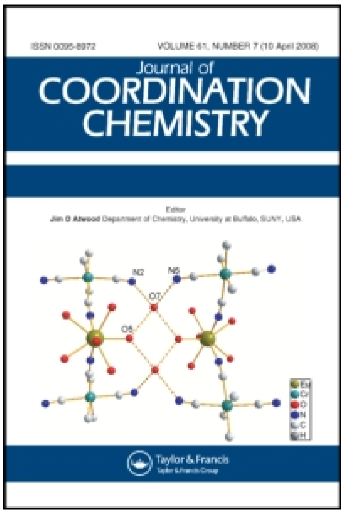

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The Isolobal Theory and Organotransition Metal Chemistry—Some Recent Advances

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THE ISOLOBAL THEORY AND ORGANOTRANSITION METAL CHEMISTRY—SOME RECENT ADVANCES

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Hoffmann's isolobal theory was largely credited for bridging the gap between inorganic complexes and carbon-based compounds. Recent advances have extended its applications to organotransition metal monomers and cluster molecules. Isolobal mapping is not only applicable among molecules and molecular fragments, but also significant in comparing organometallic reactions. Such advancement is likely to influence current trends in mechanistic chemistry. Through a concise review of some of the latest and more representative results, this article aims to highlight and illustrate the versatility and applicability of the theory. Coupled with the Polyhedral Skeletal Electron Pair theory, the isolobality principle provides a useful theoretical underpinning for some synthetic and structural characteristics of many organotransition metal compounds.

Keywords: Isolobal theory, organotransition metal compounds, organometallic reactions

1 FOREWORD

In spite of the burgeoning amount of research in organometallic chemistry over recent years, as yet the discovery, synthesis, and definition of the chemistry of many organometallic compounds have largely been serendipitous. Fortunately, with the advent of molecular orbital theory, this trend has now been reversed. The purpose of this article is to present a brief overview of the isolobal theory and to illustrate its applications in organometallic chemistry.

2. THE ISOLOBAL THEORY[1]

The isolobal theory is based on the premise that molecules contain as building blocks transition metal–ligand fragments ML_n. Of particular interest are the frontier orbitals—the highest occupied and lowest vacant molecular orbitals—which are involved in bonding to other moieties. The frontier orbitals of a particular ML_n fragment may resemble those of another $M'L'_n$, or an organic or inorganic moiety; this concept is the highlight of the isolobal theory.

One convenient approach is to consider the fragments as pieces of an octahedron (Figure 1). This is analogous to perceiving CH_3, CH_2 and CH in a tetrahedron.

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FIGURE 1 Transition metal coordination fragments.

The valence orbitals of transition metals are the nd, $(n + 1)s$ and $(n + 1)p$ orbitals, where $n = 3, 4, 5$. Bonding requires six equivalent octahedral hybrids; the s, p_x, p_y, p_z, $d_{x^2-y^2}$ and d_{z^2} orbitals are utilised. Three d functions, viz d_{xy}, d_{yz} and d_{xz}, collectively known as the t_{2g} set, are left unhybridised (Figure 2).

If six 2-electron ligands are attached to the metal atom or ion to form an octahedral complex, the six hybrids would be involved in strong M–L σ-bonds, together with their strongly anti-bonding σ* counterparts. The ligand electrons fill the σ-orbitals, while the electrons from the metal atom or ion, if any, occupy the t_{2g} set (Figure 3).

If, instead, there are only five ligands, five of the hybrids interact strongly and are removed from the frontier orbital region, leaving a hybrid orbital unused and relatively low-lying in energy. This hybrid, together with the t_{2g} set, constitute the valence active orbitals (Figure 4).

Consider the case of d^7-ML_5, for example the fragment $Mn(CO)_5$ where three electron pairs fill the t_{2g} set; the remaining electron goes into the hybrid pointing away from the fragment. This situation is similar to that of the methyl radical (Figure 5).

It is therefore not surprising to note that, whereas CH_3 has a rich radical chemistry, $Mn(CO)_5$ resembles a radical in many of its reactions, e.g. dimerization, initiation of radical chains, etc. The common organometallic compound $Mn(CO)_5(CH_3)$ can be rationalised in terms of codimerisation of the $Mn(CO)_5$ and CH_3 fragments.

If, as in the above case, the number, symmetry properties, approximate energy and shape of the frontier orbitals of two fragments and the number of electrons in them are similar, the two fragments are said to be isolobal to each other, and may be

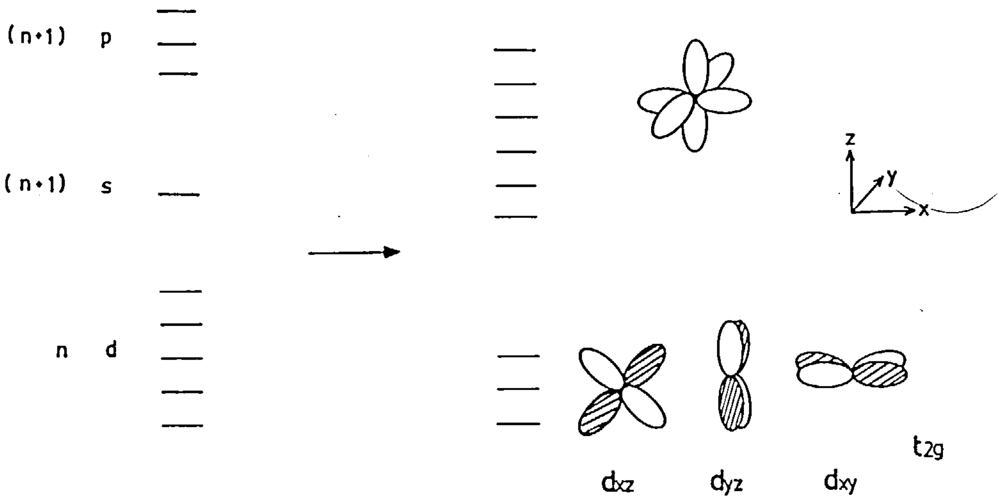


FIGURE 2 Valence orbitals of transition metals.

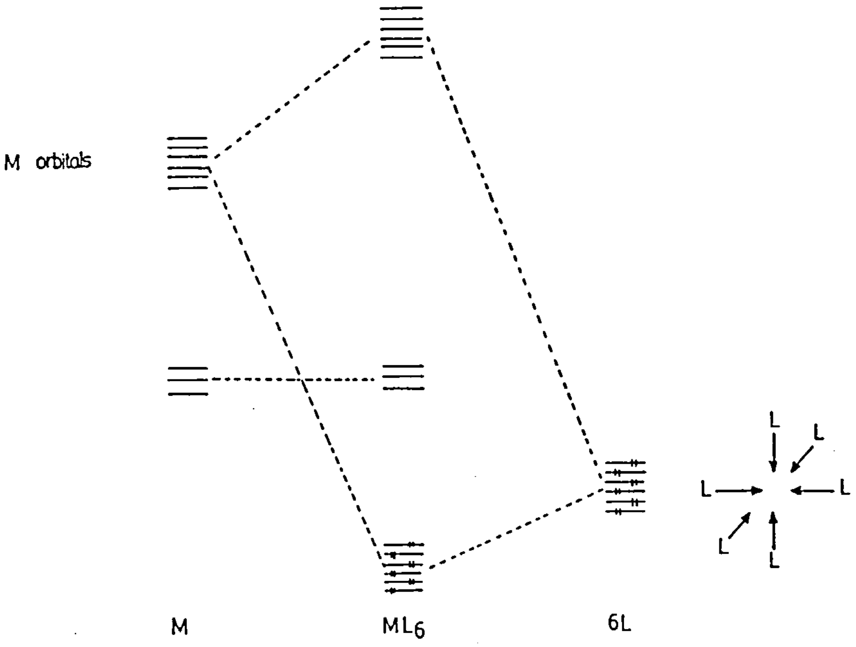


FIGURE 3 Orbital interactions in ML_6 octahedral complexes.

