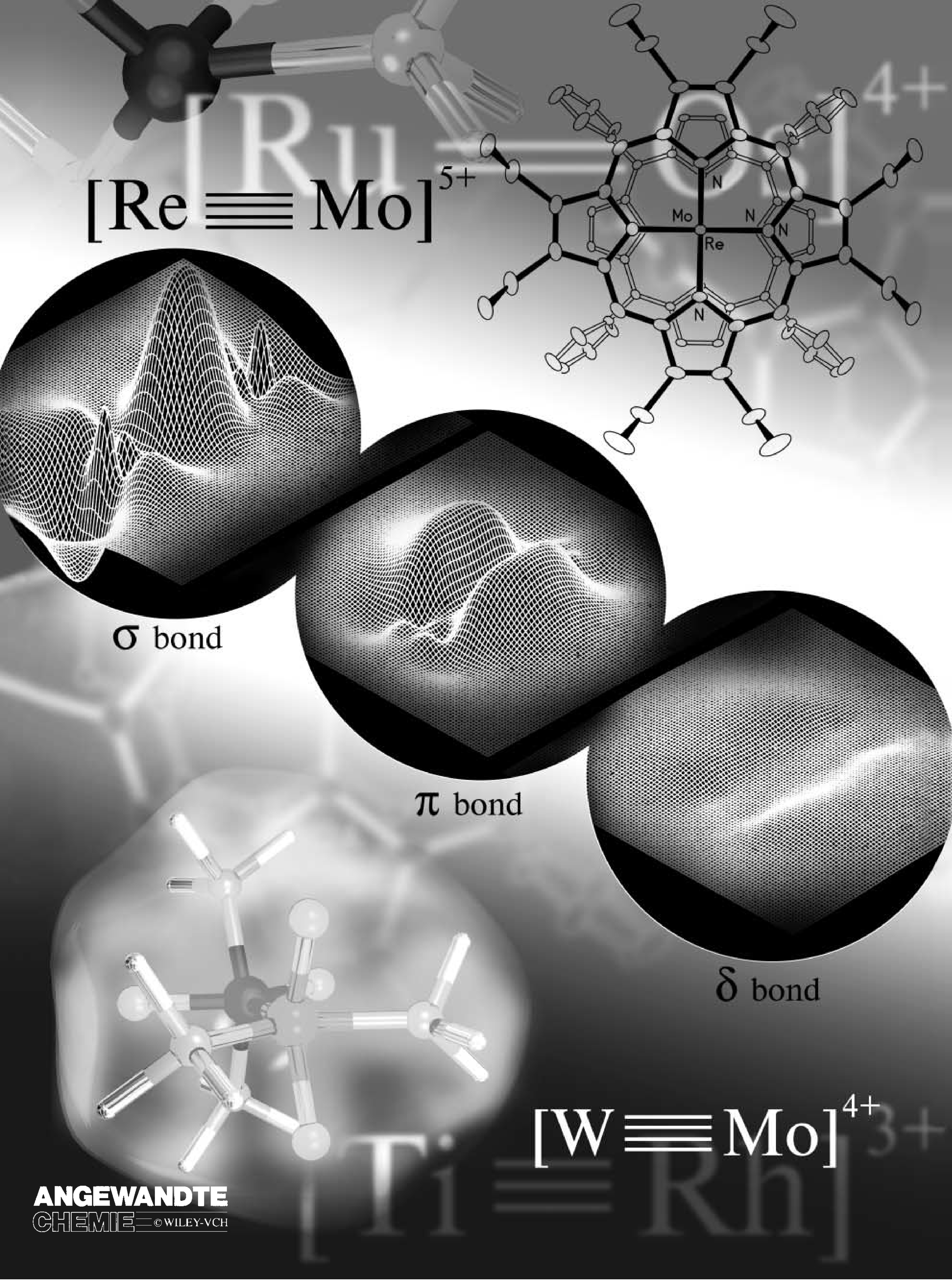
[Ru=Os]4+
[Re≣Mo]5+
Mo
Re
N
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N
σ bond
π bond
δ bond
[W≣Mo]4+
[Ti≡Rh]3+
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Heterodinuclear Transition-Metal Complexes with Multiple Metal–Metal Bonds

James P. Collman* and Roman Boulatov

Interactions between a pair of transition-metals can range from weak antiferromagnetic coupling to bonds of the highest multiplicity known in chemistry, for example, quadruple in isolatable compounds. Tremendous effort has been invested in studying homodinuclear transition-metal–metal bonds. In contrast, relatively little attention has been devoted to heterodinuclear analogues, as it is substantially more challenging to prepare and handle such entities. Yet, in this largely unexplored area of transition-metal chemistry, novel chemical interactions with unprecedented reactivities are likely to be found. Heterodinuclear analogues of diatomic transition-metal dimers being yet inaccessible, dinuclear complexes with Werner-type ligands provide examples of high-multiplicity bonds between different d elements in their least-perturbed form. Such compounds provide an opportunity to probe fundamental issues of chemical bonding between transition-metals, by revealing how and to what extent such bonds are affected by differences in the two metals. Complexes wherein electronically unsaturated heterodinuclear cores are stabilized by π-acidic ligands (such as CO) hold the potential of new chemical reactions (including catalytic) that capitalize on the synergetic effect of two transition-metal centers.

Keywords: bond theory · cluster compounds · electronic structure · metal–metal interactions · transition-metals

1. Introduction

It seems probable that no multiple bonds between two different transition-metals existed in nature (or, at least on this planet) until chemists attempted to synthesize them. This situation illustrates the progress made over the past 50 years in the area of di- and polynuclear transition-metal complexes. Species which we now know have homonuclear multiple metal–metal bonds were prepared as early as the 19th Century (e.g. $[Cr_2(\mu\text{-}O_2CMe)_4(H_2O)_2]$[1]) but it was not until 1956 when Figgis and Martin suggested that the diamagnetism of chromium acetate is a result of what they thought was a weak (5 kcal mol^{-1}) quadruple bond between the Cr atoms.[2] This appears to be the first explicit mentioning of a multiple metal–metal bond in the literature. In 1964 Cotton proposed that the $[Re_2Cl_8]^{2-}$ ion contains an extremely strong $Re\overset{4}{-}Re$ bond (the δ component alone was estimated at 60 kcal mol^{-1}).[3, 4] Since then, numerous dinuclear compounds have been synthesized wherein bonds between two identical transition-metal atoms have some multiple character.[5–9] Tremendous effort has been invested in studying such species experimentally as well as theoretically.[10–14]

In contrast, relatively little attention has been devoted to mixed-metal dinuclear transition-metal complexes, such work being hampered by synthetic challenges. Yet it is this largely unexplored area of transition-metal chemistry where novel chemical interactions, which may have unprecedented properties and unusual reactivities, are likely to be found.

Although diatomic transition-metal dimers can be prepared in the gas phase,[15] isolatable dinuclear cores must be stabilized by auxiliary ligands. Two distinct classes of unsaturated dinuclear compounds are known, those with and without π-acidic ligands. In complexes with only Werner-type ligands (e.g. those with weak or no π-acidity), a subset of metal d orbitals interacts weakly with ligand orbitals so that, in the first approximation, the metal–metal bonding can be considered as isolated from metal–ligand interactions. In contrast, π-acidic ligands (e.g. CO) significantly affect the metal–metal interaction by extensive mixing between metal and ligand orbitals of π symmetry.[16, 17] While compounds of these two classes differ in the nature of metal–metal bonding, they manifest related structural (e.g. short metal–metal separations) and reactivity patterns.

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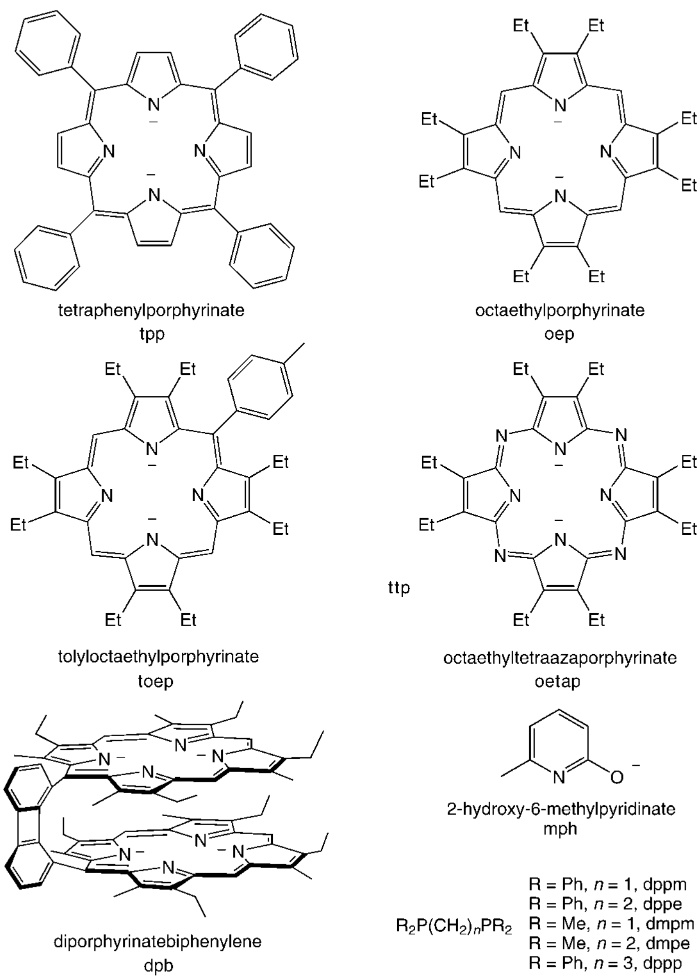
2. Heterodinuclear Complexes Without π-Acidic Ligands.

