

Similar MO treatments are possible for tetrahedral and square planar complexes but are increasingly complicated.

## 19.7 Organometallic Compounds

This section gives a brief overview of the vast and burgeoning field of organometallic chemistry. The term *organometallic* is somewhat vague since definitions of *organo* and *metallic* are themselves necessarily imprecise. We use the term to refer to compounds that involve at least one close M–C interaction: this includes metal complexes with ligands such as CO, CO<sub>2</sub>, CS<sub>2</sub> and CN<sup>−</sup> but excludes “ionic” compounds such as NaCN or Na acetate; it also excludes metal alkoxides M(OR)<sub>n</sub> and metal complexes with organic ligands such as C<sub>5</sub>H<sub>5</sub>N, PPh<sub>3</sub>, OEt<sub>2</sub>, SMe<sub>2</sub>, etc., where the donor atom is not carbon. A permissive view is often taken in the literature of what constitutes a “metal” and the elements B; Si, Ge; As, Sb; Se and Te are frequently included for convenience and to give added perspective. However, it is not helpful to include as metals all elements less electronegative than C since this includes I, S and P. Metal carbides (p. 297) and graphite intercalation compounds (p. 293) are also normally excluded. Further treatment of organometallic compounds will be found throughout the book under each individual element.

No area of chemistry produces more surprises and challenges and the whole field of organometallic chemistry continues to be one of great excitement and activity. A rich harvest of new and previously undreamed of structure types is reaped each year, the rewards of elegant and skilful synthetic programmes being supplemented by an unusual number of chance discoveries and totally unsuspected reactions. Synthetic chemists can take either a buccaneering or an intellectual approach (or both); structural chemists are able to press their various techniques to the limit in elucidating the products formed; theoretical chemists and reaction kineticists, though badly

outpaced in predictive work, provide an invaluable underlying rationale for various aspects of the continually evolving field and just occasionally run ahead of the experimentalists; industrial chemists can exploit and extend the results by developing numerous catalytic processes of immense importance. The field is not new, but was transformed in 1952 by the recognition of the “sandwich” structure of dicyclopentadienyliron (ferrocene).<sup>(22,23)</sup> Compendia and extended reviews<sup>(24–27)</sup> are available on various aspects, and continued progress is summarized in annual volumes.<sup>(28,29)</sup>

The various classes of ligands and attached groups that occur in organometallic compounds are summarized in Table 19.2, and these will be briefly discussed in the following paragraphs. Aspects which concern the general chemistry of carbon will be emphasized in order to give coherence and added significance to the more detailed treatment of the organometallic chemistry of individual elements given in other sections, e.g. Li (p. 102), Be (p. 127), Mg (p. 131), etc.

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<sup>22</sup> G. WILKINSON, M. ROSENBLUM, M. C. WHITING and R. B. WOODWARD, *J. Am. Chem. Soc.* **74**, 2125–6 (1952). For some personal recollections on the events leading up to this paper, see G. WILKINSON, *J. Organometallic Chem.* **100**, 273–8 (1975).

<sup>23</sup> J. S. THAYER, *Adv. Organometallic Chem.* **13**, 1–49 (1975).

<sup>24</sup> G. WILKINSON, F. G. A. STONE and E. W. ABEL (eds.), *Comprehensive Organometallic Chemistry*, 9 Vols., Pergamon Press, Oxford, 1982, 9569 pp. E. W. ABEL, F. G. A. STONE and G. WILKINSON (eds.), *Comprehensive Organometallic Chemistry II*, 14 Vols, Pergamon Press, Oxford, 1995, approx. 8750 pp.

<sup>25</sup> F. A. COTTON and G. WILKINSON, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988, particularly Chaps. 22–29, pp. 1021–334.

<sup>26</sup> *Dictionary of Organometallic Compounds*, Chapman and Hall, London, Vols. 1–3, (1984), J. BUCKINGHAM (ed.); Supplement 1 (1985)–Supplement 5 (1989), Index (1990), J. F. MACINTYRE (ed).

<sup>27</sup> *The Chemistry of the Metal–Carbon Bond*, Wiley, Chichester, Vols. 1–3 (1985), F. R. HARTLEY and S. PATAI (eds.); Vol. 4 (1987), Vol. 5 (1989), F. R. HARTLEY (ed.).

<sup>28</sup> F. G. A. STONE and R. WEST (eds.), *Advances in Organometallic Chemistry*, Academic Press, New York, Vol. 1 (1964)–Vol. 40 (1996).

<sup>29</sup> *Organometallic Chemistry Reactions*, Wiley, Vol. 1, (1967)–Vol. 12 (1981).