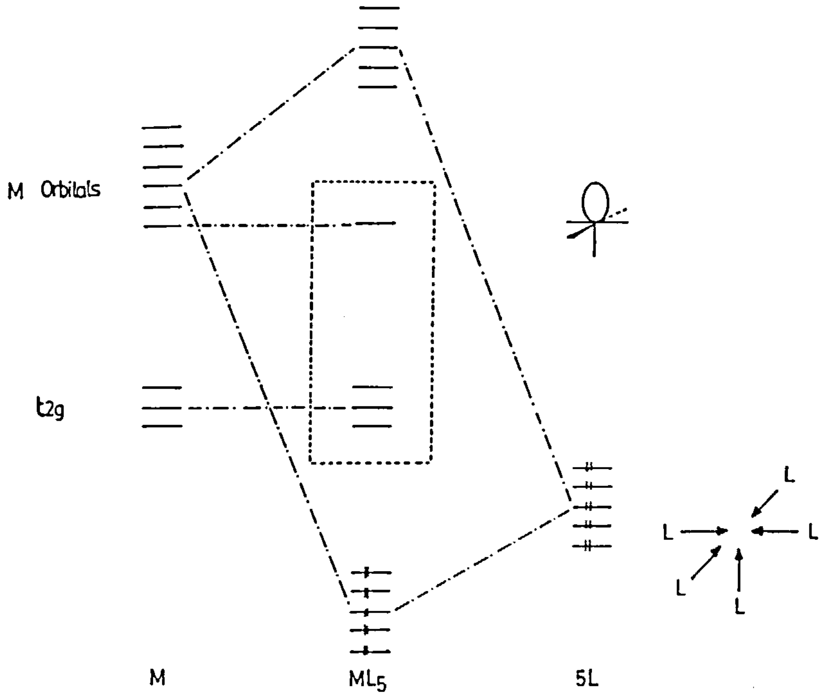


FIGURE 4 Orbital interactions in five-coordinate ML_5 complexes.

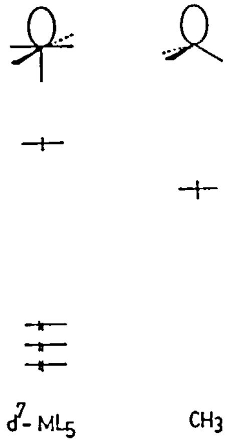


FIGURE 5 Isolobal analogy between d^7–ML_5 and methyl radicals.

represented thus:

$CH_3 \xleftrightarrow[\circ]{} Mn(CO)_5$

Other isolobal relationships may be constructed using similar arguments. These may be summarised as follows:

Hydrocarbon fragment	*Transition metal coordination number from which isolobal mapping is derived*				
	9	*8*	*7*	*6*	*5*
CH_3	$d^1 - ML_8$	$d^3 - ML_7$	$d^5 - ML_6$	$d^7 - ML_5$	$d^9 - ML_4$
CH_2	$d^2 - ML_7$	$d^4 - ML_6$	$d^6 - ML_5$	$d^8 - ML_4$	$d^{10} - ML_3$
CH	$d^3 - ML_6$	$d^5 - ML_5$	$d^7 - ML_4$	$d^9 - ML_3$	—

Hoffmann also demonstrated that, if two axial ligands (z-direction) are removed from ML_5 (octahedral case) and ML_4, then the d_{z^2} orbital joins the t_{2g} set in becoming non-bonding, and the number of unused hybrids would remain the same.

$d^m - ML_n \xleftrightarrow[\circ]{} d^{m+2} - ML_{n+2} \quad n = 4, 5$

Mingos and coworkers,[2] in drawing parallels between transition metal clusters and boranes, introduced the concept of the skeletal electron pair count and related it to frontier orbital theory. For transition metals, 12 electrons are used in metal–ligand bonding involving six valence orbitals of the metal. Hence, this number has to be subtracted from the total number of electrons in the fragment to compute the number n of electrons in the frontier orbitals, i.e.

$n = v + x - 12$

v = no. of metal valence electrons

x = no. of electrons contributed by ligands

For non-transition elements,

$n = v + x - 2$

Two fragments are isolobal if the number of electrons in the frontier orbitals are the same.

$$\text{e.g. } d^7 - ML_5: \quad v + x - 12 = 7 + 10 - 12 = 5$$
$$CH_3: \quad v + x - 2 = 4 + 3 - 2 = 5$$

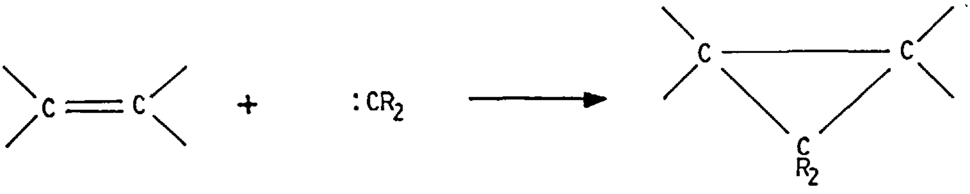
$$d^7 - ML_5 \xleftrightarrow[\sigma]{} CH_3, \text{ as before.}$$

3. ORGANIC REACTIONS: MAPPING M–C AND C–C BOND MAKING AND BREAKING

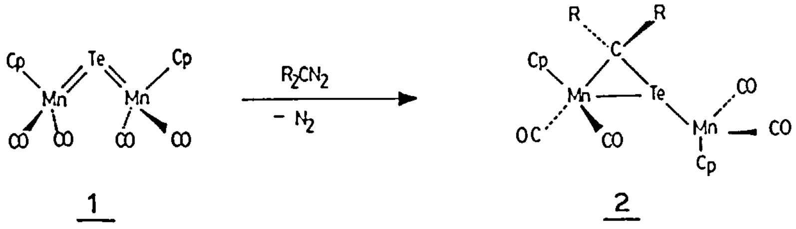
At present, the mechanisms of most organometallic reactions remain unfathomed; this trend is fortunately on the decline. By drawing on the immense wealth of organic reaction mechanisms, it is possible, by means of isolobal analogies, to propose plausible mechanisms for certain organometallic reactions.

The cycloaddition of a carbene to the double bond of an alkene to form cyclopropane is a well-known reaction in organic chemistry (Scheme 1). Hence, we expect a carbene or carbene analogue to react in a similar manner with an "inorganic alkene" to form a metallocyclopropane. Some representative examples are given below.