2.1. Molecular Structure and Metal–Metal Bonding.

All reported complexes of this class are listed in Table 1 (see also Scheme 1).[18–41] The compounds are stable at room temperature under anaerobic and anhydrous conditions, and most of them have been characterized crystallographically. The four major metal-donor-atom geometries observed in homodinuclear complexes[10] are also represented in heterodinuclear compounds (Scheme 2), although only one example of the face-sharing bi-octahedral (FSBO) and $(ML_3)_2$ stereochemical types are known. Edge-sharing bi-octahedral (ESBO) and FSBO complexes contain two and three donor atoms, respectively, that coordinate to both metal centers. Dinuclear complexes of the $(ML_3)_2$ and $(ML_4)_2$ structural types comprise two flattened trigonal- (ML_3) or square-pyrimadial (ML_4) units, connected face-to-face by a metal–metal bond and, in some cases, by the backbone(s) of bridging ligands. High metal–metal bond multiplicities result in intermetal distances that are 0.2–0.9 Å shorter than single bonds between the same metal ions in a comparable coordination environment.



Scheme 1. Structures of some Werner-type ligands used to stabilize transition-metal heterodinuclear cores.

Useful qualitative description of metal–metal bonding in most heterodinuclear transition-metal complexes is given by simple molecular orbital (MO) diagrams derived for the highest symmetry accessible within the corresponding structural type (Figure 1). In an ESBO complex each ML_4 fragment has three metal-localized orbitals (derived from the nonbonding t_{2g} set in the O_h symmetry), the positive overlap of which generates the σ, π, and δ MOs of the M_2^{x+} core. Because of the relatively long intermetal separations, the δ overlap is particularly weak and is effectively nonbonding (nb), so that the maximum formal metal–metal bond order in an ESBO complex is two. Among the MOs of the M_2^{x+} core only the δ orbital is of the right symmetry to interact with orbitals of the bridging ligands; these π-donor interactions destabilize the δ MO and often invert the δ/δ* order (δ* < δ).[42, 43] Small HOMO/LUMO gaps (≈1000 cm^{-1}) and the $^1A_1$ ground state ($\sigma^2\pi^2(\delta/\delta^*)^2$) observed in the ESBO heterodi-

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Table 1. Heterodinuclear cores stabilized by Werner-type ligands arranged by structural type.[a]

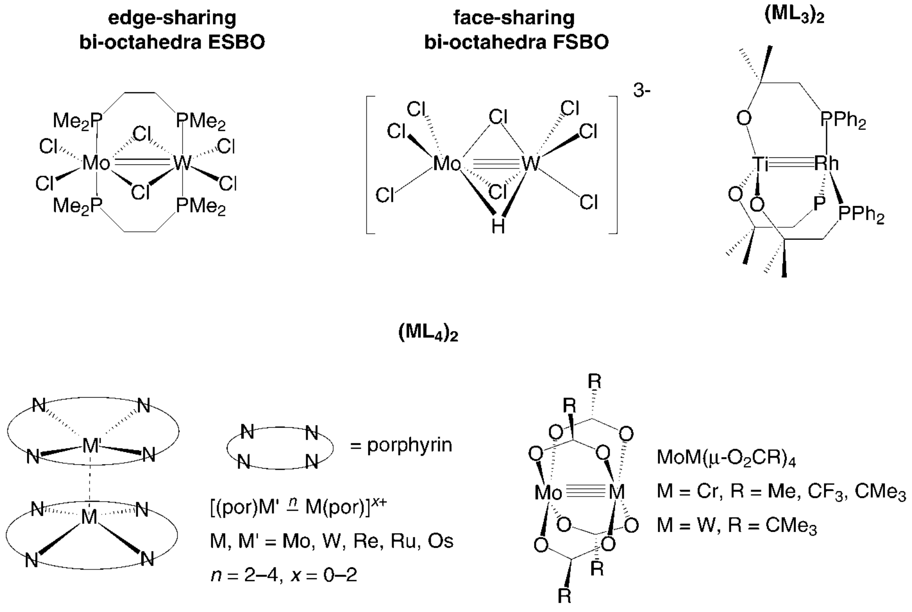
Heterodinuclear core	Ground-state configuration[b]	Examples[c]	M–M′ separation [Å] M$\cdots$M′	 Single bond[e]	Synthesis[d]
ESBO					
$Mo{=}W^{6+}$	$\sigma^2\pi^2(\delta^{nb})^2$	5 isomers of $[MoWCl_4(\mu\text{-}Cl)_2(PP)_2]$ (PP = dppe, dppm)[18, 19]	2.682(1)–2.7320(6)	2.92	reaction 6
		$[MoWCl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)]$[20]	2.4932(6)	2.92	
FSBO					
$Mo{\equiv}W^{6+}$	$\sigma^2\delta^4$	$[MoWCl_6(\mu\text{-}Cl)_2(\mu\text{-}H)]^{3-}$[21, 22]	2.445(3)	2.92	reaction 7
$(ML_3)_2$					
$Ti{\equiv}Rh^{3+}$	see text	$[Ti(\mu{:}\eta^1,\eta^1\text{-}OCMe_2CH_2PPh_2)_3Rh]$[23]	2.2142(11)	2.92	reaction 3
$(ML_4)_2$					
$Ru{=}Os^{4+}$	$\sigma^2\pi^4(\delta^{nb})^4\pi^{*2}$	[(oep)OsRu(oetap)],[24] [RuOs(dpb)][25]			reaction 1
$Mo\overset{n}{-}Ru^{5+}$ $n \geq 2.5$	$\sigma^2\pi^4(\delta^{nb})^2(\delta^{nb}/\pi^*)^1$[f]	$[(oep)MoRu(tpp)]^+$[26][g]	2.181(2)	2.88	reaction 1
$Mo\overset{n}{-}Os^{5+}$ $n \geq 2.5$	$\sigma^2\pi^4(\delta^{nb})^2(\delta^{nb}/\pi^*)^1$[f]	$[(oep)MoOs(tpp)]^+$[27]	2.238(3)	2.96	reaction 1
$M\overset{n}{-}M'^{4+}$ M = Mo, W; M′ = Ru, Os, $n > 2$	$\sigma^2\pi^4(\delta/\delta^{nb})^2\pi^{*2}$ (MoRu)	[(oep)MM′(tpp)][26, 27]			reaction 1
$Mo\overset{3.5}{-}W^{5+}$	$\sigma^2\pi^4\delta^1$	$[MoW(\mu\text{-}O_2CCMe_3)_4I]$[21]	2.194(2)	2.92	
$Mo\overset{3.5}{-}Ru^{5+}$	$\sigma^2\pi^4\delta^2(\delta^*/\pi^*)^1$[f]	$[(tpp)MoRu(oep)]^+$[26][g]	2.211(2)	2.88	reaction 1
$W\overset{3.5}{-}Ru^{5+}$	$\sigma^2\pi^4\delta^2(\delta^*/\pi^*)^1$[f]	$[(oep)WRu(tpp)]^+$[27]	2.297(2)	2.90	reaction 1
$Cr\overset{4}{-}Mo^{4+}$	$\sigma^2\pi^4\delta^2$	$[CrMo(\mu\text{-}O_2CMe)_4]$[28]	2.050(1)	no data	reaction 4
		$[CrMo(\mu\text{-}L)_4]$ (L = O_2CCF_3;[28] O_2CCMe_3;[29] mph[30])			ligand exchange
$Mo\overset{4}{-}W^{4+}$	$\sigma^2\pi^4\delta^2$	$[MoW(\mu\text{-}mph)_4]$[31]	2.091(1)	2.92	reaction 5
		$[MoW(\mu\text{-}O_2CCMe_3)_4]$[32]	2.080(1)	2.92	reaction 5
		$[P_2Cl_2MoWCl_2P'_2]$ (P, P′ = PMe_2Ph, $PMePh_2$, PMe_3);[33, 34] $[MoWBr_4P_4]$ (P = PMe_2Ph, $PMePh_2$)[35]	2.207(1)–2.2092(7)	2.92	reaction 2
		$[MoWX_4(\mu\text{-}PP)_2]$ (X = Cl, Br; PP = dppm, dppe, dmpe, dmpm)[35, 36]	2.2110(7)–2.243(1)	2.92	ligand exchange
		[(por)MoW(por)] (por = toep, oep)[37]			reaction 5
$Mo\overset{4}{-}Re^{5+}$	$\sigma^2\pi^4\delta^2$	$[(tpp)MoRe(oep)]^+$[38]	2.2350(12)	2.98	reaction 1

[a] See Scheme 1 for chemical structures of oep, oetap, tpp, toep, dpb, mph, and molecular formulas of bidentate phosphanes. Multiple bonds between two different transition-metal atoms may be present in several other dinuclear complexes; there is either insufficient evidence to ascertain whether the bond is multiple, or the compounds were not adequately characterized. A mixture of diamagnetic $[(PMe_3)_3Cl_nMo(\mu\text{-}Cl)(\mu\text{-}S)WCl_m(PMe_3)_2]$ ($n = 1, m = 2$; $n = 2, m = 1$) was prepared from $[S{=}WCl_2(PMe_3)_3]$ and $[MoCl_2(PMe_3)_4]$;[39] these complexes may have the ESBO geometry and one Mo=W bond. Formation of $[Mo{\equiv}W(NMe_2)_6]$ (as a mixture with the homodimers) in a reaction between $LiNMe_2$ and a solid with an empirical composition MoW_2Cl_{12} was claimed based on mass-spectrometric evidence.[40] Finally, an ESBO ion, $[CrMoCl_9]^{3-}$, possibly with a formal Cr≡Mo bond ($\sigma^2\delta^4$), may form in a reaction between $[MoCl_6]^{2-}$, $CrCl_2$, and Cl^- ions.[41] [b] See Figure 1. The δ^{nb} notation designates weakly or non-interacting metal-based orbitals of δ symmetry. [c] See Scheme 2. [d] See Scheme 3. [e] The M–M′ separation averaged over all structures deposited in Cambridge Crystallographic Structural Database (CCSD) as of October 2001 and designated as having a single M–M′ bond. [f] The nature of the SOMO is presently unknown.[26, 27] [g] Both the eclipsed and staggered conformers are present in the solid state (Figure 2).[27]

nuclear complexes,[18, 19] are consistent with this qualitative picture and indicate that the weak room-temperature paramagnetism of these compounds arises from thermally populated (δδ*) excited states.