**Table 19.2** Classification of organometallic ligands according to the number of attached C atoms<sup>(a)</sup>

Number	Examples
$\eta^1$ , monohapto	Alkyl ( $-\text{R}$ ), aryl ( $-\text{Ar}$ ), perfluoro ( $-\text{R}_f$ ), acyl ( $-\text{CR}$ ), $\sigma$ -allyl ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ), $\sigma$ -ethynyl ( $-\text{C}\equiv\text{CR}$ ), CO, CO <sub>2</sub> , CS <sub>2</sub> , CN <sup>-</sup> , isocyanide (RNC), <div style="text-align: center;"> <math>\begin{array}{c} \text{O} \\    \\ \text{C} \end{array}</math> </div> carbene ( $=\text{CR}_2$ , $=\text{C}\begin{array}{l} \text{OR}' \\ \text{R} \end{array}$ , $=\text{C}\begin{array}{l} \text{OR} \\ \text{NHAr} \end{array}$ , $=\text{C}_{\text{cyclo}}$ , etc.) carbyne ( $\equiv\text{CR}$ , $\equiv\text{CAr}$ ), carbido (C)
$\eta^2$ , dihapto	Alkene ( $\text{>C}=\text{C}<$ ), perfluoroalkene (e.g. C <sub>2</sub> F <sub>4</sub> ), alkyne ( $-\text{C}\equiv\text{C}-$ ), etc. [non-conjugated dienes are bis-dihapto]
$\eta^3$ , trihapto	$\pi$ -Allyl ( $\text{>C}-\text{C}-\text{C}<$ )
$\eta^4$ , tetrahapto	Conjugated diene (e.g. butadiene), cyclobutadiene derivatives
$\eta^5$ , pentahapto	Dieryl (e.g. cyclopentadienyl derivatives, cycloheptadienyl derivatives)
$\eta^6$ , hexahapto	Arene (e.g. benzene, substituted benzenes) cycloheptatriene, cycloocta-1,3,5-triene
$\eta^7$ , heptahapto	Tropylium (cycloheptatrienyl)
$\eta^8$ , octahapto	Cyclooctatetraene

<sup>(a)</sup>Many ligands can bond in more than one way: e.g. allyl can be  $\eta^1$  ( $\sigma$ -allyl) or  $\eta^3$  ( $\pi$ -allyl); cyclooctatetraene can be  $\eta^4$  (1,3-diene),  $\eta^4$  (chelating, 1,5-diene),  $\eta^6$  (1,3,5-triene),  $\eta^6$  (bis-1,2,3,-5,6,7- $\pi$ -allyl),  $\eta^8$  (1,3,5,7-tetraene), etc.

### 19.7.1 Monohapto ligands

Alkyl and aryl derivatives of many main-group metals have already been discussed in previous chapters, and compounds such as PbMe<sub>4</sub> and PbEt<sub>4</sub> are made on a huge scale, larger than all other organometallics put together (p. 371). The alkyl and aryl groups are usually regarded as 1-electron donors but it is important to remember that even a monohapto 1-electron donor can bond simultaneously to more than 1 metal atom, e.g. to 2 in Al<sub>2</sub>Me<sub>6</sub> (p. 259), 3 in Li<sub>4</sub>Bu<sub>4</sub>' (p. 105) and 4 in [Li<sub>4</sub>Me<sub>4</sub>]<sub>n</sub>. Similarly, an  $\eta^1$  ligand such as CO, which is often regarded as a 2-electron donor, can bond simultaneously to either 1, 2 or 3 metal atoms (p. 928). There is thus an important distinction to be drawn between (a) hapticity (the number of C atoms in the organic group that are closely associated with a metal atom), (b) metal connectivity (the number of M atoms simultaneously bonded to the organic group), and (c) the number of ligand electrons formally involved in bonding to the metal atom(s). The

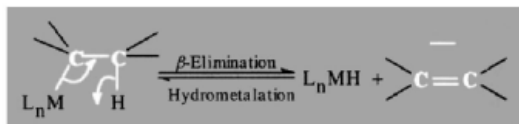
metal connectivity is also to be distinguished from the coordination number of the C atom, which also includes all other atoms or groups attached to it: e.g. the bridging C atoms in Al<sub>2</sub>Me<sub>6</sub> are monohapto with a metal connectivity of 2 and a coordination number of 5.

Although zinc alkyls were first described by E. Frankland in 1849 and the alkyls and aryls of most main group elements had been prepared and often extensively studied during the subsequent 100 y, very few such compounds were known for the transition metals even as recently as the late 1960s. The great burst of more recent activity stems from the independent suggestion<sup>(30,31)</sup> that M-C bonds involving transition elements are not inherently weak and that kinetically stable complexes can be made by a suitable choice of organic groups. In particular, the use of groups which have no  $\beta$ -hydrogen atom (e.g.  $-\text{CH}_2\text{Ph}$ ,

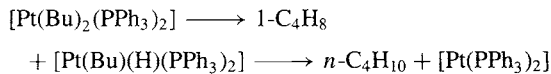
<sup>30</sup> M. R. COLLIER, M. F. LAPPERT and M. M. TRUELOCK, *J. Organometallic Chem.* **25**, C36-8 (1970).

<sup>31</sup> G. YAGUPSKY, W. MOWAT, A. SHORTLAND and G. WILKINSON, *J. Chem. Soc., Chem. Commun.*, 1369-71 (1970).

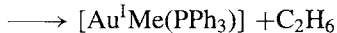
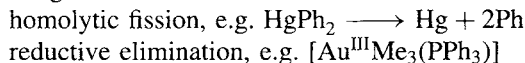
$-\text{CH}_2\text{CMe}_3$ , or  $-\text{CH}_2\text{SiMe}_3$ ) often leads to stable complexes since this prevents at least one facile decomposition route namely  $\beta$ -elimination.