In the reaction sequence (Scheme 2),[3] since both (η^5-C_5H_5)Mn(CO)$_2$ and the bridging tellurium are isolobal to CH_2, the Mn=Te double bond can be considered to be similar to that in an alkene. Formation of such a three-membered ring in **2** through the transfer of an alkylidene group to the Mn=Te double bond can hence be treated as the organometallic counterpart of the cyclopropanation of olefins. Multiple bond formation between the metals and the bridging ligand (obsd. Mn–Te = 2.46Å) in complex **1** occurs at the expense of any possible metal–metal interaction (obsd. Mn–Mn = 4.21Å). However, the reverse is observed in the sulphido analogue of a congeneric complex $Re_2(\mu\text{-}S)(\eta^5\text{-}C_5H_5)_2(CO)_4$ (obsd. Re–Re = 2.95Å), which can be viewed as isolobal to cyclopropane.

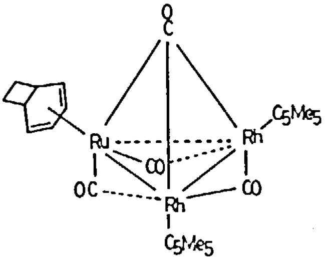


SCHEME 1 Cycloaddition of a carbene to an alkene.



SCHEME 2 Diazoalkanation of $(\mu_2\text{-Te})Mn_2(\eta^5\text{-}C_5H_5)_2(CO)_4$.

Similarly, complex 3, $RuRh_2(\mu\text{-CO})(\mu_3\text{-CO})(CO)_2(\eta^4\text{-}C_8H_{10})(\eta^5\text{-}C_5Me_5)_2$, which is obtained by mixing $Ru(\eta^6\text{-}C_8H_{10})$ (cod) (cod = cyclo-octa-1,5-diene) with $Rh(CO)_2(\eta^5\text{-}C_5Me_5)$ in toluene at 60°C can be treated as a cycloaddition product between the fragment $Ru(CO)_2(\eta^4\text{-}C_8H_{10})$, which is isolobal to a carbene, and the "inorganic alkene", $Rh_2(\mu\text{-CO})_2(\eta^5 - C_5Me_5)_2$.[4]



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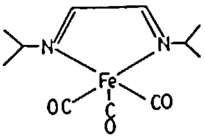
The interesting compound 5, in which the 1,4-diaza-1,3-butadiene ligand bridges the two iron atoms asymmetrically, was obtained by the reaction of 4 with $Fe_2(CO)_9$.[5] It was proposed that $Fe_2(CO)_9$ served as a source of $Fe(CO)_4$ (isolobal with carbene) which added to one of the Fe=CO double bonds in 4 to form the intermediate 6, after which 5 is formed with loss of a molecule of carbon monoxide.



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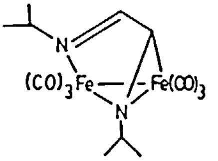

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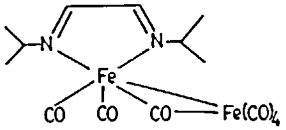

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It may be noted that reactions involving the cycloaddition of an "inorganic carbene" to an alkene are numerous and well documented; these are equivalent to introducing an alkene ligand to a metal complex. However, a distinction must be made between the two modes of coordination (Figure 6), the diagnostic factor being the C–C bond length.

An unusual application of the isolobal theory arises in the area of pericyclic reactions. By making the isolobal substitution $L_nM \leftrightarrow CH$, the conversion of 8 to 9[6]

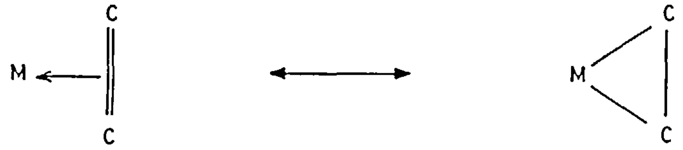
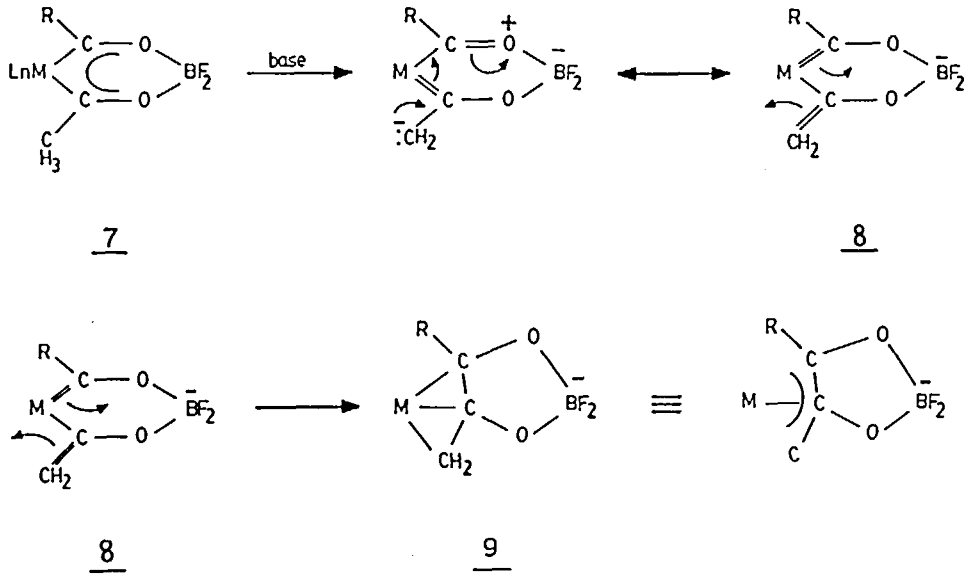


FIGURE 6 Coordination modes in metal ethylene complexes.

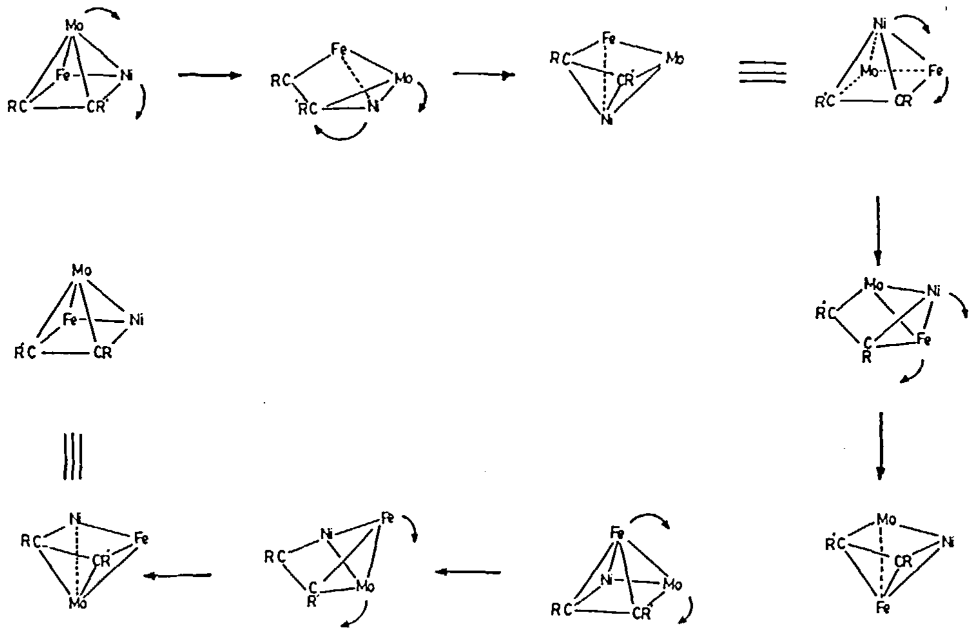
in Scheme 3 represents the thermally allowed $[p_{\pi}2_a + p_{\pi}2_s]$ ring closure, in analogy to the reverse reaction of the pericyclic ring opening of bicyclo[1.1.0]butanes to give *trans*, *trans*-1,3-butadienes.[7] This comparison can be understood if one draws the analogy between the metalla-moiety, M, in 8 and 9 to an sp^2–CH and sp^3–CH fragment respectively. Hence, 8 and 9 would evidently be related to a transoid 2-metalla-1,3-butadiene and a 1-metalla-bicyclo[1.10]butane, respectively.