The magnetic properties of the only reported FSBO heterodinuclear ion, $[MoWCl_6(\mu\text{-}Cl)_2(\mu\text{-}H)]^{3-}$, have not been studied. Based on the MO diagram in Figure 1, this $(d-d)^6$ complex should have a $\sigma^2\delta^4$ ground state and a triple Mo–W bond. This MO diagram is likely to be applicable to the MoW^{6+} core as it correctly describes the ground-state configurations of all W_2^{6+} and most Mo_2^{6+} congeners.[13, 44]

The $(ML_4)_2$ geometry is the only common structural type in which a quadruple bond is possible. The overlap of effectively nonbonding, with



Scheme 2. Structures of select heterodinuclear transition-metal complexes (structural type listed in bold).

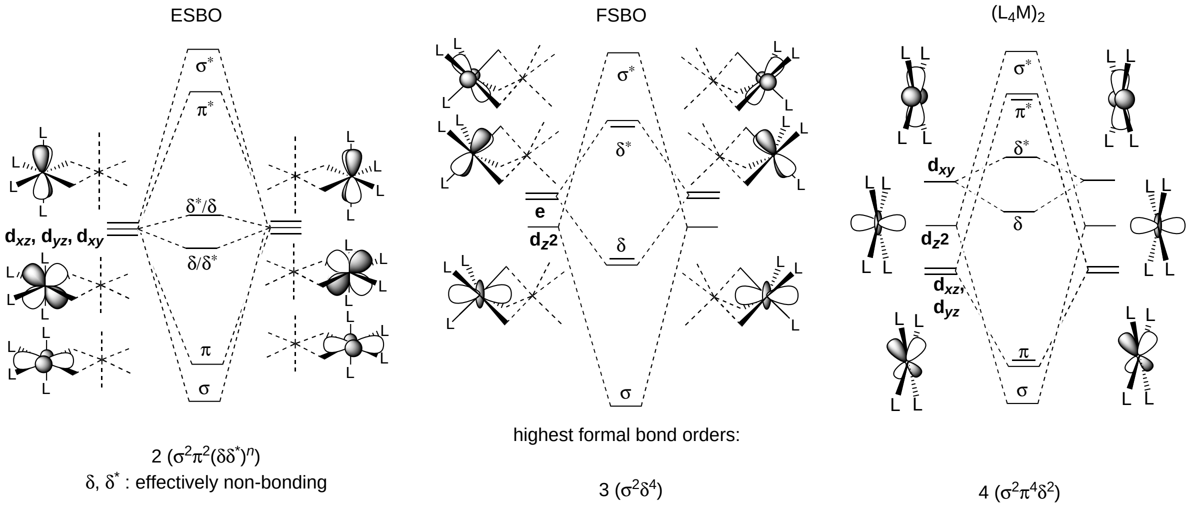


Figure 1. Qualitative MO diagrams of the metal–metal bonding between transition metal atoms in three major structural types of dinuclear complexes without π-acidic ligands. In the ESBO the d_{xz} and d_{yz} orbitals are rotated 45° around the axial L-M-L axis relative to their orientation in a t_{2g} set in O_h symmetry. In the FSBO the e set is comprised of a pair of strongly mixed d_{xz}/d_{yz} and $d_{xy}/d_{x^2-y^2}$ orbitals.[10]

respect to the metal–ligand interactions, d_{xy}, d_{xz}, d_{yz} and d_{z^2} orbitals of the ML_4 fragments generates the σ, two π, and a δ MOs of the metal–metal core. The δ overlap, which depends on the L-M-M-L dihedral (torsion) angle (χ) as cos2χ, is maximum in the eclipsed conformation (χ = 0°) and is annihilated if the L_4M moieties are staggered (χ = 45°). The diamagnetism and the eclipsed solid-state conformation of all known $(d-d)^8$ heterodinuclear complexes suggest a $\sigma^2\pi^4\delta^2$ ground state and quadruple M–M′ bonds. The electronic stabilization from maximal δ overlap over rides increased nonbonding repulsions in the sterically least-favorable eclipsed conformation of $(L_4M)_2$-type heterodinuclear complexes without bridging ligands: $(d-d)^8$ $[MoWX_4P_4]$ (X = Cl, Br, P = phosphane)[33–35] and $[(tpp)MoRe(oep)]^+$,[38] and $(d-d)^9$ $[(oep)WRu(tpp)]^+$.[27] In contrast, the $(d-d)^9$ $MoRu^{5+}$ derivative exists in the solid state as an equimolar mixture of an eclipsed and a staggered conformer (Figure 2).[27] Such a situation is unprecedented among homodinuclear compounds and may arise from the electronic stabilization engendered by the δ bond being comparable to the difference in noncovalent ligand–ligand interactions between the two conformers.

The MO diagram in Figure 1 predicts a diamagnetic $\sigma^2\pi^4(\delta^{nb})^4$ ground-state configuration for a $(d-d)^{10}$ complexes, as is indeed observed for homodinuclear $[(por)_2Re_2]$[45] and $[(por)_2M'_2]^{2+}$ (M′ = Ru, Os; por = oep, tpp).[46] However, isoelectronic structurally analogous heterodinuclear complexes, $[MM'(por)_2]$ (M = Mo, W; M′ = Ru, Os; por = oep, tpp), have a triplet $^3A_2$ ground state, consistent with the $\sigma^2\pi^4\delta^2\pi^{*2}$ electronic configuration (in the absence of a crystal structure it is unknown if the δ orbital is bonding).[26, 27] The origin of the inversion ($\pi^* < \delta^*$) in heterodinuclear $(d-d)^{10}$ cores is not yet known. Whereas the $\delta^* \approx \pi^*$ or $\pi^* < \delta^*$ ordering in most homodinuclear $Ru_2^{4/5+}$ and $Os_2^{4/5+}$ complexes is caused by π-donor interactions between the δ* orbitals and orbitals of bridging ligands,[10, 47] the stereoelectronic properties of the porphyrin do not allow such orbital interactions. Because the $[MM'(por)_2]$ species have a rare among dinuclear transition-metal complexes π^{*2} HOMO,[44] they may be interesting objects to study the electron correlation effects in bimetallic derivatives of heavy transition elements.

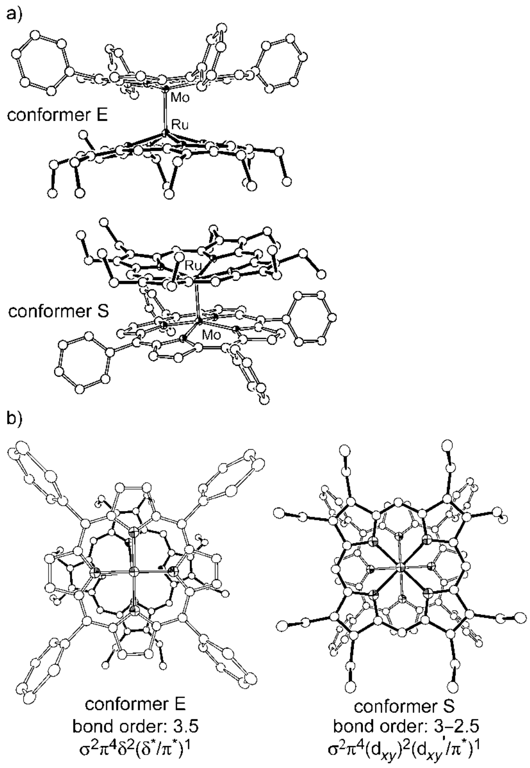


Figure 2. ORTEP drawings of $(d-d)^9$ $[oep)MoRu(tpp)]^+$ (tpp is drawn with open bonds, oep with bold bonds). a) half the unit cell containing one molecule of an eclipsed (E) and a staggered (S) conformer; b) view along the Mo–Ru vector for each conformer; the perspective is exaggerated to show better the relative arrangement of the macrocycles. Unlabeled spheres with shaded octants represent the N atoms; counterions, solvent molecules, and hydrogen atoms are omitted; thermal ellipsoids are for 50% (a) or 25% (b) probability.

A triple Ti–Rh bond in $[Ti(\mu\text{-}OCMe_2CH_2PPh_2)_3Rh]$ was suggested to arise from one $Ti(d_\sigma)-Rh(d_\sigma)$ and two dative $Rh(d_\pi) \rightarrow Ti(d/p_\pi)$ interactions.[23] The generic MO diagram for $(ML_3)_2$-type complexes predicts a single ($\sigma^2\pi^4\pi^{*4}$) bond, but it is probably a less adequate depiction of this polar "early–late" Ti–Rh bond.[14, 48] Notably, no multiple homonuclear Ti–Ti and Rh–Rh bonds are yet known.

The one-electron orbital description of the metal–metal bond, discussed above, is useful in categorizing dinuclear transition-metal complexes and qualitatively rationalizing many of their properties. However, any *quantitative* treatments of a metal–metal bond must incorporate extensive configuration interactions as the separations of the energies of the MOs comprising such bonds are comparable to the energy of interactions among many electrons confined to a dimetallic core.[10, 44, 49] This importance of excited states (Table 2) is seen, for example, in that, in contrast to early main-group elements,[50] a multiplicity of a transition-metal–metal bond derived from computational studies is always substantially lower than that obtained from simple MO arguments (formal bond order, FBO) and may differ significantly among isoelectronic structurally analogous dinuclear complexes.

Very few computational studies of heterodinuclear metal–metal bonds have been reported, apparently because of the difficulty in dealing with the intrinsic dissymmetry of such entities.[51] Cr–Mo bonding in the most studied heterodinuclear complex, $[CrMo(\mu\text{-}O_2CH)_4]$, was found to be more similar to that in the Mo_2^{4+} rather than Cr_2^{4+} analogues (Table 2).[51–54] Qualitatively, the difference was ascribed to higher covalency of the Cr–Mo bond resulting from the improved overlap of the 3d orbitals with more polarizable and diffuse 4d orbitals of the Mo.[51] The slight polarity of the $^{\delta-}Cr\overset{4}{-}Mo^{\delta+}$ bond was ascribed[51, 52] to different radial distributions of 3d and 4d orbitals.