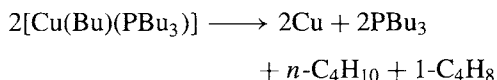
The reverse reaction (formation of metal alkyls by addition of alkenes to  $\text{M}-\text{H}$ ) is the basis of several important catalytic reactions such as alkene hydrogenation, hydroformylation, hydroboration, and isomerization. A good example of decomposition by  $\beta$ -elimination is the first-order intramolecular reaction:



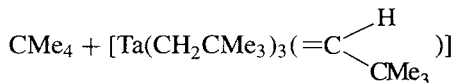
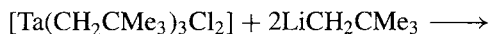
$\beta$ -Elimination reactions have been much studied but should not be over emphasized since other decomposition routes must also be considered. Amongst these are:



binuclear elimination (or formation of Bu radicals) e.g.



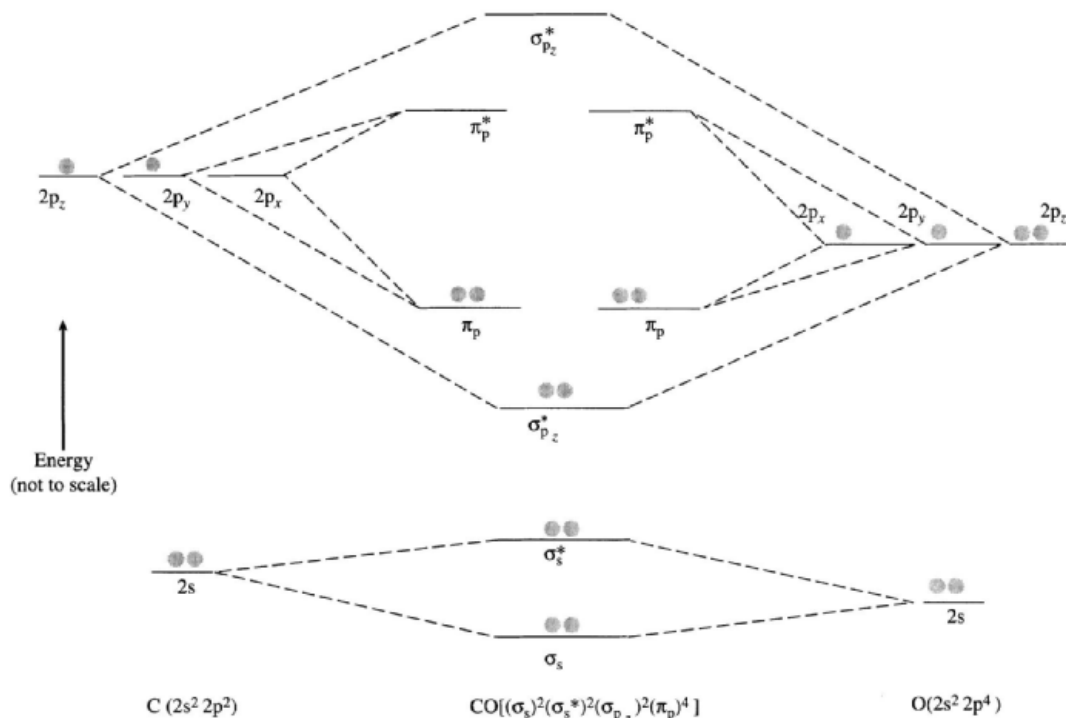
$\alpha$ -Elimination to give a carbene complex, e.g.



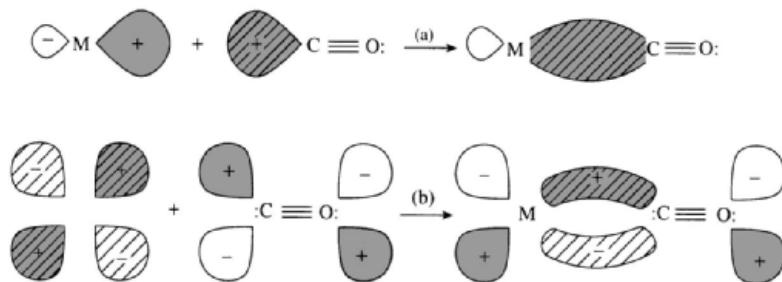
Stabilization of  $\eta^1$ -alkyl and -aryl derivatives of transition metals can be enhanced by the judicious inclusion of various other stabilizing ligands in the complex, even though such ligands are known not to be an essential prerequisite. Particularly efficacious are potential  $\pi$  acceptors (see below) such as  $\text{AsPh}_3$ ,  $\text{PPh}_3$ ,

$\text{CO}$  or  $\eta^5\text{-C}_5\text{H}_5$  in combination with the heavier transition metals since the firm occupation of coordination sites prevents their use for concerted decomposition routes. Steric protection may also be implicated. Similar arguments have been used to interpret the observed increase in stability of  $\eta^1$  complexes in the sequence alkyl < aryl < *o*-substituted aryl < ethynyl ( $-\text{C}\equiv\text{CH}$ ).