SCHEME 3 Ring closure reactions of $L_nM(\eta^2\text{-}C_2RMeO_2BF_2)$ (where $L_nM = Fe(\eta^5\text{-}C_5H_5)(CO)$, *cis*-$Mn(CO)_4$ or *cis*-$Re(CO)_4$; R = Me or i-Pr).

This reflects the tremendous potential in improving on the current dearth of work on "inorganic pericyclic reactions", applying the Woodward–Hoffmann rules[8] and drawing upon the plethora of organic pericyclic reactions.

The novel square pyramidal clusters $(RC{\equiv}CR')MM'Fe(CO)_3$ (where $M = (C_5H_5)Ni$; $M' = (C_5H_5)Mo(CO)_2$, $Co(CO)_3$, $(C_5H_5)Ni$) have been shown to be fluxional[9] on the NMR time scale. The proposed mechanism of isomerisation, which is shown below, is related to that of $C_5H_5^+$.[10] This can easily be rationalised by the fact that M and M′ are isolobal with CH and $Fe(CO)_3$ with CH^+ (Scheme 4).



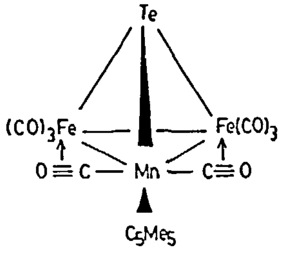
SCHEME 4 Isomerisation mechanism of $(RC{\equiv}CR')(\eta^5\text{-}C_5H_5)NiM'Fe(CO)_3$ (where $M' = (\eta^5\text{-}C_5H_5)Mo(CO)_2$, $Co(CO)_3$, $Ni(\eta^5\text{-}C_5H_5)$).

4. ORGANIC COMPOUNDS: STRUCTURAL SIMILARITIES BETWEEN CARBON- AND METAL-BASED SPECIES

The isolobal relationship may be used to recognise structural relationships between organometallic and organic molecules, and as a predictive tool to devise logical syntheses of novel organometallic compounds.

Organic pericyclic compounds in a variety of shapes (e.g. adamantane, cubane, basketane, tetrahedrane etc.) have been synthesised; it is therefore possible to envisage many complex compounds and metal clusters of a similar nature.

The reaction between $Fe_2(CO)_9$ and $(\mu\text{-Te})[(\eta^5\text{-}C_5Me_5)Mn(CO)_2]_2$[11] yielded **10**. Since $(\eta^5\text{-}C_5Me_5)Mn(CO)_2$, Te and $Fe(CO)_3$ are isolobal with CH^-, CH^- and CH^+ respectively, **10** is thus an organometallic analogue of tetrahedrane, **11**. The formation of **10** may be viewed as the appropriate isolobal analogy relating to



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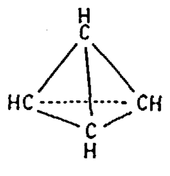

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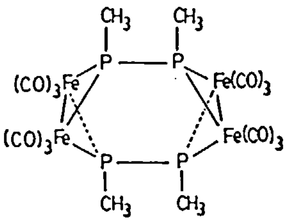
$(\mu_3\text{-Te})Co_2Fe(CO)_9$.[12] The product of this reaction is different from that involving the unsubstituted cyclopentadienyl ligand,[3] probably due to steric and electron-releasing properties of the methyl substituents.

Vahrenkamp *et al.*[13–15] asserted that complexes of composition $[(CO)_3FeER]_n$ (where E = P,As) are analogous to the organic cage compounds $(CH)_{2n}$. Among the novel compounds synthesised are the tetrahedrane analogue $[(CO)_3Fe(PBu^t)]_2$[13] and the cubane analogue $[(CO)_3Fe(AsCH_3)]_4$.[14] The more recent example is $[(CO)_3\text{-}Fe(PCH_3)]_4$,[15] **12**, whose organic counterpart **13** is hitherto unknown.

After the work of Lindner *et al.*,[16] monocycloalkanes have also found counterparts in the realm of organometallic chemistry in the novel compounds $L_nM[\eta^2\text{-}PPh_2(CH_2)_n]$ (where n = 1, 2, 3; $L_nM = (\eta^5\text{-}C_5H_5)Mo(CO)_2$).



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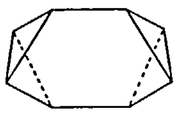

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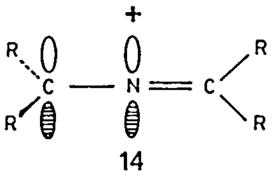
Heteroallenes possessing a central nitrogen atom usually adopt a linear structure,[17,18] **14**, except in the case of electronic stabilisation through the formation of stable amidinium fragments where amino-substituents are attached to the 1- and 3-positions, as depicted in **15**. If a CR_2 group is replaced by the isolobal $(\eta^5\text{-}C_5H_5)_2\text{-}ZrCl$ fragment, the related compounds $(\eta^5\text{-}C_5H_5)_2Zr(\text{-N=CHR})Cl$ (where R = CH_3, C_6H_5, CH_2Ph), **16**, are obtained.[19,20] As with the organic heteroallenes, the Zr–N–C chain is approximately linear, demonstrating the absence of stabilisation.



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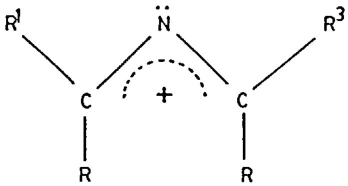

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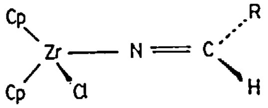
The unexpected product from the reaction between a nickel chelate $(R_2PC_2H_4PR_2)\text{-}NiCl_2$ and $HP(SiMe_3)_2$ is a diphosphorus complex, $(R_2PC_2H_4PR_2)_2Ni_2(\mu\text{-}P_2)$ (where R = Et,Ph).[21] Since $Ni(R_2PC_2H_4PR_2)$ is isolobal with the methylene group, the nickel diphosphorus complex can be viewed as a bicyclobutane derivative.[21] Similar complexes with the diphosphorus ligand bonded to two 15-electron metal–metal bonded fragments, which are isolobal to CH group, have been reported[22–24] bearing a *closo* tetrahedral structure.



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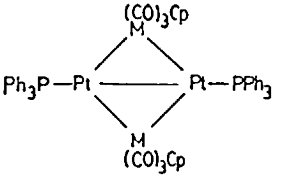
5. ORGANOMETALLIC COMPOUNDS: IDENTIFYING SEEMINGLY UNRELATED MOLECULES

With the advent of the isolobal theory, it now seems almost trivial to substitute one or more fragments of organometallic compounds.