Stranger et al. have carried out broken-symmetry DFT calculations on series of $(d-d)^6$ FSBO $[MM'Cl_9]^{3-}$ and ESBO $[MM'Cl_6(\mu\text{-}PH_2CH_2PH_2)]$ complexes (M, M' = Cr, Mo, W).[43, 55] Among heterodinuclear compounds of these types only $[MoWCl_6(PP)_2]$ (PP = dmpm, dppm, dppe) have been reported.[19] In a notable contrast to the tetracarboxylates, weak antiferromagnetic coupling was found for both the Cr_2^{6+} and the hypothetical $CrMo^{6+}$ cores as opposed to strong Mo–Mo bonds in the Mo_2^{6+} congeners.

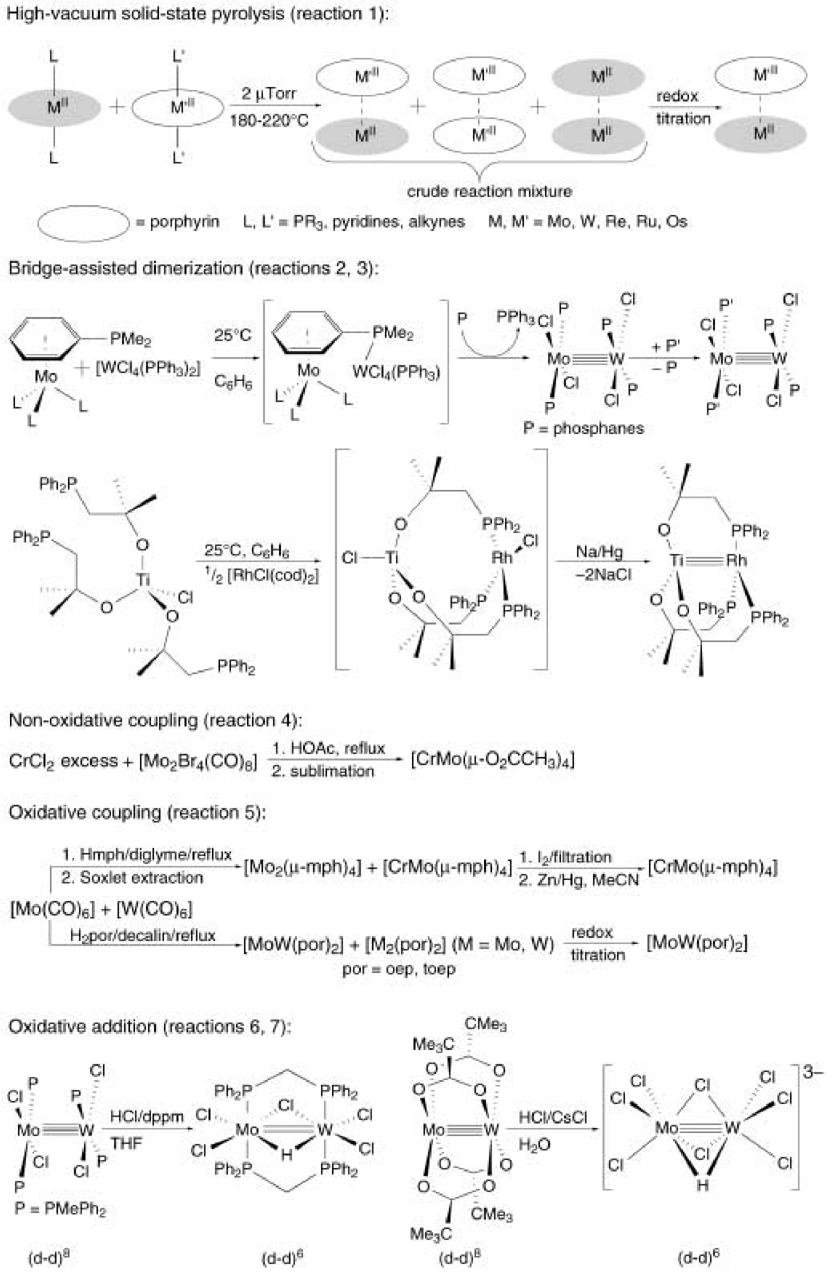
Table 2. Computed orbital population of quadruple M–M' bonds in $[MM'(\mu\text{-}O_2CH)_4]$ (M, M' = Cr, Mo).[a]

Core	σ	π	δ	δ*	π*	σ*	Net bond order
Cr_2	1.48	2.59	1.09	0.91	1.41	0.52	1.16
CrMo	1.78	3.39	1.41	0.59	0.61	0.22	2.58
Mo_2	1.89	3.69	1.65	0.35	0.31	0.11	3.23

[a] Adapted from ref. [51].

2.2. Synthesis

The most versatile synthesis of heterodinuclear cores is high-vacuum solid-state pyrolysis of mononuclear metalloporphyrins stabilized by thermally labile axial ligands (Scheme 3, Reaction 1). The loss of these ligands at 180–220 °C generates four-coordinate metalloporphyrin fragments that recombine randomly to yield a mixture of homo- and heterodinuclear bisporphyrin compounds. The latter are isolated by cycles of selective oxidation and reduction based on different redox potentials of homo- and heterodimers and different solubilities of neutral and cationic metalloporphyrins in nonpolar solvents ("redox titration").[46]



Scheme 3. Representative syntheses of heterodinuclear transition-metal complexes.

The success of this synthetic strategy is based in large part on the unique attributes of the porphyrin as an auxiliary ligand to stabilize dinuclear metal cores. First, pyrolysis is applicable to a wide range of 4d and 5d metals[56] as suitable mononuclear metalloporphyrin precursors are known for almost every transition element. Second, the yields of heterodimers can be optimized in a rational way, by selecting mononuclear precursors of similar thermal stabilities. The latter are adjusted by the appropriate choice of the porphyrin and axial ligands. For example, less σ-basic porphyrins tend to give more thermally stable derivatives with identical combinations of metals and axial ligands, whereas alkylphosphanes are lost several times faster than pyridines or acetylenes are. Third, because a porphyrin can not be displaced from most metal ions, scrambling of porphyrin ligands does not complicate syntheses of heteroleptic heterodinuclear derivatives. The latter are better suited for crystallographic studies as they are free of the solid-state disorder in which both crystallographic sites have fractional occupancy by both metals. Fourth, the combined magnetic anisotropy of the two macrocycles in a bismetalloporphyrin produces a characteristic ^{1}H NMR spectrum resonance pattern, which is sufficient to establish formation of the dinuclear derivative without crystallographic characterization. In addition, series of metal–metal bonded bisporphyrins with identical metal-donor-atom geometries but containing various spectroscopic markers and/or of varying stereoelectronic characteristics are accessible by using porphyrins with appropriate peripheral substituents. Fifth, pyrolysis is readily applicable to 2nd and 3rd row transition-metal complexes of porphyrin-like ligands, such as tetraazaporphyrins, phthalocyanines, and corroles. Because electronic properties of these macrocycles differ from those of the porphyrin, they may stabilize metal cores, which are otherwise inaccessible.

Heterodinuclear complexes of non-porphyrin ligands have been prepared by a variety of less general routes. Clever methods have been used to synthesize unbridged MoW^{4+}[57] and bridged $TiRh^{3+}$[23] cores. Formation of the metal–metal bond is facilitated and the selectivity of dimerization is significantly improved by precoordinating metal fragments with a suitable bridging ligand (Reactions 2 and 3, Scheme 3).[58] Neither method has yet been extended to other multiply bonded heterodinuclear cores.[57, 59] A reaction between $[Mo_2Br_4(CO)_8]$ and $CrCl_2$ in refluxing acetic acid yields $[MoCr(\mu\text{-}OCCH_3)_4]$ in a good yield (Scheme 3, Recation 4).[29] $[MoW(\mu\text{-}L)_4]$ ($L = O_2CCMe_3$[32] or mph[31]) and $[MoW(por)_2]$ (por = toep, oep)[37] have been prepared by oxidative coupling of $[Mo(CO)_6]$ and $[W(CO)_6]$ in the presence of the corresponding ligand (Scheme 3, Reaction 5).

A variety of other MoW^{4+} derivatives have been obtained by ligand substitution in $[MoW(\mu\text{-}O_2CCMe_3)_4]$[60] or in $[MoWCl_4(PMe_3)_4]$,[34–36, 61] but this approach does not yield novel heterodinuclear cores. However, oxidative addition of HCl[20, 21] or two Cl atoms (from CH_2Cl_2 or $PhICl_2$[19]) to such complexes generates doubly and triply bonded MoW^{6+} cores (Scheme 3, Reactions 6–7).

2.3. Physicochemical Properties

With the exception of the force constants of metal—metal bonds $\kappa(MM')$, in bismetalloporphyrins, physicochemical data are limited to Group 6 derivatives (Table 3).[10, 19, 21, 34–37, 57, 60–67] In most cases, the properties of the congeners show monotonic and expected trends.

Out of 17 crystallographically characterized heterodinuclear cores, there is one example each of a MM′ bond being shorter (in $[MoW(\mu\text{-}O_2CCMe_3)_4]$) or longer (in the $[MoW(\mu\text{-}Cl)_2(\mu\text{-}H)Cl_6]^{3-}$ ion) than either homonuclear analogue (entries 3 and 6, respectively).[10, 57, 62, 68–70] Bond-length trends in similar compounds of the 2nd and 3rd row transition metals have been ascribed to the relative importance of bond lengthening, as a result of core–core repulsions (which accounts for longer W–W bonds relative to Mo–Mo ones), and bond shortening as a result of relativistic phenomena (e.g. shorter W–L than Mo–L bonds).[10] A nonlinear trend in metal–metal separations may result if the relative contributions of these effects are significantly different for a heterodinuclear core than for the homonuclear congeners. However, the metal–metal separations may also be substantially affected by the stereoelectronic requirements of relatively rigid bridging-ligand sets.

