Towards Rational Syntheses of the Elusive Metallocarbohedrenes: Density Functional Prescriptions for Electronic and Geometric Structures

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Abstract: The metallocarbohedrenes are binary molecular clusters containing metal atoms linked by acetylenediide C_2 groups. Hundreds of these molecules have been generated, detected and reacted in the gas phase since the prototype, $[Ti_8(C_2)_6]$, was reported in 1992, but none has yet been synthesised pure in bulk: the time gap between detection and preparation increasingly exceeds that of the fullerenes. We report here the results of density functional calculations of geometrical and electronic structure of more than 150 postulated metallocarbohedrenes, stabilised by terminal ligation, in order to recognise the more electronically favourable and less reactive targets. At least 38 metallocarbohedrenes have been identified as having a spin singlet ground state, with a relatively large (> 0.5 eV) energy gap between HOMO and LUMO, and an appropriate HOMO energy. In addition, a considerable number of electronically stable metallocarbohedrenes are predicted to have highly paramagnetic ground states, potentially useful in molecular magnetism. The geometrical principles for enclosing but unstrained coordination of metal sites by terminal ligands are outlined. Mechanisms for rational syntheses are considered in the context of reaction type and precursor selection, including issues of oxidation and reduction, and kinetic versus thermodynamic control. This leads to many diverse reactions suggested for the rational syntheses of metallocarbohedrenes. Some preliminary experimental results are presented.

Keywords: cluster compounds · density functional calculations · electronic structure · geometric structure · ligands · metallocarbohedrenes · synthesis design

Introduction

Metallocarbohedrenes[1] are molecules that contain only metal and carbon, and so far are known only in the gas phase. The prototype metallocarbohedrene, $[Ti_8(C_2)_6]$, reported in 1992,[2] was formed as a cation by expansion of $Ti_{x(g)}$ clusters in low-pressure methane, and detected by mass spectrometry. Since that time there have been numerous publications dealing with the formation, detection and reactions of metallocarbohedrenes in the gas phase, and theoretical evaluations of their structures and properties. More than one hundred metallocarbohedrenes and their relatives and derivatives have been reported: they contain C_1, C_2, C_3 and possibly higher C_n moieties, clustered with metals.[3–7]

However, there has been no substantiated report of the preparation of any pure metallocarbohedrene in a condensed phase.[8] The state of metallocarbohedrene chemistry can be compared with that of fullerene chemistry before the Huffman–Kratschmer experiments of 1990:[9] intriguing and unconventional molecules are known in the gas phase, but without bulk samples. Structural analogies between elemental fullerenes and binary metallocarbohedrenes were evident from the outset,[2, 10] but now there is a wider variety and probably larger number of metallocarbohedrenes than of fullerenes.

The principal constituent of the metallocarbohedrenes is the C_2 group bound to a number (often four) of metal atoms. They can also be regarded as binary metal acetylenediide (C_2^{2-}) clusters,[11] but are distinct from the better known acetylide clusters containing RC_2^-.[12, 13] Diagram **1** indicates characteristic features of metallocarbohedrenes, with σ and π components of C_2 interacting with different M atoms, while **2** symbolises the related metal carbide (C_1) nanoclusters that sometimes form with metallocarbohedrenes in the gas phase.[4, 7] Both types contain peripheral undercoordinated metal atoms.

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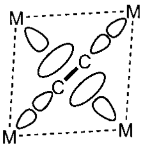

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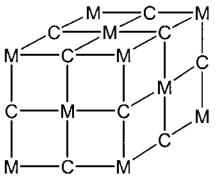

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There are two general approaches to the generation of bulk sample of species such as metallocarbohedrenes: one is *preparation*, relying on thermodynamic stability and therefore using high-energy processes; the second is rational organometallic *synthesis*, designed mechanistically, involving controlled assembly via intermediates under much less energetic conditions, as molecular *chimie douce*.[14] For fullerenes the high-energy preparative methods are successful, but the rational chimie douce approach is still a challenge.

The high-energy preparation of metallocarbohedrenes (met-cars) needs to avoid the thermodynamic sink of non-molecular metal carbide solids, and therefore is likely to involve condensation from the gas phase into a matrix of ligands that can cap the peripheral coordination sites. Heterogeneous solids with properties assignable to met-cars have been obtained by high-energy arc methods, but they were too reactive to be isolated or purified, and many other species were present.[8] In this paper we focus instead on the rational syntheses of binary metal acetylenediide clusters. We will focus on the protypical and most commonly observed composition $\{M_8(C_2)_6\}$, which has also been the subject of many theoretical investigations.[6, 7, 10, 15–21]

Structure: A considerable number of symmetric structures have been proposed and evaluated for prototypical $[Ti_8(C_2)_6]$, with the T_d structure **3** understood to be the most stable.[6, 7, 10, 15, 16, 19, 22, 23] This structure **3** (Figure 1) is best conceived as a tetrahedron of inner metal atoms ($^{i}M_4$) tetracapped with four outer metal atoms ($^{o}M_4$), with the C_2 groups aligned with the long diagonals of the six $^{i}M_2{}^{o}M_2$ rhombi over the surface of the $^{i}M_4{}^{o}M_4$ tetracapped tetrahedron.