The next group of  $\eta^1$  ligands comprise the isoelectronic species,  $\text{CO}$ ,  $\text{CN}^-$  and  $\text{RNC}$ . They are closely related to other 14-electron (10 valence electron) ligands such as  $\text{N}_2$  and  $\text{NO}^+$  (and also to tertiary phosphines and arsines, and to organic sulfides, selenides, etc.), and it is merely the presence of C as the donor atom which classifies their complexes as organometallics. All have characteristic donor properties that distinguish them from simple electron-pair donors (Lewis bases, p. 198) and these have been successfully interpreted in terms of a synergic or mutually reinforcing interaction between  $\sigma$  donation from ligand to metal and  $\pi$  back donation from metal to ligand as elaborated below.  $\text{CO}$  is undoubtedly the most important and most widely studied of all organometallic ligands and it is the prototype for this group of so-called  $\pi$ -acceptor ligands. The currently accepted view of the bonding is represented diagrammatically in Figs. 19.17 and 19.18. Figure 19.17 shows a schematic molecular orbital energy level diagram for the heteronuclear diatomic molecule  $\text{CO}$ . The AOs lie deeper in O than in C because of the higher effective nuclear charge on O; consequently O contributes more to bonding MOs and C contributes more to the antibonding MOs. It can be seen that all the bonding MOs are filled and, in this description, the  $\text{CO}$  molecule can be said to have a triple bond  $:\text{C}\equiv\text{O}:$  with the lone-pair on carbon weakly available for donation to an acceptor. The top part (a) of Fig. 19.18 shows the formation of a  $\sigma$  bond by donation of the lone-pair into a suitably directed hybrid orbital on M, and the lower part (b) shows the accompanying back donation from a filled metal d orbital into the vacant antibonding  $\text{CO}$  orbital having  $\pi$  symmetry (one node) with respect to the bonding axis. This



**Figure 19.17** Schematic molecular energy level diagram for CO. The 1s orbitals have been omitted as they contribute nothing to the bonding. A more sophisticated treatment would allow some mixing of the 2s and  $2p_z$  orbitals in the bonding direction (z) as implied by the orbital diagram in Fig. 19.18.



**Figure 19.18** Schematic representation of the orbital overlaps leading to M–CO bonding: (a)  $\sigma$  overlap and donation from the lone-pair on C into a vacant (hybrid) metal orbital to form a  $\sigma$  M←C bond, and (b)  $\pi$  overlap and the donation from a filled  $d_{xz}$  or  $d_{yz}$  orbital on M into a vacant antibonding  $\pi_p^*$  orbital on CO to form a  $\pi$  M→C bond.

at once interprets why CO, which is a very weak  $\sigma$  donor to Lewis acids such as  $BF_3$  and  $AlCl_3$ , forms such strong complexes with transition elements, since the drift of  $\pi$ -electron density from M to C tends to make the

ligand more negative and so enhances its  $\sigma$ -donor power. The pre-existing negative charge on  $CN^-$  increases its  $\sigma$ -donor propensity but weakens its effectiveness as a  $\pi$  acceptor. It is thus possible to rationalize many chemical

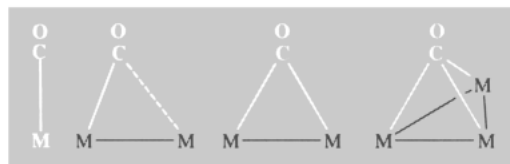
**Table 19.3** Known neutral binary metal carbonyls. Osmium also forms  $\text{Os}_5(\text{CO})_{16}$ ,  $\text{Os}_5(\text{CO})_{19}$ ,  $\text{Os}_6(\text{CO})_{18}$ ,  $\text{Os}_6(\text{CO})_{20}$ ,  $\text{Os}_7(\text{CO})_{21}$  and  $\text{Os}_8(\text{CO})_{23}$ . Carbonyls of elements in the shaded area are either very unstable or anionic or require additional ligands besides CO for stabilization

3	4	5	6	7	8	9	10	11	12
	Ti	$\text{V}(\text{CO})_6$	$\text{Cr}(\text{CO})_6$	$\text{Mn}_2(\text{CO})_{10}$	$\text{Fe}(\text{CO})_5$ $\text{Fe}_2(\text{CO})_9$ $\text{Fe}_3(\text{CO})_{12}$	$\text{Co}_2(\text{CO})_8$ $\text{Co}_4(\text{CO})_{12}$ $\text{Co}_6(\text{CO})_{16}$	$\text{Ni}(\text{CO})_4$	Cu	
	Zr	Nb	$\text{Mo}(\text{CO})_6$	$\text{Tc}_2(\text{CO})_{10}$ $\text{Tc}_3(\text{CO})_{12}$	$\text{Ru}(\text{CO})_5$ $\text{Ru}_2(\text{CO})_9$ $\text{Ru}_3(\text{CO})_{12}$	$\text{Rh}_2(\text{CO})_8$ $\text{Rh}_4(\text{CO})_{12}$ $\text{Rh}_6(\text{CO})_{16}$	Pd	Ag	
	Hf	Ta	$\text{W}(\text{CO})_6$	$\text{Re}_2(\text{CO})_{10}$	$\text{Os}(\text{CO})_5$ $\text{Os}_2(\text{CO})_9$ $\text{Os}_3(\text{CO})_{12}$	$\text{Ir}_2(\text{CO})_8$ $\text{Ir}_4(\text{CO})_{12}$ $\text{Ir}_6(\text{CO})_{16}$	Pt	Au	

observations by noting that effectiveness as a  $\sigma$  donor decreases in the sequence  $\text{CN}^- > \text{RNC} > \text{NO}^+ \sim \text{CO}$  whereas effectiveness as a  $\pi$  acceptor follows the reverse sequence  $\text{NO}^+ > \text{CO} \gg \text{RNC} > \text{CN}^-$ . By implication, back donation into antibonding CO orbitals weakens the CO bond and this is manifest in the slight increase in interatomic distance from 112.8 pm in free CO to  $\sim 115$  pm in many complexes. There is also a decrease in the C–O force constant, and the drop in the infrared stretching frequency from  $2143 \text{ cm}^{-1}$  in free CO to  $2125\text{--}1850 \text{ cm}^{-1}$  for terminal COs in neutral carbonyls has been interpreted in the same way.