For a number of heterodinuclear complexes, metal–metal vibration frequencies, $\nu(MM')$, identified by resonance Raman spectroscopy, have been used to calculate $\kappa(MM')$ within the diatomic-oscillator approximation. However, opinions differ[10, 71] as to whether comparisons of such diatomic force constants among homologous complexes of different metals provide meaningful information on the relative strengths of metal–metal bonds.

In contrast to light main-group elements, where C=O and N=O bonds are substantially stronger than the homonuclear analogues, such as C=C, O=O, and N=N, O=O, no unambiguous examples of a similar effect are known for metal–metal bonds between transition-metal atoms. Although $\kappa(MoW)$ in $[MoWCl_4(PMe_3)_4]$ was found to be larger than those in the homodinuclear analogues (Table 3, entry 9), it is unclear if this small difference is meaningful within the diatomic-oscillator approximation. While force constants in the $[MM'(\mu\text{-}mph)_4]$ series (M, M′ = Cr, Mo, W) increase monotonically from Cr_2 to MoW, the very low value of $\kappa(W_2)$ appears to be either underestimated or represent unusually large ligand perturbation (entry 8).

With the exception of the recently reported $\kappa(Mo_2)$, $\kappa(MoW)$, and $\kappa(W_2)$ values that change monotonically (entry 10)[72–74] but might be systematically underestimated,[72] a decrease in the force constants of both homo- and heteronuclear 4d–4d and 5d–5d bonds with the number of d electrons is described by the same linear function in all known metalloporphyrins (Figure 3). Remarkably, force constants of isoelectronic homo- and heteronuclear 4d–4d or 5d–5d bonds of different charge ($\kappa(WOs^{4+}) \approx \kappa(Os_2^{6+})$) or electronic configuration ($\kappa(Ru_2^{6+}, \sigma^2\pi^4(\delta^{nb})^4) \approx \kappa(MoRu^{4+}, \sigma^2\pi^4\delta^2\pi^{*2})$) are very similar. Force constants of 4d–5d bonds are intermediate between those of the isoelectronic 4d–4d and 5d–5d analogues.

Table 3. Physicochemical properties of hetero- and homodimers of Group 6 elements.[a]

parameter	entry	FBO[a]	auxiliary ligands	Cr_2	CrMo	Mo_2	MoW	W_2
bond length [Å]	1	4	Cl_4P_4[b]			2.14(2)	2.21(2)	2.28(2)
	2	4	$(\mu\text{-}O_2CMe)_4$[62]	1.966(14)	2.050(1)	2.0934(8)		
	3	4	$(\mu\text{-}O_2CCMe_3)_4$			**2.088(1)**[10]	**2.080(1)**[32]	**2.194(10)**[c]
	4	4	$(\mu\text{-mph})_4$[57]			2.065(1)	2.091(1)	2.161(1)
	5	3.5	varies[d]			2.164(2)	2.194(2)	2.312
	6	3	$(\mu\text{-}Cl)_2(\mu\text{-}H)Cl_6^{3-}$[e]			**2.372(11)**	**2.445(3)**[21]	< **2.421(17)**
	7	2	$(\mu\text{-}Cl)_2Cl_4(PP)_2$[f]			2.76(2)	2.71(3)	2.68(1)
force constants, $\kappa(M\overset{4}{-}M')$, mdyne [Å][g]	8	4	$(\mu\text{-mph})_4$	4.73	5.04	5.10	**5.47**	**4.71**
	9	4	$Cl_4(PR_3)_4$[60]			**3.54** (R = Me)	**3.84** (R = Me)	**3.65** (R = Bu)
	10	4	$(\text{oep})_2$[37, 72]			2.72	2.89	4.08
^{31}P NMR chemical shifts, δ [ppm]	11	4	$Cl_4(PMe_3)_4$			**– 8.3**	**– 27.9 (Mo); 11.2 (W)**	**– 7.3**
	12	2	$Cl_4(\mu\text{-}Cl)_2(PP)_2$[f]			**≈ 10**	**≈ – 130 (Mo), ≈ 130 (W)**	**≈ – 10**
diamagnetic anisotropy [$Å^3$][h]	13	4	$Cl_4(PP)_2$			-4.45×10^{-3}	-5.1×10^{-3}	-5.7×10^{-3}
$^1(\delta^2) \rightarrow {}^1(\delta\delta^*)$ [nm][i]	14	4	$Cl_4(PMe_3)_4$			582	635	657
rotation barrier [kcal mol^{-1}][37]	15	4	$(\text{toep})_2$			10.8(1)	10.6(1)	12.9(1)
$E^{ox}_{1/2}$ $(MM'^{4+/5+})$ [V][57]	16	4	$(\mu\text{-mph})_4$	1.01 (irrever.)	0.35	0.20	– 0.16	– 0.35
	17	4	$Cl_4(PR_3)_4$			0.64 (R = Me)	0.42 (R = Me)	0.04 (R = Bu)
$E^{ox}_{1/2}$ $(MM'^{4+/3+})$ [V][57]	18	4	$Cl_4(PR_3)_4$			– **1.92** (R = Me)	– **1.86** (R = Me)	– **2.16** (R = Bu)
IP_δ [eV][57]	19	4	$(\mu\text{-mph})_4$	6.8	6.0	5.89	5.60	5.3
	20	4	$Cl_4(PMe_3)_4$			6.44	6.11	5.81
	21	4	$(\mu\text{-}O_2CCMe_3)_4$			6.75	6.34	5.93
$M\overset{4}{-}M$ bond strength [kcal mol^{-1}][10]	22	4	$(\mu\text{-}O_2CMe)_4$	≈ 45	≈ 55	≈ 75		

[a] Entries in bold indicate a non-monotonic trend. See Scheme 1 for structures of oep, toep, mph, and formulas of the bidentate phosphane ligands, electrochemical data versus the saturated calomel electrode (SCE); FBO = formal bond order. [b] The average of six, nine, and five homologues, respectively, containing both monodentate and bridging phosphane ligands.[34–36, 61] [c] The W_2 homologue is not characterized; the value is the average W – W separation in five tetracarboxylate dimers. [d] $[Mo_2(\mu\text{-}SO_4)_4(H_2O)_2]^{3-}$;[63] $[MoW(\mu\text{-}O_2CCMe_3)_4I]$;[21] $[W_2Br_2(\mu\text{-}O_2CCMe_3)_3(thf)_2]$.[64] [e] For Mo_2^{6+}, the average of four compounds; the W_2 congener has not been studied crystallographically; the value is the average W – W separation in two $[W_2(\mu\text{-}Cl)_3Cl_6]^{3-}$ ions,[65, 66] which is likely to be longer than the W–W bond in $[W_2(\mu\text{-}Cl)_2(\mu\text{-}H)Cl_6]^{3-}$ based on comparison of the corresponding Mo_2 derivatives. [f] The average M – M′ separation in three derivatives (PP = dppe, dppm, dmpm).[19] [g] See Figure 3 for metal – metal force constants in bismetalloporphyrins. [h] The average value of two ($[Mo_2X_4(\mu\text{-dmpm})_4]$, X = Br, I),[36] five ($[MoWCl_4(\mu\text{-PP})_4]$, PP = dppe, dppm, dmpm, dmpe (two isomers)),[61] and three ($[W_2X_2(\mu\text{-dppm})_2]$, X = Cl, Br; and $[W_2Cl_4(\mu\text{-dppe})_2]$)[35] homologues, respectively. [i] See ref. [35] for more examples.

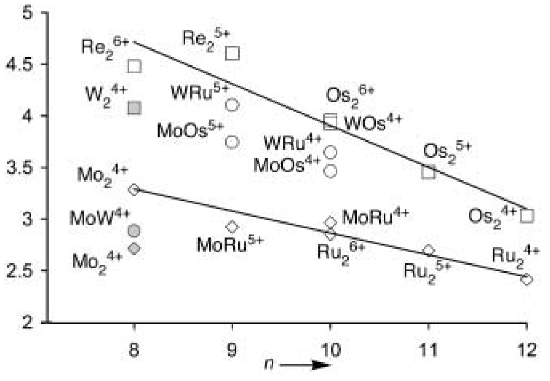


Figure 3. Correlation between the number of d electrons (n), and the force constant κ, of a 4d – 4d (◇), 5d – 5d (□), or 4d – 5d (○) metal – metal bonds in porphyrin-stabilized bimetallic cores. Solid lines are linear least-squares fits of the data for "same-series" bonds. The gray data points represent force constants that may be systematically underestimated.[72]

The substantially different ^{31}P NMR spectroscopy chemical shifts in $[MoWCl_4(PMe_3)_4]$ and $[MoWCl_4(\mu\text{-}Cl)_2(PP)_4]$ relative to those in the homonuclear congeners (Table 3, entries 11, 12) is qualitatively consistent with the partial ionic character of the $^1(\delta^2)$ ground state,[75] which results in a polar $^{\delta-}$Mo–W$^{\delta+}$ bond in a non-centersymmetric Mo – W core. Interestingly, although magnetic anisotropies of N=O and C=O bonds are substantially higher than those of the C=C bonds, anisotropies of the quadruple bonds (Table 3, entry 13), albeit the largest known, increase monotonically from Mo_2 to W_2.[35]

The complex δ manifold of a $(d-d)^8$ metal – metal bond (Figure 4) has been remarkably well studied in the Mo_2^{4+} core.[12, 75, 76] In contrast, only the $^1(\delta^2)-{}^1(\delta\delta^*)$ gap (determined from UV/Vis spectra of $[MoWCl_4(PR_3)_4]$ compounds,[35] Table 3, entry 14) and the low limit on the $^1(\delta^2)-{}^1(d_{xy}d_{xy})$ energy difference (δ barrier[77, 78]) are known for a heteronuclear bond. The δ barrier and the (partially off-