For example,[25] the fragment $M(CO)_3(\eta^5\text{-}C_5H_5)$ (where M = Cr, Mo, W) bridges the compound **17** in the same way as the phosphido ligand does in **18**.[26]



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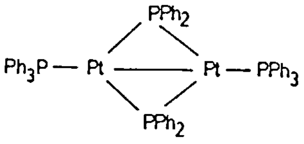

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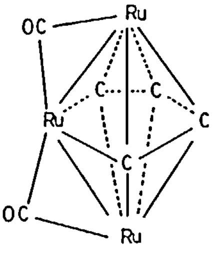
Sappa and coworkers,[27] by progressive substitution and invoking the isolobal relationship between $(\eta^5\text{-}C_5H_5)Ni$ and CH, were successful in synthesising a series of related compounds, $Ru_3(CO)_8(C_2Ph_2)_2$ and $Ru_3(CO)_8(HC_2Bu^t)_2$, **19**, $NiRu_3(\eta^5\text{-}C_5H_5)(CO)_8(C_6H_9)$, **20**, and $Ni_2Ru_3(\eta^5\text{-}C_5H_5)_2(CO)_8(C_2Ph_2)$, **21**.

Stone[28] first noted that the $Au(PPh_3)$ group is isolobal with the hydrogen atom. Prior to this, several works[29,30] had been described in which the $Au(PPh_3)$ ligand occupies the role of a hydride in a related compound. Recent works include those of Barrientos-Penna *et al.*,[31] which describe the compound $(\eta^5\text{-}C_5H_5)ReAu(PPh_3)(p\text{-}N_2C_6H_4OMe)(CO)$ as related to $(\eta^5\text{-}C_5H_5)ReH(CO)(p\text{-}N_2C_6H_4OMe)$.[32]



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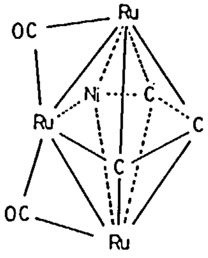

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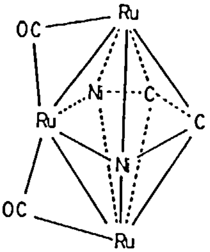

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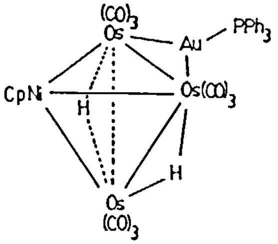
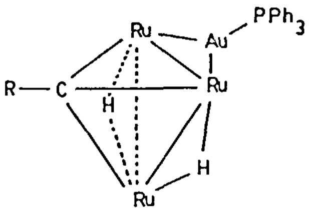
In the light of the compound $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9$,[33] the existence of the compound $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}AuPPh_3)(CO)_9$, **22**,[34] might also be expected from the isolobal relationship of hydrogen with $Au(PPh_3)$.



22

The fact that the ligand CR is isolobal with $\text{Ni}(\eta^5\text{–C}_5\text{H}_5)$ and that $\text{–C}\equiv\text{C–Bu}^t$ is equivalent to $\text{Ni}(\eta^5\text{–C}_5\text{H}_5)$ plus two hydrogens enables us to make further comparisons of the novel compound **22** with $\text{Ru}_3(\mu_3\text{–COMe})(\mu\text{–H})_2(\text{AuPPh}_3)(\text{CO})_9$, **23**,[35] and $\text{Ru}_3\text{Au}(\text{CO})_9(\text{C}_2\text{Bu}^t)(\text{PPh}_3)$, **24**.[36]



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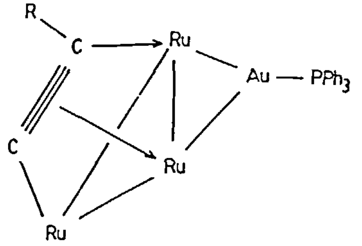

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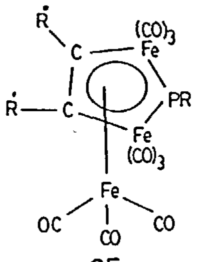
The compound **25**[37] can be accounted for by the existence of a similar compound[38] in which the ligands BR and S occupy the positions of Fe(CO)_3 and PR, respectively.

Moreover, the Fe(CO)_3 and PR fragments are considered to be isolobal with RC^+ and RC^-, respectively. If the extra electron can be assumed to be donated by the central iron atom, the C–C–Fe–P–Fe ring may be treated as an organometallic equivalent of the ubiquitous cyclopentadienyl ligand. This possibility has far-reaching implications.



$R = p\text{-CH}_3\text{O-C}_6\text{H}_4$
$\dot{R} = \text{C}_6\text{H}_5$
$\ddot{R} = \text{H or C}_6\text{H}_5$

25

An intriguing bridge substitution invokes the analogy[39] shown in Figure 7. Hence it is not surprising that the compound $[\text{Zn}(\eta^5\text{–C}_5\text{H}_5]_2(\mu\text{–C}_5\text{H}_5)[\mu\text{–Ni}(\eta^5\text{–C}_5\text{H}_5)(\text{PPh}_3)]$, **26**, strongly resembles $[\text{Zn}(\eta^5\text{–C}_5\text{H}_5)]_2[\mu\text{–N}(\text{SiMe}_3)_2]\,(\mu\text{–C}_5\text{H}_5)$.[40]

Stone *et al.*,[41,42] established the structural and electronic relationship between a

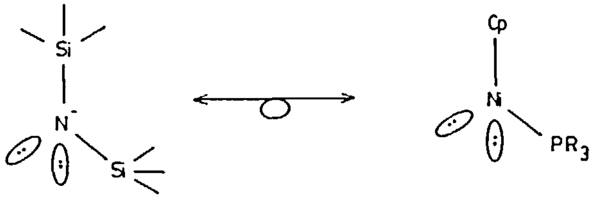
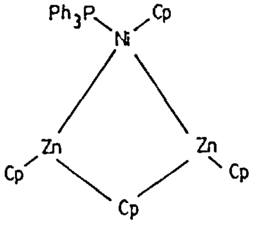


FIGURE 7 Isolobal relationship between $[\text{N(SiR}_3)_2][\text{N(SiR}_3)_2]^-$ and $[\text{Ni}(\eta^5\text{–C}_5\text{H}_5)(\text{PR}_3)]^-$.

platinum monomer, $Pt(RC_2R)_2$, and a triangulo platinum-ditungsten complex, $PtW_2(\mu\text{-}CR)_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, **27**, (where $R = C_6H_4Me\text{-}4$). Such isolobal mapping is justified if one can realise the isolobal analogy between the CR group and the tungsten entity, $W(CO)_2(\eta^5\text{-}C_5H_5)$.