The occurrence of stable neutral binary carbonyls is restricted to the central area of the d block (Table 19.3), where there are low-lying vacant metal orbitals to accept  $\sigma$ -donated lone-pairs and also filled d orbitals for  $\pi$  back donation. Outside this area carbonyls are either very unstable (e.g. Cu, Ag, p. 1199), or anionic, or require additional ligands besides CO for stabilization. As with boranes and carboranes (p. 181), CO can be replaced by isoelectronic equivalents such as  $2e^-$ ,  $\text{H}^-$ ,  $2\text{H}^+$  or L. Mean bond dissociation energies  $\bar{D}(\text{M}–\text{CO})/\text{kJ mol}^{-1}$  increase in the sequence  $\text{Cr}(\text{CO})_6$  109,  $\text{Mo}(\text{CO})_6$  151,  $\text{W}(\text{CO})_6$  176, and in the sequence  $\text{Mn}_2(\text{CO})_{10}$  100,  $\text{Fe}(\text{CO})_5$  121,  $\text{Co}_2(\text{CO})_8$  138,  $\text{Ni}(\text{CO})_4$  147.

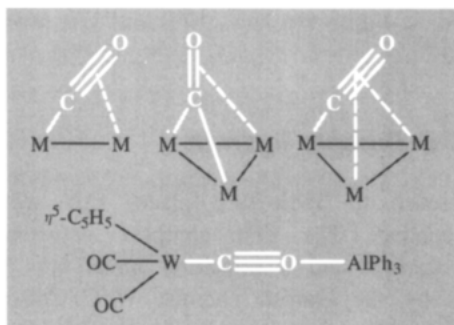
CO can act as a terminal ligand, as an unsymmetrical or symmetrical bridging ligand ( $\mu_2$ -CO) or as a triply bridging ligand ( $\mu_3$ -CO):



In all these cases CO is  $\eta^1$  but the connectivity to metal increases from 1 to 3. It is notable that in the  $\mu_2$ -bridging carbonyls the angle  $\text{M}–\text{C}(\text{O})–\text{M}$  is usually very acute ( $77\text{--}80^\circ$ ), whereas in organic carbonyls the  $\text{C}–\text{C}(\text{O})–\text{C}$  angle is typically  $120\text{--}124^\circ$ . This suggests a fundamentally differing bonding mode in the two cases and points to the likelihood of a 2-electron 3-centre bond (p. 158) for the bridging metal carbonyls. The hapticity can also rise, and structural determinations indicate that one or both of the  $\pi^*$  orbitals in CO contribute to  $\eta^2$  bonding to 1 or 2 M atoms.<sup>(32)</sup> A bis- $\eta^1$ -bridging mode has also been detected in an  $\text{AlPh}_3$  adduct,<sup>(33)</sup> reminiscent of the bridging mode in the isoelectronic  $\text{CN}^-$  ligand (p. 322):

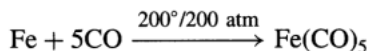
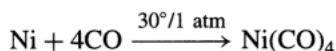
<sup>32</sup> C. P. HORWITZ and D. F. SHRIVER, *Adv. Organometallic Chem.* **23**, 219–305 (1984).

<sup>33</sup> J. M. BURLICH, M. E. LEONOWICZ, R. B. PETERSEN and R. E. HUGHES, *Inorg. Chem.* **18**, 1097–105 (1979).

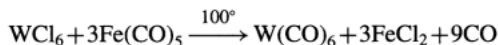
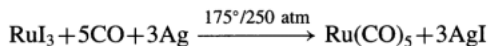
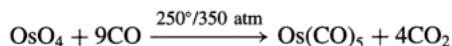


Numerous examples of metal carbonyls will be found in later chapters dealing with the chemistry of the individual transition metals. CO also has an unrivalled capacity for stabilizing metal clusters and for inserting into M–C bonds (p. 309). Synthetic routes include:

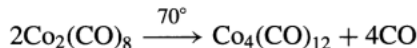
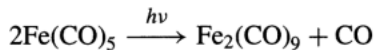
(a) direct reaction, e.g.:



(b) reductive carbonylation, e.g.:



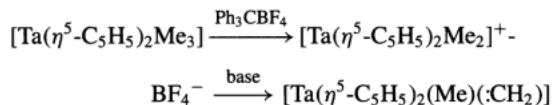
(c) photolysis or thermolysis, e.g.:



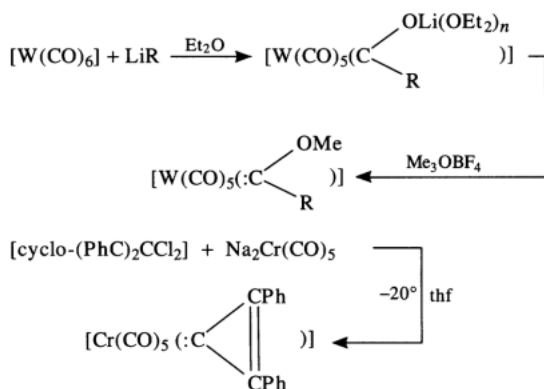
The remaining classes of monohapto organic ligands listed in Table 19.2 are carbene ( $=\text{CR}_2$ ), carbyne ( $\equiv\text{CR}$ ), and carbido (C). Stable carbene complexes were first reported in 1964 by E. O. Fischer and A. Maasböl.<sup>(34)</sup> Initially they

were of the type  $[\text{W}(\text{CO})_5(\text{C}(\text{OMe})\text{R})]$ , and it was

not until 1968 that the first homonuclear carbene complex was reported  $[\text{Cr}(\text{CO})_5(\text{C}(\text{CPh})_2)]$ ; isolation of a carbene containing the parent methylene group  $:\text{CH}_2$  was not achieved until 1975.<sup>(35)</sup>



Other preparative routes are:



The metal is in the formal oxidation state zero. As expected, the M–C bonds are somewhat shorter than M–R bonds to alkyls, but they are noticeably longer than M–CO bonds suggesting only limited double-bond character  $\text{M}=\text{C}$ , e.g.:

in $[\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{Me})(\text{CH}_2)]$	Ta–CH <sub>2</sub> 220.6 pm
	Ta–CH <sub>3</sub> 225 pm
in $[\text{W}(\text{CO})_5(\text{C}(\text{OMe})\text{Ph})]$	W–C(OMe)Ph 205 pm
	W–CO 189 pm
in $[\text{Cr}(\text{CO})_4(\text{C}(\text{OMe})\text{Me})(\text{PPh}_3)]$	Cr–C(OMe)Me 204 pm
	Cr–CO 186 pm

Carbene complexes are highly reactive species.<sup>(36)</sup>

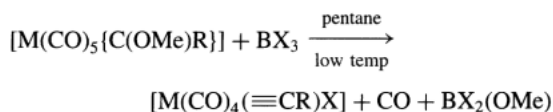
Carbyne complexes were first made in 1973 by the unexpected reaction of methoxycarbene

<sup>35</sup> R. R. SCHROCK, *J. Am. Chem. Soc.* **97**, 6577–8 (1975); L. J. GUGGENBERGER and R. R. SCHROCK, *ibid.* 6578–9.

<sup>36</sup> K. H. DÖTZ, H. FISCHER, P. HOFMANN, F. R. KREISSL, U. SCHUBERT and K. WEISS, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983, 264 pp.

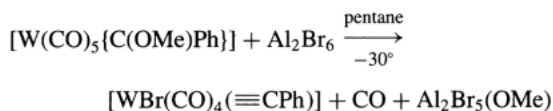
<sup>34</sup> E. O. FISCHER, *Adv. Organometallic Chem.* **14**, 1–32 (1976).

complexes with boron trihalides:



M = Cr, Mo, W; R = Me, Et, Ph; X = Cl, Br, I

Several other routes are now also available in which  $\text{BX}_3$  is replaced by  $\text{AlCl}_3$ ,  $\text{GaCl}_3$ ,  $\text{Al}_2\text{Br}_6$ ,  $\text{Ph}_3\text{PBr}_2$ , e.g.:



X-ray studies reveal the expected short M–CR distance, but the bond angle at the carbyne C atom is not always linear. Some structural data are annexed, see below. A compound which features all three types of  $\eta^1$  ligand, alkyl, alkylidene and alkylidyne, is the red, square-pyramidal tungsten(VI) complex  $[\text{W}(\equiv\text{CCMe}_3)(=\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]$  in which the W–C distance is 226 pm to neopentyl, 194 pm to neopentylidene, and 176 pm to the apical neopentylidyne ligand; the corresponding

W–C–C angles are  $125^\circ$ ,  $150^\circ$  and  $175^\circ$  respectively.<sup>(37)</sup>

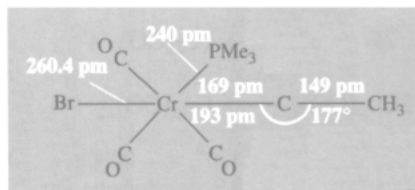
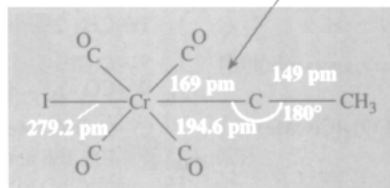
### 19.7.2 Dihapto ligands

Reference to Table 19.2 places this section in context. The first complex between a hydrocarbon and a transition metal was isolated by the Danish chemist W. C. Zeise in 1825 and in the following years he characterized the pale-yellow compound now formulated as  $\text{K}[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$ .<sup>†</sup> Zeise's salt, and a few closely related complexes such as the chloro-bridged binuclear compound  $[\text{Pt}_2(\eta^2\text{-C}_2\text{H}_4)(\mu_2\text{-Cl})_2\text{Cl}_2]$ , remained as chemical curiosities and a considerable theoretical embarrassment for over 100 y but are now seen as the archetypes of a large family of complexes based on the bonding of unsaturated organic

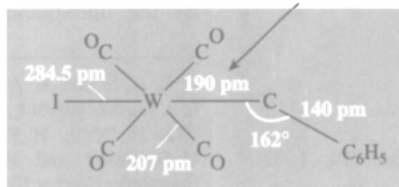
<sup>37</sup> M. R. CHURCHILL and W. J. YOUNGS, *Inorg. Chem.* **18**, 2454–8 (1979).