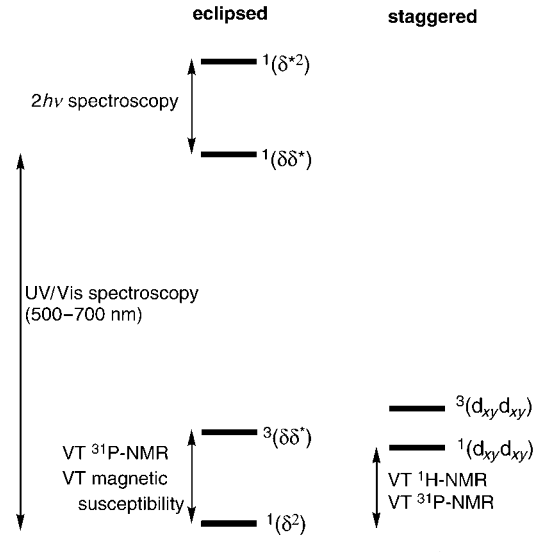


Figure 4. A qualitative diagram of the δ manifold of a $(d-d)^8$ bimetallic core; the ionic states in the staggered conformer are not shown. Experimental methods used to study particular transitions are listed.

setting) difference in noncovalent ligand–ligand interactions in the eclipsed and staggered conformations of an unbridged $(ML_4)_2$ complex are mostly responsible for the barrier of rotation around a quadruple bond. The latter was measured in $[MoW(toep)_2]$ by variable-temperature (VT) ^1H NMR spectroscopy. The ^1H NMR spectrum of a metal—metal-bonded bisporphyrin, wherein at least one of the macrocycles is of lower than fourfold symmetry and carries a group with sufficient magnetic anisotropy to affect the ^1H chemical shifts of the second porphyrin, is temperature-dependent (Figure 5).[79] A standard dynamic NMR spectroscopic analysis yields the rotation barrier; its average value for several $[Mo_2(por)_2]$ dimers ($10.2(5)\ \mathrm{kcal\,mol^{-1}}$)[46, 79] is remarkably close to the δ barrier of the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond derived from magnetic studies ($10.3(5)\ \mathrm{kcal\,mol^{-1}}$).[78] However, the rotation barriers in the $[MM'(toep)_2]$ series (M, M′ = Mo, W) are so similar (Table 3, entry 15) that any trends in the δ barrier may be obscured by decreasing noncovalent interactions from the Mo_2^{4+} to W_2^{4+} derivatives.

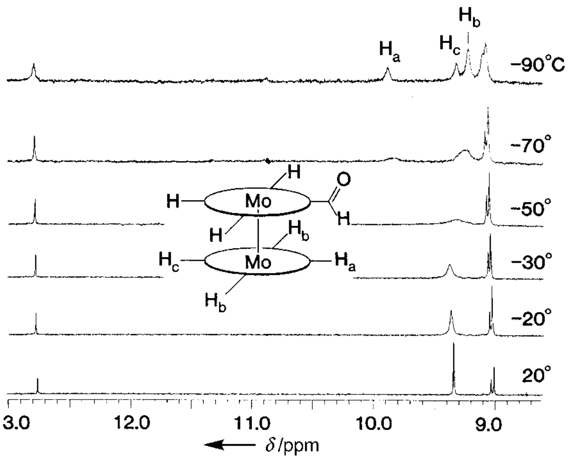


Figure 5. Variable temperature ^1H NMR spectra (300 MHz) of $[(oep)\mathrm{Mo}\overset{4}{-}\mathrm{Mo}(oep\text{-}CHO)]$. Adapted from ref. [79]; (Copyright: The National Academy of Sciences, USA).

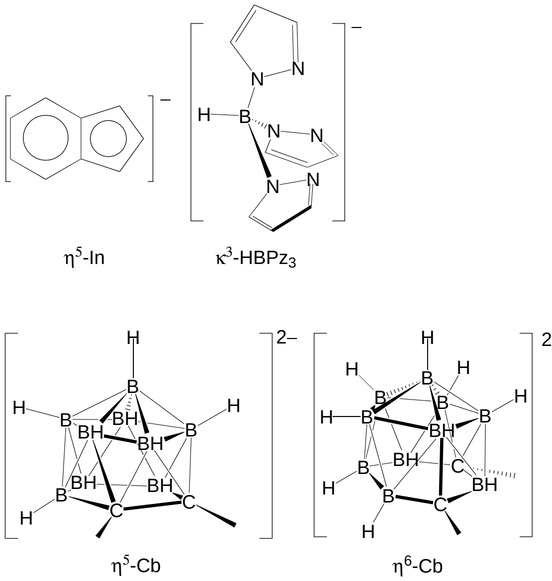
The techniques that have been used to estimate the $^1(\delta^2)-{}^3(\delta\delta^*)$ and $^1(\delta\delta^*)-{}^1(\delta^{*2})$ separations (Figure 4) in Mo_2^{4+} derivatives should be applicable to heterodinuclear cores, but this has not been done to date. The diradical $^1(\delta^2)-{}^3(\delta\delta^*)$ gap (and the δ barrier) was estimated from VT ^{31}P NMR spectroscopic studies of a series of $[Mo_2X_4(PP)_2]$ dimers (X = Cl, Br, I), wherein the bridging phosphane ligands, PP, induce a torsion angle, χ, which varies from 0° in $[Mo_2Cl_4(dmpm)_2]$ to 69° in $[Mo_2Cl_4(dppp)_2]$ (Scheme 1).[77, 78] As χ approaches 45°, the $^1(\delta^2)-{}^3(\delta\delta^*)$ separation decreases so that temperature-dependent $^1(\delta^2)-{}^3(\delta\delta^*)$ spin equilibrium induces paramagnetic shifts in ^{31}P NMR resonance signals. The $^1(\delta^2)-{}^3(\delta\delta^*)$ gap is estimated for each χ value by applying a standard contact-shift model. Extrapolation of these data to $\chi = 0°$ and $\chi = 45°$ yields $^1(\delta^2)-{}^3(\delta\delta^*)$ and $^1(d_{xy}d_{xy})-{}^3(d_{xy}d_{xy})$ separations, respectively. The difference between these two values ap-

Table 4. Representative examples of heterodinuclear transition-metal cores stabilized by π-acidic ligands.

Heterodinuclear core	n(Ve)[a]	Example[b]	M–M′ separation [Å][c] listed example	 saturated analogue	 single bond
ZrRh	30	$[Cp^*Zr(\mu\text{-}OCH_2Ph_2P)_2RhMe_2]$[86]	2.444(1)		3.08
CrMn	30	$[C_6Me_6Cr(\mu\text{-}CO)_3MnCp^*]$[87]			
MoW	32	$[Cp(PMe_3)Mo(\mu\text{-}CR)W(CO)_2(\eta^6\text{-}Cb)]$,[88] $[(CO)(\eta^5\text{-}In)Mo(\mu\text{-}L)W(CO)_2Cb]$ ($L = PPh_2$,[89] CR[90])	2.702(1)	2.708(1), 2.657(2)	2.92
MoRu	32	$[Cp(CO)Mo(\mu\text{-}Cl)(\mu\text{-}CO)Ru(CO)(PPh_3)_2]$[91]			
MoCo,[d] WCo	32	$[(\eta^6\text{-}Cb)(CO)_2M(\mu\text{-}CR)Co(\eta^4\text{-}C_4Me_4)]$[92]	2.540(1)		2.73
WCo	30	$[(\eta^4\text{-}C_4Me_4)Co(\mu\text{-}CO)_3WCp]$[93]	2.356		2.71
	32	$[Cp(O{=})W(\mu\text{-}RC{\equiv}COMe)(\mu\text{-}PPh_2)Co(CO)(PPh_2H)]$, $[Cp(OH)W(\mu\text{-}CR)(\mu\text{-}PPh_2)Co(CO)_2(PPh_2H)]$, $[CpW(\mu\text{-}CR)(\mu\text{-}PPh_2)_2Co(CO)_2]$[96]	2.612(1)	2.758(1)[95]	2.90
MoRh, WRh[d,e]	30	$[Cp(CO)M(\mu\text{-}CO)_2Rh(PPh_3)_2]$[94]	2.588(1)	2.9212(7)	2.84
WFe[e]	32	$[(CO)_3Fe(\mu\text{-}L)W(CO)_2L']$ ($L' = Cp$, $L = C(CO)(SiPh_3)$,[97] CR; $L' = pz_3BH$, $L = PPh_2$, CR) $[(CO)_2Fe(\mu\text{-}CR)(\mu\text{-}CO)(\mu\text{-}dmpm)W(pz_3BH)]$[95, 98]	2.516(1)–2.658(2)		2.79
WRu[e,f]	30	$[(\eta^5\text{-}EtMe_4C_5)W(\mu\text{-}CO)_3RuCp^*]$[99]	2.410(1)		2.90
WRh	30	$[CpLW(\mu\text{-}CO)_2Rh(PPh_3)_2]$ ($L = CO$, C_2H_4)[98]	2.587(1)		2.82
	32	$[(\eta^5\text{-}Cb)(CO)W(\mu\text{-}CO)(\mu\text{-}CR)Rh(PPh_3)_2]$[100]	2.681(1), 2.662(2)	2.796(1)[101]	2.82
WIr[e]	32	$[(\eta^5\text{-}Cb)(CO)_2W(\mu\text{-}CR)IrP_2]$ (P = monodentate phosphane)[102]	2.590(1)	2.876(1)[103]	2.83
WPt[e]	28	$[(\eta^5\text{-}CbR)W(\mu\text{-}CO)_2Pt(PEt_3)_2]$[102]	2.602(1)	2.843(2)	2.78
	30	$[Cp(C_2H_4)W(\mu\text{-}CO)_2Pt(PEt_3)_2]^+$ [104]	2.602(1)	2.795(1)	
MnFe	30	$[(\eta^4\text{-}C_4Me_4)Fe(\mu\text{-}CO)_3MnCp^*]$[87]			
MnRh	30	$[PPh_3(CO)_2Mn(\mu\text{-}CO)_2Rh(PPh_3)_2]$[94]			
FeCo, FeRh, FeIr	32	$[(\eta^6\text{-}C_6H_6)Fe(\mu\text{-}CO)_2MCp^*]$[105]			
ReRh, **ReIr**[d]	32	$[(PCy_2)_2Re(\mu\text{-}PCy_2)_2ML_2]$ (L = ½ 1,5-cod, PMe_3)[106]	2.6573(5)		2.92
ReRh	30	$[CpHRe(\mu\text{-}CO)_2Rh(PPh_3)_2]$[106]	ca. 2.54		2.90
CoRh	32	$[Cp^*Co(\mu\text{-}CO)(\mu\text{-}L)RhCp^*]$ ($L = CO$, CH_2)[107]	2.4040(5)		2.60
CoIr	32	$[LCo(\mu\text{-}CO)_2IrL']$ (L, L′ = Cp, Cp*)[108]	2.45(2)	2.624(1)	2.66
RhIr	32	$[Cp^*Rh(\mu\text{-}CO)_2IrCp^*]$[108]			