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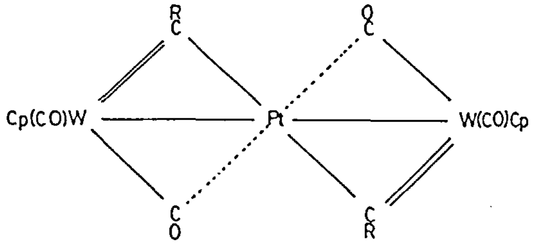

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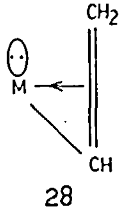
Extended Hückel calculations[43,44] indicated that isolobal mapping occurs among $[\eta^2\text{-}HC{=}CH_2]^-$ (vinyl), **28**, $[\eta^2\text{-}HC{=}CO]^-$ (ketenyl), **29**, and the more familiar 4-electron alkyne donor, $R\text{-}C{\equiv}C\text{-}R$,[45] when they are bonded to a transition metal centre.[44] Using the hypothetical octahedral d^4 complexes $[WH_5(\eta^2\text{-}H_2C{=}CH)]^{4-}$, $[WH_5(\eta^2\text{-}HC{=}CO)]^{4-}$ and $[WH_5(\eta^2\text{-}HC{\equiv}CH)]^{3-}$ as models, Templeton *et al.*[44] rationalised their isolobal analogies by demonstrating the interactions between the metal *d*-orbitals with the filled σ-orbital and π_d-orbital and the vacant π_a of the ligands. This isolobal mapping, however, cannot be extended to the η^2-ethylene complex because of the lack of the π_d-orbital in the ligand. The σ, π_d, π_a and δ correlate to the bonding $\pi_{\parallel}$, $\pi_{\perp}$ and antibonding $\pi^*_{\parallel}$ and $\pi^*_{\perp}$ orbitals, respectively. Similar analogy has been studied by Allen *et al.*[46] Further calculations[44] on the rotational profiles of related d^4 complexes that contain a π-acidic carbonyl ligand $[WH_4(CO)\,(\eta^2\text{-}HC\text{-}CO)]^{3-}$, **30**, $[WH_4(CO)(\eta^2\text{-}H_2C{=}CH)]^{3-}$, **31**, and $[WH_4(CO)(\eta^2\text{-}HC{\equiv}CH)]^{2-}$, **32**,[44,47,48] suggested that the orientation of the η^2-ketenyl ligand in the coordination sphere is dependent on the frontier orbital interactions, while that of the η^2-vinyl counterpart is sterically controlled.



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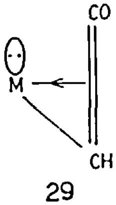

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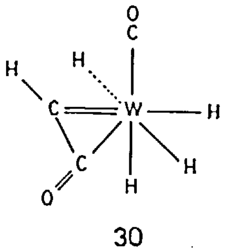

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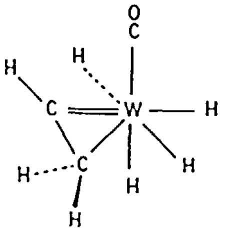

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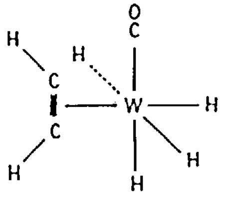

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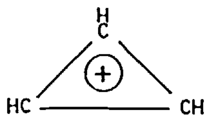
Realising the isolobal analogy between the $[WH_5]^{3-}$ d^4 fragment and the methyne cation, $[CH]^+$, both of which possess two electrons, one σ-orbital and two π-orbitals, one may immediately establish the relationship between the hypothetical d^4 anionic η^2-ketenyl, η^2-vinyl and η^2-alkyne hydrides to the familiar C_3 species, cyclopropenium ion, 33, cyclopropene, 34, and cyclopropenone, 35.[44]



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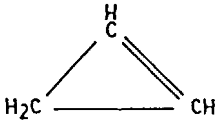

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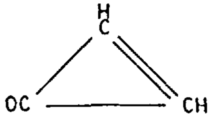

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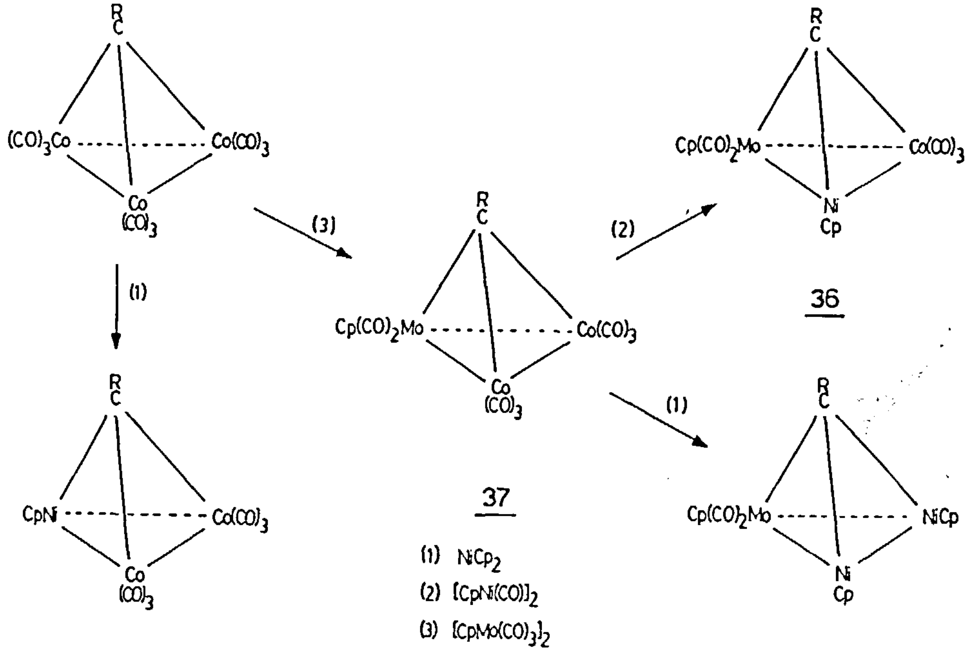
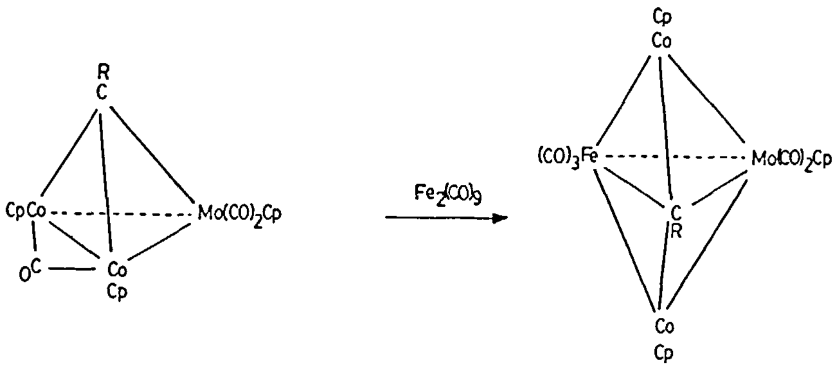
The isolability of the fragments $Co(CO)_3$, $CpMo(CO)_2$, CpNi and CH is fully exploited in a series of heterometallic clusters derived from $Co_3(CO)_9(\mu_3\text{-}CR)$ (where $R = CO_2CHMe_2$).[49] As illustrated in Scheme 5, the $Co(CO)_3$ vertices in the cluster can be replaced by their isolobal counterparts upon treatment with Cp_2Ni, $Cp_2Ni_2(CO)_2$ or $Cp_2Mo_2(CO)_6$. The generation of $CoMoNi(CO)_5(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CR)$, 36, is particularly enticing; the chirality of the molecule is evident from the different functional group on each of the vertices of the tetrahedron. Similar species have been previously reported by Vehrenkamp *et al.*[50–52] Decarbonylated cyclopentadienylation reaction of the molybdenum dicobalt cluster $Cp(CO)_2Mo(\mu_3\text{-}CR)Co_2(CO)_6$, 37, by C_5H_6 gives rise to a carbonyl-bridged complex $Co_2Mo(CO)_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CR)$, 38, which readily captures an iron tricarbonyl moiety from $Fe_2(CO)_9$ to give a rare *closo* trigonal bipyramidal cluster $Co_2FeMo(CO)_5(\eta^5\text{-}C_5H_5)_3(\mu_4\text{-}CR)$, 39, (Scheme 6).