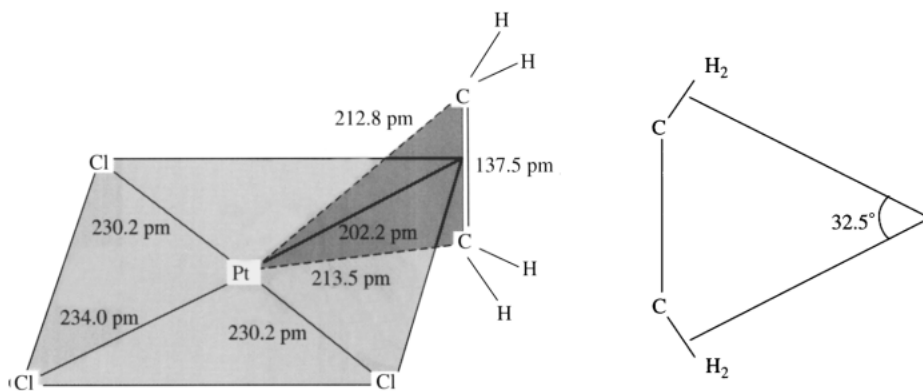
<sup>†</sup> The original reaction was obscure: Zeise heated a mixture of  $\text{PtCl}_2$  and  $\text{PtCl}_4$  in EtOH under reflux and then treated the resulting black solid with aqueous KCl and HCl to give ultimately the cream-yellow product. Subsequently the compound was isolated by direct reaction of  $\text{C}_2\text{H}_4$  with  $\text{K}_2[\text{PtCl}_4]$  in aqueous HCl.

This is the shortest known Cr–C distance cf. 217–222 pm in Cr–C single bonds and 191 pm in  $\text{Cr}(\text{CO})_6$



Cf. 227–232 pm for W–C single bond and 206 pm in  $\text{W}(\text{CO})_6$





**Figure 19.19** Structure of the anion of Zeise's salt,  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_2)\text{Cl}_3]^-$ ; standard deviations are Pt–Cl 0.2 pm, Pt–C 0.3 pm, and C–C 0.4 pm.

molecules to transition metals. The structure of the anion of Zeise's salt has been extensively studied and neutron diffraction data<sup>(38)</sup> are in Fig. 19.19. Significant features are (a) the C=C bond is perpendicular to the PtCl<sub>3</sub> plane and is only 3.8 pm longer than in free C<sub>2</sub>H<sub>4</sub>, (b) the C<sub>2</sub>H<sub>4</sub> group is significantly distorted from planarity, each C being 16.4 pm from the plane of 4H, (c) the angle between the normals to the CH<sub>2</sub> planes is 32.5°, and (d) there is an unambiguous *trans*-effect (p. 1163), i.e. the Pt–Cl distance *trans* to C<sub>2</sub>H<sub>4</sub> is longer than the 2 *cis*-Pt–Cl distances by 3.8 pm (19 standard deviations).

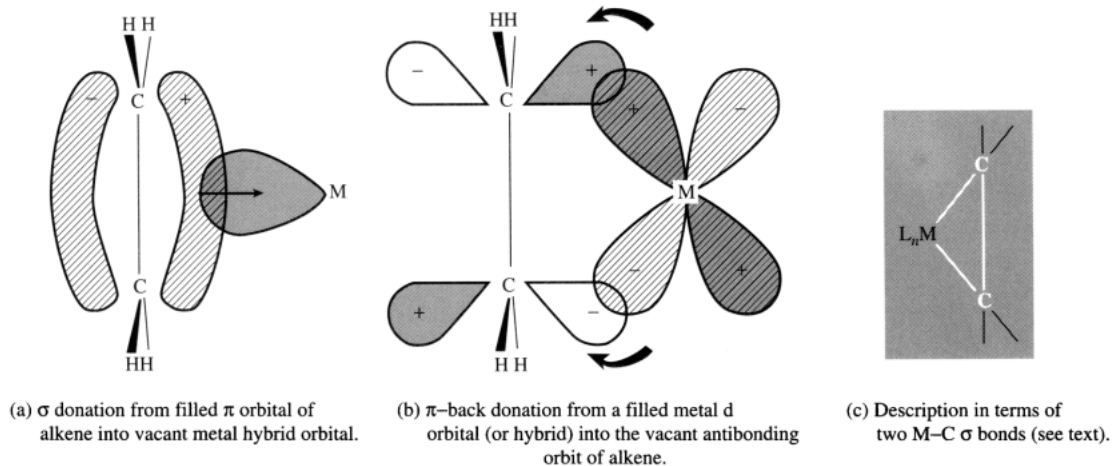
The key to our present understanding of the bonding in Zeise's salt and all other alkene complexes stems from the perceptive suggestion by M. J. S. Dewar in 1951 that the bonding involves electron donation from the  $\pi$  bond of the alkene into a vacant metal orbital of  $\sigma$  symmetry; this idea was modified and elaborated by J. Chatt and L. A. Duncanson in a seminal paper in 1953 and the Dewar–Chatt–Duncanson theory forms the basis for most subsequent discussion. The bonding is considered to arise from two interdependent components as illustrated schematically in Fig. 19.20 (a) and (b). In the first part,  $\sigma$  overlap between the filled  $\pi$  orbital of