[a] The number of valence electrons in the M–M′ core; $n = 34$ corresponds to an electronically saturated dinuclear organometallic complex with a single M—M′ bond if both metal centers satisfy the 18-electron rule. [b] $Cp = C_5H_5^-$; $Cp' = C_5H_4Me^-$; $Cp^* = C_5Me_5^-$; $R = \text{-}C_6H_4(p\text{-}Me)$; see Scheme 4 for chemical structures of In, $HBpz_3$, and Cb. [c] The "saturated analogue" is a complex derived from the corresponding unsaturated compound by ligand addition; the "average single" bond refers to the M—M′ separation averaged over *all* structures designated as having a single M—M′ bond in CCSD (the October 2001 release). [d] A MM′ core in bold indicates the core was studied crystallographycally. [e] See ref. [102] for additional examples. [f] See ref. [109] for additional examples.

proximates to the δ barrier. Notably, even at $\chi = 45°$, where the $d_{xy}-d_{xy}$ overlap is annihilated, $^1(d_{xy}d_{xy})$ remains lower that $^3(d_{xy}d_{xy})$ because of configuration interactions.[80] A series of MoW^{4+} derivatives with varying values of χ, which would be necessary to extend this method to heterodinuclear metal–metal bonds may be obtained from $[MoWCl_4(PMe_3)_4]$ by using the well-developed phosphane-substitution method.[35, 36]



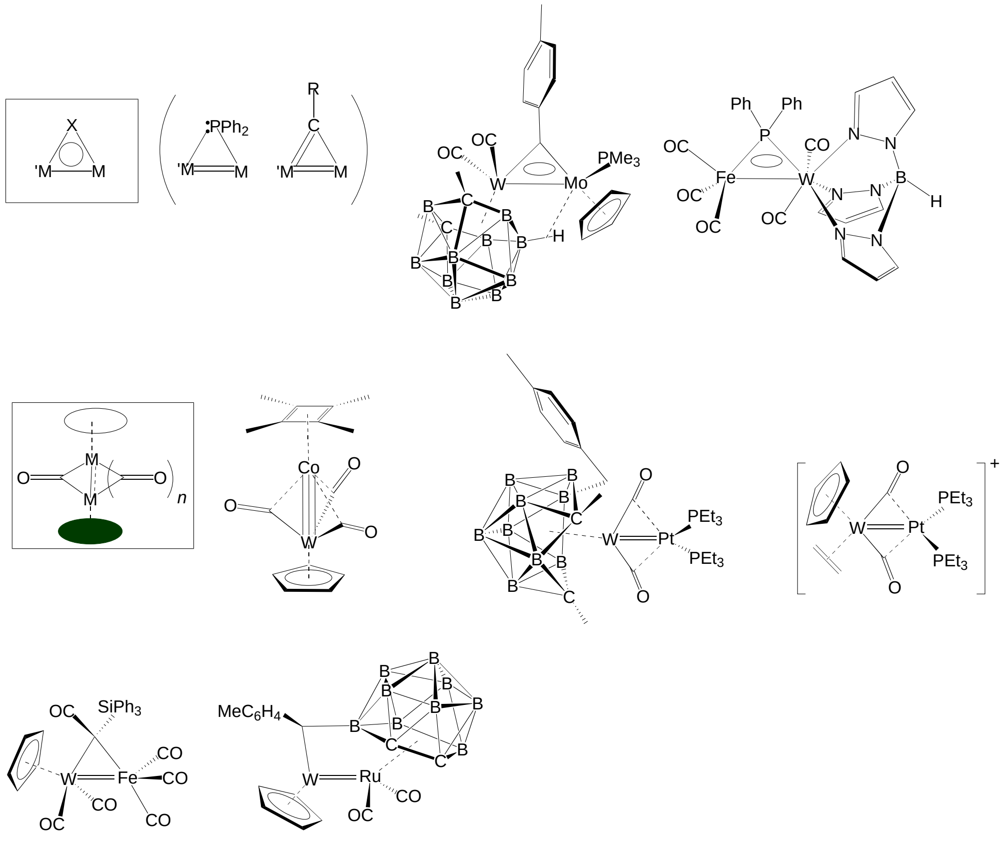
Scheme 4. Select polyhapto (polydentate) ligands used to stabilize unsaturated heterodinuclear cores in organometallic complexes.

The ionic ($^1(\delta^{*2})$, $^1(\delta\delta^*)$) states of the Mo_2^{4+} core have been studied by two photon spectroscopy (Figure 4).[76] Induced fluorescence from the $^1(\delta\delta^*)$ state is observed upon two-photon $^1(\delta^2 \rightarrow \delta^{*2})$ excitation followed by rapid nonradiative decay to the $^1(\delta\delta^*)$ state. The $^1(\delta\delta^*)-{}^1(\delta^{*2})$ gap (4800 cm^{-1}), estimated from the difference in the $^1(\delta^2 \rightarrow \delta\delta^*)$ and $^1(\delta^2 \rightarrow \delta^{*2})$ transition maxima, is comparable to the $^1(\delta^2)-{}^3(\delta\delta^*)$ gap (4840 cm^{-1}) measured by VT ^{31}P NMR spectroscopy.

Finally, the difference between the energies of the electron in a singly occupied δ and δ* orbitals (ΔW), which is indicative of the strength of the δ interaction, is given by the $^2(\delta \rightarrow \delta^*)$ transition frequency in optical absorption spectra of $(d-d)^{7/9}$ dinuclear compounds. The latter should be easily accessible by one-electron oxidation or reduction of corresponding quadruple-bonded heterodinuclear complexes. Unfortunately, optical methods are not easily applicable to metalloporphyrins, as their absorption spectra are dominated by the porphyrin chromophore.

2.4. Reactivity

Reactivity of heterodinuclear complexes has been little studied, and again most available data are on Group 6 metals. The susceptibility of MoW^{4+} and $MoCr^{4+}$ cores toward



1 **2**

Scheme 5. Structures of representative unsaturated heterodinuclear organometallic compounds arranged by structural type. In carboranes only those B-bound H atoms that participate in agostic interactions are shown.

oxidative and nucleophilic additions appears intermediate between that of the more robust Mo_2^{4+} and more reactive Cr_2^{4+} and W_2^{4+} congeners. For example, unlike W_2^{4+} cores, the Mo_2^{4+}, and MoW^{4+} analogues are not oxidized by acetic acid. On the other hand, the Cr$\overset{4}{-}$Mo bond is readily cleaved by Cl^- ions[81] and acetonitrile[28] (in acidic media), to yield mononuclear Cr species and Mo_2 dimers. Likewise, $[MWCl_4P_4]$ but not the Mo_2 analogue, is oxidized by CH_2Cl_2 (to $[MWCl_6P_4]$, M = Mo or W; P = mono- or bidentate phosphanes)[19] and oxidative addition of HCl to the MoW^{4+} and W_2^{4+} cores occurs at significantly milder conditions than to the Mo_2^{4+} core.[20, 82]

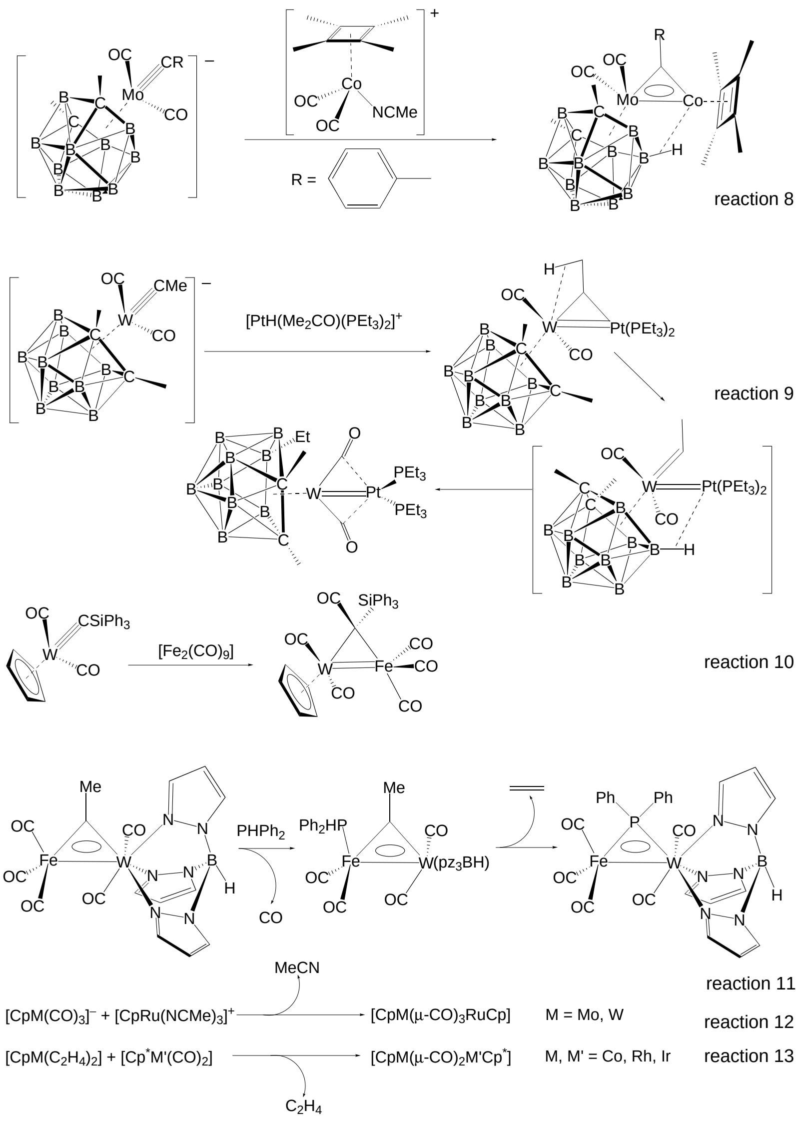
In $[CrMo(\mu\text{-}O_2CMe)_4]$ the modest affinity of the Cr^{II} center to axial ligation contrasts dramatically with that of $[Cr_2(\mu\text{-}O_2CMe)_4]$, which can not be isolated in the condensed phase without axial ligands or without strong intermolecular association through carbonyl oxygen atoms.[10] Higher covalency of the Mo–Cr bond (Section 2.1.) was suggested[51] to account for this difference. In $[MoWCl_4(PMePh_2)_4]$ Mo-bound phosphanes are more labile, as could be expected, thereby allowing synthesis of a heteroleptic heterodinuclear complex, $[(PMe_3)_2Cl_2MoWCl_2PMePh_2)_2]$.[34] Finally, dimerization of MoW^{4+} moieties yields approximately equimolar amounts of both isomers of a rectangular Mo_2W_2 core, which suggests the absence of preference for formation of homo- over heterometallic bonds.[83]