SCHEME 5 Substitution reactions in $Co_3(CO)_9(\mu_3\text{-}CR)$ (where $R = CO_2CHMe_2$).



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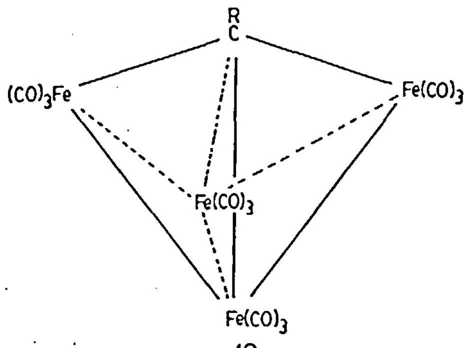
SCHEME 6 Reaction between $(\mu_2\text{-CO})(\mu_3\text{-CR})MoCo_2(\eta^5\text{-}C_5H_5)_3(CO)_2$ and $Fe_2(CO)_9$.

Complex 39 is structurally related to *closo*-$CpNiRu_3(CO)_8(C_5H_7)$, which can be isolated from the mixture containing *nido*-$HRu_3(CO)_9(C_5H_7)$ and $Cp_2Ni_2(CO)_2$.[53] The metal atoms in 39 adopt a butterfly arrangement, with the alkylidyne ligand completing the equatorial plane in the trigonal bipyramidal framework. The structure is comparable to an isoelectronic 60-electron tetra-iron alkylidyne cluster anion $[Fe_4(CO)_{12}(\mu_4\text{-CR})]^-$ (where $R = CO_2CH_3$), 40.[54,55] Conversion of 39 to 40 can be visualised by replacing two CoCp units with the isolobal $Fe(CO)_3$ fragments and the three-electron $CpMo(CO)_2$ with a two-electron $Fe(CO)_3$ moiety, which has three frontier orbitals.



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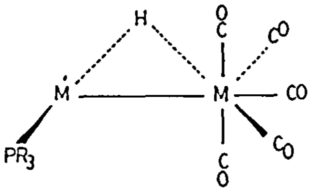
6. ORGANOMETALLIC REACTIONS: ISOLOBAL MECHANISMS

In spite of only a minority of organometallic reactions being currently understood, nonetheless the isolobal theory enables chemists to predict the behaviour of some compounds and to propose novel reaction pathways.

For example, the nucleophilic behaviour of the selenium bridge in $(\mu\text{-Se})[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ towards CH_3I[56] is emulated in a reaction with the isolobal $(\eta^5\text{-}C_5H_5)Mn(CO)_2$.[57]

The anion $[MH(CO)_5]^-$ (where M = Cr, Mo, W) has a known propensity to combine with $M(CO)_5$ fragments,[58-60] the anion $[M_2(\mu\text{-}H)(CO)_{10}]^-$ being formed in the process. The fragments $M(CO)_5$ and $M'(PR_3)^+$ (where M' = Au and Ag) are isolobally related in possessing a vacant frontier orbital pointing away from ML_n. Hence, in a manner similar to the one described above, the $[MH(CO)_5]^-$ and $M'(PR_3)^+$ fragments combine to yield $(R_3P)M'(\mu\text{-}H)M(CO)_5$, **41**.[61]



M	M	R
Cr, Mo, W	Au	Ph
Cr, W	Ag	Me

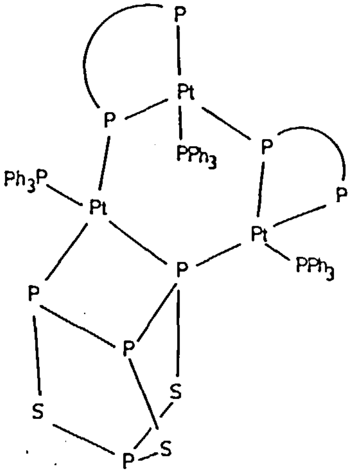
41

A complex in which the P_4S_3 molecule serves as a ligand is a product of the following reaction:[62]

$$Pt(C_2H_4)(PPh_3)_2 + P_4S_3 \rightarrow [Pt(\mu\text{-}P_4S_3)(PPh_3)]_3$$

The formation of the trinuclear compound **42** involves the loss of C_2H_4 and a phosphine ligand from each molecule of reactant, $Pt(C_2H_4)(PPh_3)_2$, with insertion of an LL'Pt moiety into a P–P bond of the P_4S_3 molecule, **43**. Such a progress is analogous to that which leads to the formation of the dinuclear complex[63] $[Ir(\mu\text{-}P_4S_3)(Cl)(CO)(PPh_3)]_2$; note the isolobal relationship between $Ir(Cl)(CO)(PPh_3)$ and PtLL'.

Abstraction of the chlorine atoms from $Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}PRCl)$ yields $Fe_3(CO)_{10}$-$(\mu_3\text{-}PR)$ in the presence of excess $Fe_2(CO)_9$ and $Fe_4(CO)_{11}(\mu_4\text{-}PR)_2$ when reduced by zinc metal.[64] The intermediate $Fe_2(CO)_6(\mu\text{-}PR)$, **44**, was observed spectroscopically; its relative stability may be explained by the fact that the system



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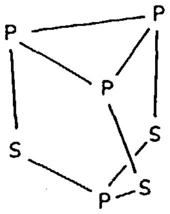

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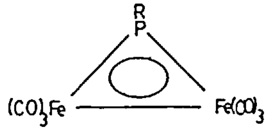

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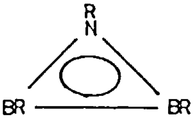

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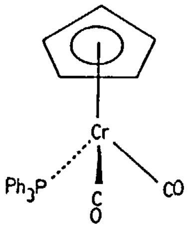
possesses the two π-electrons requisite for Hückel aromaticity and is related to the inorganic aromatic compound **45**.

The 17-electron $CpCr(CO)_2(PPh_3)$ radical, **46**, which is isolobal to the methyl radical, has lately been characterised structurally by Baird *et al.*[65] It adopts a "three-legged piano stool" configuration,[66] with the carbonyl ligands substantially closer to each other (OC–Cr–CO angle = 80.9°) than they are to the phosphine (P–Cr–CO angle = 93.4°). Such distortion may be attributed to the presence of the singly occupied orbital between CO and PPh_3.[67] The authors[65] reported an unexpected hydrogen migration between $CpCr(CO)_3H$[68] and $[CpCr(CO)_3]_2$.[69,70]



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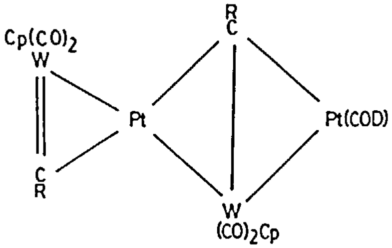
The mechanism may involve metal–metal bond cleavage, thus yielding a $CpCr(CO)_3$ radical, followed by facile transfer of hydrogen. Realising the isolobal relationship between $CpCr(CO)_3$ and the methyl radical, one can immediately parallel such facile transfer to the simplest organic reaction—e.g. the coupling reaction between H and CH_3, forming methane.

