9	0, 1		2, 0	1, 6	1, 2	0, 1					
Mo ^{15,16}	1, 1	1, 0	11, 25	17, 26	7, 28	1, 1	1, 0	5, 11	3, 20	1, 2	0, 2	1, 0	0, 2	1, 0	0, 2	0, 2
Tc ^{17,18}			0, 1	5, 5	3, 5			1, 2	1, 2	1, 1	0, 1			2, 0		
Ru	0, 1	2, 1	12, 25	19, 9	11, 8		0, 1	2, 13	4, 4	0, 2	0, 2			0, 2		1, 1
Rh	2, 1	0, 2	11, 25	12, 18	11, 14		1, 0	5, 13	6, 7	0, 2	1, 1	0, 1	0, 2	0, 2		0, 2
Pd		0, 1	9, 15	14, 13	6, 6			8, 7	4, 10	1, 2	1, 1		0, 1	0, 1		1, 1
Ag		1, 0	4, 2	8, 6	8, 2	1, 0		2, 3	4, 6	2, 1		1, 0	1, 0	1, 0		1, 2
Cd ¹⁹				3, 14	12, 10			2, 0	6, 4	0, 3				1, 2		0, 1
La§				1, 1	4, 7				1, 0	1, 0						
Ce§			0, 2	0, 1	4, 4				0, 1	1, 0						
Pr§			1, 1	1, 0	2, 5					2, 0						
Nd§				2, 2	7, 5					1, 0						
Sm§			0, 1	2, 1	8, 6											
Eu§			0, 1	0, 1	3, 6											
Gd§			0, 1	1, 0	2, 4											
Tb§					1, 0											
Dy§				2, 1	1, 2					0, 1						
Ho§					0, 1											
Er§			0, 1	1, 1	4, 4					1, 0						
Tm§											0, 1					
Yb§			0, 2	2, 2	3, 2					2, 0						1, 0
Lu§			1, 2	1, 0	0, 1					0, 1						
Hf ¹³			2, 4	1, 0	2, 2			0, 2		1, 0						
Ta ²³	1, 0		5, 7	4, 1	4, 2			2, 2	2, 4	0, 2				1, 0		
W ^{24,159}	0, 2	1, 1	9, 20	10, 7	4, 12	1, 0	1, 0	4, 6	7, 5	1, 2	1, 0	1, 0	0, 1	0, 1		1, 1
Re	0, 2	0, 1	10, 13	9, 9	11, 12	1, 0	0, 1	4, 5	4, 3	0, 2	0, 1	1, 0	0, 2	0, 2		0, 2
Os	0, 2	2, 0	12, 11	9, 7	6, 6		1, 0	4, 6	3, 3	0, 2	1, 0	1, 0	1, 0	0, 1		0, 1
Ir	1, 1	1, 1	11, 12	12, 4	3, 4	1, 0	1, 0	5, 9	5, 5	0, 2		1, 0	0, 2	0, 2		0, 2
Pt	2, 0	0, 1	4, 25	11, 13	8, 10	1, 0	0, 1	6, 13	8, 11	0, 2	0, 1	1, 0	0, 2	1, 0	0, 2	0, 2
Au ²⁵		0, 1	4, 3	6, 0	4, 0			5, 3	7, 3	0, 1				0, 1		1, 0
Hg ²⁶		1, 0	8, 3	10, 5	11, 2		0, 1	3, 2	2, 6	1, 2		1, 0	0, 2	0, 1	0, 1	0, 2
Th§	1, 0		1, 2	0, 3	5, 8			1, 0	0, 1	0, 1						
U§		0, 1	1, 5	7, 5	16, 18	1, 2		1, 0	1, 1	0, 2				0, 1		

*No entries for Pm, Pa, and Ac. †Superscripts refer to entries in Appendix 1. §See references 1, 20–23 in Appendix 1.

state is not always well defined, where no assignment was possible then this is indicated by (–) rather than the roman numeral used elsewhere. Finally, cases where the ligand oxidation state is variable are identified (*e.g.* for O₂, *o*-quinones *etc.*) by references to the footnotes at the end of Table 9.6.3.3.

9.6.3.3. Use of the 'Note' column

The 'Note' column refers to the footnotes collected in Appendix 1. These record additional information as follows:

(a) notable features of the distribution of distances, *e.g.* likely bias due to dominance by one structure of substructure, skewness, bimodality (subdivisions of the entry usually follow, which remove these features whenever possible); (b) further details of the chemical substructure, such as the exclusion of structures with particular *trans* ligands; (c) details of exclusion criteria used for a given entry or group of entries, such as the constraint that the two *M*–Cl distances, in bridging (μ_2) chloride complexes, differ by <0.1 Å (section 10.1.1.2); (d)