3. Electronically Unsaturated Heterodinuclear Organometallic Species

In a dimetallic core stabilized by π-acidic ligands (e.g. CO), the metal–metal bonding, which is significantly affected by extensive π-acceptor-ligand–metal interactions,[16] does not necessarily lead to concentration of the electron density in the immediate space between two metal centers. These interactions do not necessarily lead to concentration of the electron density in the immediate space between two metal atoms. Identification of specific metal–metal MOs is often not possible or productive and assignment of a metal–metal bond order often relies on the assumption that at least one metal center should satisfy the 18-electron rule. The situation is even more ambiguous if the 18-electron configuration is not obligatory for either metal (e.g. those in Groups 4, 5, 8, and 9). While it is debatable if the metal–metal interactions in unsaturated dinuclear organometallic compounds (i.e. those with 32 or fewer valence electrons) should be viewed as multiple metal–metal bonds,[16, 84] such complexes manifest structures and reactivities which are related to those of dinuclear complexes with Werner-type ligands.

A recent explosion of interest in heterodinuclear organometallic compounds[14, 85] is motivated in large part by the promises of substrate activation by the bimetallic species, particularly by reactions based on the dissymmetry of a heterodinuclear core. Although most such complexes are electronically saturated, unsaturated heteronuclear organometallic species are particularly attractive as their greater reactivity is not dependent on ligand or dimer dissociation to create reaction sites in the coordination spheres of the metal center(s). Such complexes have also been studied as precursors for mixed-metal clusters[85] and models of materials with strong metal-support interactions (SMSI).

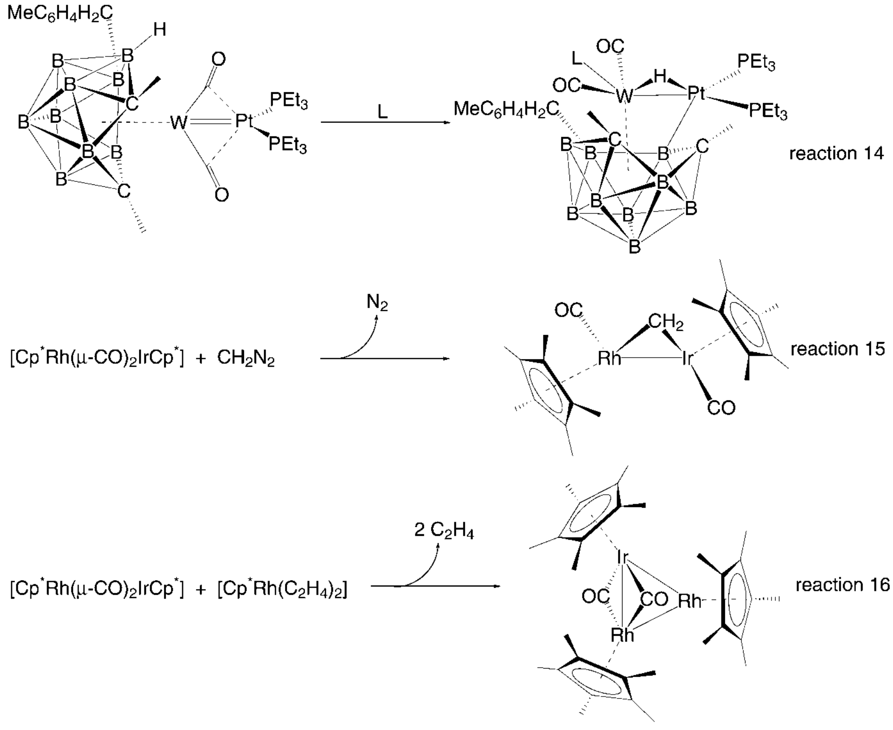
Unsaturated heterodinuclear organometallic complexes are significantly more numerous than their counterparts without π-acidic ligands and such complexes are known for most transition metals (Table 4).[86–109] Although their coordination spheres may be made up of a variety of donor molecules, most contain at least one polyhapto (or chelating) ligand (Scheme 4). These ligands sterically disfavor a nucleophilic attack on, or oligomerization of, unsaturated metal cores thereby stabilizing the complexes.[110]



Scheme 6. Representative syntheses of unsaturated organometallic heterodinuclear complexes. In carboranes, only those B-bound H atoms that participate in agostic interactions are shown.

The dominant structural motifs (boxed structures, Scheme 5) are based on 1) a trinuclear core resulting from a metal–metal bond bridged by either an alkylidyne or a phosphide group and 2) on the $[Cp_2M_2(CO)_x]$ ($Cp = C_5H_5^-$) structure,[16] although heterodimers often contain a single Cp-related ligand. Other structures are less common (compounds **1** and **2**, Scheme 5).

The dimetallocyclopropene-type complexes, the synthesis and chemistry of which has been developed by F. G. A. Stone and co-workers,[102] have been obtained by addition of a metal alkylidyne to a mononuclear complex with labile ligand(s), occasionally followed by other transformations (Scheme 6, Reactions 8–10). Some μ-alkylidyne complexes can be converted into μ-phosphide analogues (Reaction 11). Syntheses of other heterodimers include reactions between $[LM(CO)_x]^-$ ions (L is a ligand in Scheme 4) and labile cationic complexes and recombination of unsaturated mononuclear fragments generated in situ (Reactions 12 and 13, respectively).



Scheme 7. Representative reactions of unsaturated heterodinuclear organometallic complexes. In the carborane only the B–H unit that adds to Pt is shown.

The intermetal distances in unsaturated organometallic compounds are significantly shorter than those in structurally related saturated MM′ cores (Table 4). Although the latter often contain an additional ligand, which increases unfavorable noncovalent interactions around the metal, the observed metal—metal-bond elongation is significantly greater than could be expected from the more congested arrangement alone. This effect indicates that electronic saturation leads to the population of MOs with M–M′ antibonding character.[16]

The reactivity of unsaturated heterodinuclear organometallic compounds (Scheme 7) is often consistent with the presence of multiply bonded MM′ cores. This reactivity includes inertness to substrates that react readily with mononuclear metal centers with half the valence electrons of the dinuclear core. For example, neither 30-electron $[CpHRe(\mu\text{-}CO)_2Rh(PPh_3)_2]$ nor 32-electron $[Cp(CO)_2Mo(\mu\text{-}CO)(\mu\text{-}Cl)Ru(CO)(PPh_3)_2]$ reacts with H_2,[91, 106] even though H_2 readily adds to mononuclear 16-electron Rh and Ru centers. In contrast, in certain carborane-stabilized complexes coordination of an exogenous ligand to one metal center induces intramolecular B–H activation at the other metal center (Reaction 14, Scheme 7). In addition, ligands, such as SO_2, CH_2 (from CH_2N_2), and metal fragments isolobal with CH_2 (e.g. RhCp*; $Cp^* = C_5Me_5^-$) add readily across MM′ bonds (Reactions 15 and 16).

4. Summary and Outlook

Stabilization of heterodimetallic cores by Werner-type ligands yields complexes wherein the ligands do not significantly perturb the metal–metal bonding. These complexes provide an opportunity to probe fundamental issues of bonding between transition metals and to discover new types of chemical bonds. An intriguing issue is the origin of the "inverted" ground-state configuration of Group 6 and 8 metal–metal cores (e.g. $\sigma^2\pi^4\delta^2\pi^{*2}$ in $MoRu^{4+}$ compared to $\sigma^2\pi^4(\delta^{nb})^4$ in the isoelectronic isostructural Ru_2^{6+} derivatives). More systematic studies of the δ MOs in MoW^{4+} cores, accessible with existing synthetic and physical techniques, may reveal interesting differences with the well-studied Mo_2^{4+} δ manifold. However, the lack of preparative methodologies remains the major impediment to systematic studies of multiple bonds between different transition-metal ions. Only solid-state high-vacuum pyrolysis of metalloporphyrins is applicable to a broad range of transition metals. In contrast, with the exception of $[Ti(\mu\text{-}OCMe_2CH_2PPh_2)_3Rh]$, no heterodinuclear species in non-porphyrin environments are known outside Group 6.

Metal–metal bonding in unsaturated dinuclear organometallic species is significantly attenuated by π-acceptor-ligand–metal interactions. These complexes are relatively easily accessible and include pairs of almost every transition-metal atom, thereby comprising a pool of compounds which can be searched for novel reactivities. Such complexes have a potential use as catalysts wherein one metal center serves as a reservoir of reducing equivalents for multielectron processes, such as small molecule activation.[111] A number of processes, if performed by a mononuclear catalyst, would require unreasonably large changes in its oxidation state and thus are unlikely to be catalytic. Unsaturated heterodimetallic compounds may also be synthetically advantageous precursors to higher-nuclearity mixed-metal clusters.

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