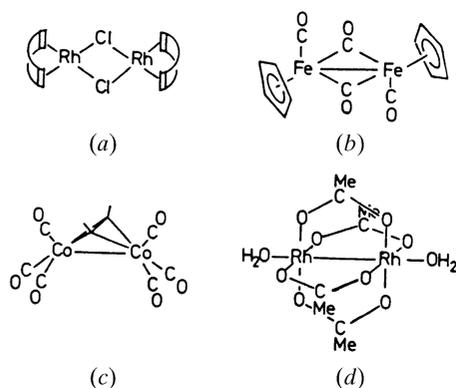


## 9.6. TYPICAL INTERATOMIC DISTANCES: ORGANOMETALLIC COMPOUNDS AND COMPLEXES

## 9.6.2.2. Program system

All calculations were performed on a University of Bristol VAX 11/750 computer. Programs *BIBSER*, *CONNSEER*, *RETRIEVE* (Allen *et al.*, 1979) and *GEOSTAT* (Murray-Rust & Raftery, 1985*a,b*), as locally modified, were used. A stand-alone program was written to implement the selection criteria, whilst a new program (*STATS*) was used for statistical calculations described below. It was also necessary to modify *CONNSEER* to improve the precision with which it locates chemical substructures. In particular, the program was altered to permit the location of atoms with specified coordination numbers. This was essential in the case of carbon so that atoms with coordination numbers 2, 3, and 4 (equivalent to formal hybridization state  $sp^1$ ,  $sp^2$ ,  $sp^3$ ) could be distinguished easily and reliably. Considerable care was taken to ensure that the correct molecular fragment was located by *GEOSTAT* in the generation of geometrical tabulations. Searches were conducted for all metals together and statistics for individual metal elements and subdivision of the entry for a given metal carried out subsequently. An important modification to *GEOSTAT* allowed for calculation of metal-atom coordination number with due allowance for multihapto ligands and  $\mu_2$  ligands. Thus,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>,  $\eta^6$ -C<sub>6</sub>H<sub>6</sub>, and other  $\eta^5$  and  $\eta^6$  ligands were assigned to occupy 3 coordination sites,  $\eta^3$  and  $\eta^4$  ligands such as allyls and dienes to occupy 2 coordination sites, and  $\eta^2$  ligands such as alkenes 1 site, and so on. The approach taken in dealing with ( $\mu_2$ ) bridging ligands was that when a metal-metal bond is bridged by one atom of a ligand [*e.g.* as in Cl, CO, OMe *etc.* as in (a), (b) below] then only the non-metal atom is counted as occupying a coordination site. For the relatively rare case of bridging polyhapto ligands (in which the bridging atoms are linked by direct bonds), the assignment follows logically, thus,  $\mu_2$ - $\eta^2$ ,  $\eta^2$ -alkyne, see (c) below, occupies one site on each metal. Bridging ligands that do not have one atom bonded to both metals [*e.g.* acetate in (d) below] contribute to metal coordination numbers as do terminal ligands. In examples (a)–(d) below, the metal atoms therefore have coordination numbers as follows: (a), Rh 4; (b), Fe 6; (c), Co 4; (d), Rh 6. For cases where coordination number is very difficult to assign, notably where a metal atom is bonded to more than one other metal atom as in metal cluster complexes, no assignment was attempted.



The non-location of hydrogen atoms presents major difficulties, both in the determination of coordination numbers for metal atoms, and for correct identification of ligands (*e.g.* to distinguish methoxide from methanol). Care was therefore taken to exclude cases where any ambiguity existed [*e.g.* no data taken for  $M$ –(OCH<sub>3</sub>) and  $M$ –O(H)CH<sub>3</sub> distances when both are present in a structure in which hydrogen-atom positions were not reported].

## 9.6.2.3. Classification of bonds

The classification of metal–ligand bonds in Table 9.6.3.3 is based on the ligating contacting atom. Thus, all metal–boron distances appear in sections 2.1–2.3 of Table 9.6.3.3, all metal–carbon distances in sections 3.1–3.22, and so on. Where intra-ligand interatomic distances (*e.g.* P–C distances in tertiary phosphines) are given in Table 9.6.3.3, they are averaged over all metals and precede the individual metal–ligand interatomic distances for that ligand.

Table 9.6.3.3 is designated: (i) to appear logical, useful, and reasonably self-explanatory to chemists, crystallographers, and others who may use it; (ii) to permit a meaningful average value to be cited for each bond length. With reference to (ii), it was considered that a sample of bond lengths could be averaged meaningfully if: (a) the sample was unimodally distributed; (b) the sample standard deviation ( $\sigma$ ) was reasonably small, ideally less than *ca* 0.04 Å; (c) there were no conspicuous outlying observations – those that occurred at  $> 4\sigma$  from the mean were automatically eliminated from the sample by *STATS*, other outliers were inspected carefully; (d) there were no compelling chemical reasons for further subdivision of the sample. It should be noted that Table 9.6.3.3 is not intended to be complete in covering all possible ligands. The purpose of the table is to provide information on the interatomic distances for ligands of the greatest *chemical* importance, notably for those that are simple and/or common.

## 9.6.2.4. Statistics

Where there are less than four independent observations of a given bond length, then each individual observation is given explicitly in Table 9.6.3.3. In all other cases, the following statistics were generated by the program *STATS*.

(i) The unweighted sample mean,  $d$ , where

$$d = \sum_{i=1}^n d_i/n$$

and  $d_i$  is the  $i$ th observation of the bond length in a total sample of  $n$  observations. Recent work (Taylor & Kennard, 1983, 1985, 1986) has shown that the unweighted mean is an acceptable (even preferable) alternative to the weighted mean, where the  $i$ th observation is assigned a weight equal to  $1/\text{var}(d_i)$ . This is especially true where structures have been pre-screened on the basis of precision.

(ii) The sample median,  $m$ . This has the property that half of the observations in the sample exceed  $m$ , and half fall short of it.

(iii) The sample standard deviation,  $\sigma$ , where

$$\sigma = \left[ \sum_{i=1}^n (d_i - d)^2 / (n - 1) \right]^{1/2}.$$

(iv) The lower quartile for the sample,  $q_l$ . This has the property that 25% of the observations are less than  $q_l$  and 75% exceed it.

(v) The upper quartile for the sample,  $q_u$ . This has the property that 25% of the observations exceed  $q_u$  and 75% fall short of it.

(vi) The number ( $n$ ) of observations in the sample.

The statistics given in Table 9.6.3.3 correspond to distributions for which the automatic  $4\sigma$  cut-off (see above) had been applied, and any manual removal of additional outliers (an infrequent operation) had been performed. In practice, a very small percentage of observations were excluded by these methods. The major effect of removing outliers is to improve