Stone and coworkers pioneered the synthesis of heterometallic cluster compounds using, especially, tungsten-carbyne as the sython based on isolobal mapping between different transition metal moieties.[28,71–76] Such "rational" syntheses not only illustrate the utility and versatility of Hoffmann's isolobal principle but also signify a breakthrough in the advance of cluster chemistry. Related to this, the latest trends in cluster syntheses have resorted to designed manipulations[77–82] rather than serendipity.[83] The latest attempts by Stone *et al.*[84–87] include the synthesis of a diplatinum–ditungsten bridging alkylidyne cluster, $Pt_2W_2(CO)_4(\eta^5\text{-}C_5H_5)_2(cod)(\mu\text{-}CR)_2$ (where $R = C_6H_4Me\text{-}4$), **47**, by mixing $Pt(cod)_2$ with the trinuclear $PtW_2(CO)_4(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CR)_2$,[88] **27**. This cluster expansion reaction demonstrates the ability of the PtW_2 compound to coordinate to another metal fragment via a C=W bond. This mirrors a well-documented property of the $Pt(alkyne)_2$ complex: it can couple with a platinum(0) entity to yield a bridging alkyne platinum dimer. These types of organometallic or cluster expansion reactions, which are given theoretical support by the isolobal theory and the polyhedral skeletal electron pair (PSEP) principle, have been well demonstrated in Stone's works.

Seemingly unrelated reactions may be mechanistically linked. Tyler *et al.*[89,90] have



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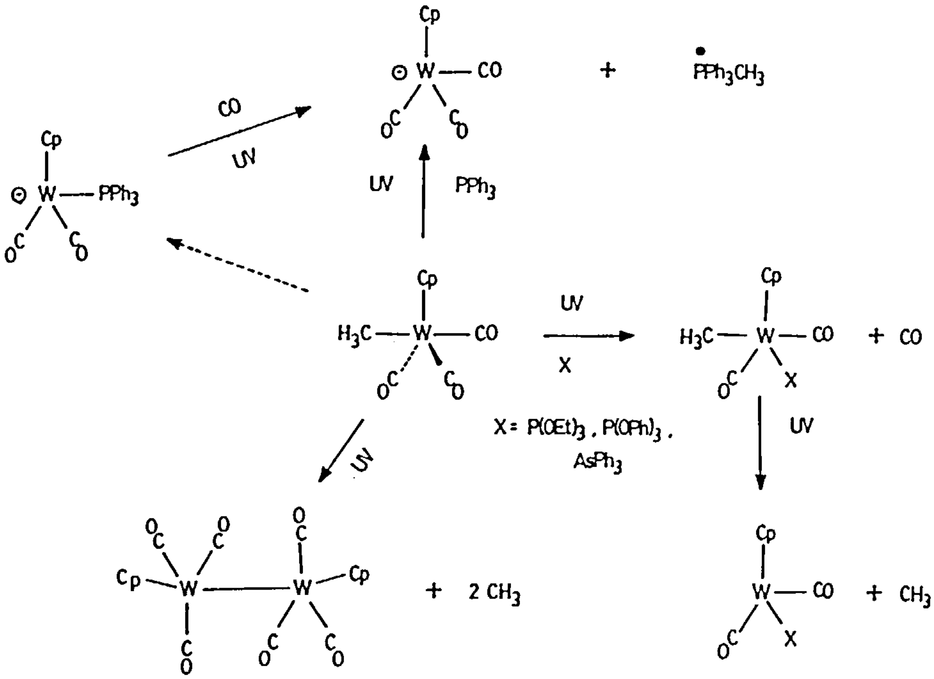
recently applied the isolobality principle in discussing the mechanistic chemistry of the photochemical reduction of $CpW(CO)_3(CH_3)$ in the presence of triphenylphosphine (Scheme 7) and the photochemical disproportionation of a metal–metal bonded dimer, $Cp_2Mo_2(CO)_6$. The former reaction yields $[CpW(CO)_3]^-$ via an intermediate of the phosphoranyl radical PPh_3Me, while the latter reaction gives $[CpMo(CO)_3]^-$ and $[CpMo(CO)_3L]^+$ (or $[CpMo(CO)_2L_2]^+$) via a 19-electron intermediate $CpMo(CO)_2L_2$.[91] The analogy is evident upon the realisation of the isolobal relationship among the methyl radical, $CpMo(CO)_3$ and $CpMo(CO)_2L$.[92] More importantly, the key intermediates involved in these two reactions are also isolobally connected. These analogies immediately imply that the two apparently unconnected reactions are mechanistically isolobal to each other. These observations are likely to have a significant influence in the latest trends of research in organometallic reaction mechanisms.



SCHEME 7 Photochemical reduction of $(\eta^5\text{-}C_5H_5)W(CO)_3(CH_3)$.

7. CONCLUSION

Isolobal theory[1,93,94] represents one of the most beautiful generalisations in contemporary inorganic chemistry. Within the last decade, vigorous progress has been achieved and new findings are emerging continually. As highlighted in this article, the applications of this principle are no longer confined to bridging the gap between carbon-based and metal-based molecules, but extended to linking other main-group entities to transition metal fragments, and metal monomers and dimers to cluster compounds. The latest works have reflected its influence on mechanistic chemistry, catalytic behaviour of organotransition metal complexes, inorganic chiral molecules, and ligand migration and transformations. Nowadays, numerous organometallic compounds are synthesised based on this analogy, and the applications seem limitless.

Recent advances have further reinforced the kinship between Hoffmann's isolobal analogy and Wade and Mingos' PSEPT.[83,95–98] The concepts of these principles provide a theoretical underpinning for many of the current metal cluster and organometallic reactions. Since the recent appearance of a few excellent reviews on the isolobality principle,[28,92,99] novel ideas and applications have surfaced, and have had significant impact on the latest trends in organotransition metal cluster synthesis. Continued interest in this area seems inevitable, while the immediate future of the theory lies in many directions. The synthesis of heterometallic complexes containing early and late metals as functional groups, which are believed to be catalytically active, are likely to take advantage of isolobal analogies. The use of d^3- and d^4-metal–metal multiple bonded dimers as a sython for cluster synthesis has attracted recent attention but so far little success has been met. A closer relationship between these synthetic strategies and the isolobal theory is likely to emerge in the near future.

It must be stressed that predictions based on isolobal analogies are not always successful. The theory fails to predict the thermodynamic or kinetic stability of hypothetical complexes. There are also shortcomings in taking the eccentricities of individual species, metal fragments and ligands alike, into consideration. These limitations are illustrated in bonding descriptions in cluster chemistry.[100,101] Isolobal mapping between intrinsically different but isolobally related fragments such as BH and $Fe(CO)_3$ needs judicial consideration, owing to the vast difference in the electronic and steric natures of the transition metal and main group entities. The theory is fundamentally a symmetry-based concept[102–107] that takes little account of the energetics of interligand interactions. Nonetheless, it provides a useful tool for expanding the horizons of organometallic chemistry.

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