ethene and a suitably directed vacant hybrid metal orbital forms the “electron-pair donor bond”. This is reinforced by the second component, (b), which derives from overlap of a filled metal d orbital with the vacant antibonding orbital of ethene; these orbitals have  $\pi$  symmetry with respect to the bonding axis and allow  $\text{M} \rightarrow \text{C}_2$   $\pi$  back bonding to assist the  $\sigma_{\text{C}_2 \rightarrow \text{M}}$  bond synergically as for CO (p. 927). The flexible interplay of these two components allows a wide variety of experimental observations to be rationalized: in particular the theory convincingly interprets the orientation of the alkene with respect to the metal and the observed lengthening of the C–C bond. However, the details of the distortion of the alkene from planarity are less easy to quantify on the model and evidence is accumulating which suggests that the extent of  $\pi$  back bonding may have been overemphasized for some systems in the past. At the other extreme back donation may become so dominant that C–C distances approach values to be expected for a single bond and the interaction would be described as oxidative addition to give a metallacyclopropane ring involving two 2-electron 2-centre M–C bonds (see Fig. 19.20(c)).

For example, tetracyanoethylene has a formal C=C double bond (133.9 pm) in the free ligand but in the complex  $[\text{Pt}[\text{C}_2(\text{CN})_4]\{\text{PPh}_3\}_2]$  the C–C distance (152 pm) is that of a single bond and the CN groups are bent away from the

<sup>38</sup> R. A. LOVE, T. F. KOETZLE, G. J. B. WILLIAMS, L. C. ANDREWS and R. BAU, *Inorg. Chem.* **14**, 2653–7 (1975).

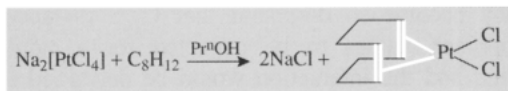




**Figure 19.20** Schematic representation of the two components, (a) and (b), of an  $\eta^2$ -alkene-metal bond.

Pt and 2P atoms; moreover, the 2P and 2C that are bonded to Pt are nearly coplanar, as expected for Pt<sup>II</sup> but not as in (tetrahedral) 4-coordinate Pt<sup>0</sup> complexes. [Rh(C<sub>2</sub>F<sub>4</sub>)Cl(PPh<sub>3</sub>)<sub>2</sub>] affords another example of the tendency to form a metallacyclopropane-type complex (C-C 141 pm) with pseudo-5-coordinate Rh<sup>III</sup> rather than a pseudo-4-coordinate  $\eta^2$ -alkene complex of Rh<sup>I</sup>. However, the two descriptions are not mutually exclusive and, in principle, there can be a continuous gradation between them.

Compounds containing M- $\eta^2$ -alkene bonds are generally prepared by direct replacement of a less strongly bound ligand such as a halide ion (cf. Zeise's salt), a carbonyl, or another alkene. Chelating dialkene complexes can be made similarly, e.g. with *cis-cis*-cycloocta-1,5-diene (cod):



Numerous examples are given in later sections dealing with the chemistry of individual transition metals. Few, if any,  $\eta^2$ -alkene or -diene complexes have been reported for the first three transition-metal groups (why?), but all later groups are well represented, including Cu<sup>I</sup>, Ag<sup>I</sup> and Au<sup>I</sup>. Indeed, an industrial method for the

separation of alkenes uses the differing stabilities of their complexes with CuCl. For many metals it is found that increasing alkyl substitution of the alkene lowers the stability of the complex and that *trans*-substituted alkenes give less stable complexes than do *cis*-substituted alkenes. For Rh<sup>I</sup> complexes F substitution of the alkene enhances the stability of the complex and Cl substitution lowers it.

Alkyne complexes have been less studied than alkene complexes but are similar. Preparative routes are the same and bonding descriptions are also analogous. In some cases, e.g. the pseudo-4-coordinate complex [Pt( $\eta^2$ -C<sub>2</sub>Bu'<sub>2</sub>)Cl<sub>2</sub>(4-toluidine)] (Fig. 19.21) the C≡C bond remains short and the alkyne group is normal to the plane of coordination; in others, e.g. the pseudo-3-coordinate complex [Pt( $\eta^2$ -C<sub>2</sub>Ph<sub>2</sub>)-(PPh<sub>3</sub>)<sub>2</sub>] (Fig. 19.22), the alkyne group is almost in the plane (14°) and the attached substituents are bent back to an angle of 140° suggesting a formulation intermediate between 3-coordinate Pt<sup>0</sup> and 4-coordinate Pt<sup>II</sup>. One important difference between alkynes and alkenes is that the former have a triple bond which can be described in terms of a  $\sigma$  bond and two mutually perpendicular  $\pi$  bonds. The possibility thus arises that  $\eta^2$ -alkynes can function as bridging ligands and several such complexes have been characterized.