In **3** each C_2 group forms two σ bonds to the two ^{o}M atoms, and the two π-bonding orbitals of C_2 are directed towards ^{i}M. The local coordination of each ^{o}M is $^{o}M(\sigma\text{-}C_2)_3$ in a spire motif (**3s**, Figure 1),[21, 24] while the local coordination of each ^{i}M is $^{i}M(\pi\text{-}C_2)_3$ in a wheel motif (**3w**). The $^{i}M-^{i}M$ and $^{i}M-^{o}M$ distances are variable under the T_d symmetry of **3**.

Isomers of $\{M_8(C_2)_6\}$ arise by rotation of C_2 groups over the M_4 quadrilaterals on the surface of the M_8 polyhedron, as first enunciated by Benard et al.[16] There are seven topological isomers containing C_2 groups each bonded only in σ and π modes to the M_8 polyhedron, and the other six (with symmetry lower than that of **3**) are illustrated also in Figure 1, and identified by their point group symmetry. In these other six isomers all metal atoms are bound by both σ-C_2 and π-C_2, except that in C_{2v} two M atoms have only π-C_2 (**3w**) and two M atoms have only σ-C_2 (**3s**), in the D_{3d} prolate two M atoms have only σ-C_2 (**3s**), and in the D_{3d} oblate two M atoms have only π-C_2 (**3w**). These isomers are relevant to the question of theoretical prediction of favourable synthesis targets, because some of the $\{M_8(C_2)_6\}$ cores are calculated to have total energies not very different from that of **3**. Table 1 presents our calculated relative energies, for M = Ti, Zr, V, Nb, Cr, Mo and Fe. Note that for $[V_8(C_2)_6]$ and $[Nb_8(C_2)_6]$ the C_{2v} isomer is as stable as **3**, and for $[Fe_8(C_2)_6]$ all seven isomers have comparable energies. The relative energies of additionally ligated isomers of the $\{M_8(C_2)_6\}$ core, relevant here, are not yet known.

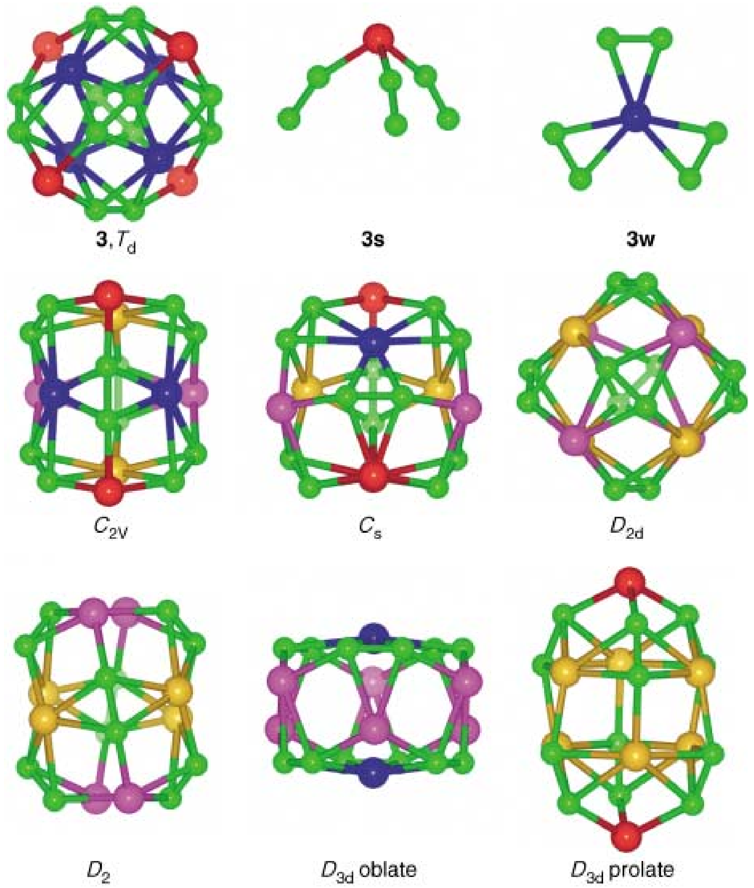

Figure 1. Structures and structural components of metallocarbohedrenes $\{M_8(C_2)_6\}$: C green. Complex **3** is the T_d isomer, with an inner tetrahedron of metals ^{i}M (blue) capped with an outer tetrahedron of metals ^{o}M (red), generating six rhombi $\{(^{i}M)_2(^{o}M)_2\}$ each craddling a C_2 group over the long diagonal of the rhombus. Complex **3** is comprised of four spire substructures $^{o}M(\sigma\text{-}C_2)_3$ (**3s**, M red) and four wheel substructures $^{i}M(\pi\text{-}C_2)_3$, (**3w**, M blue). In the other six isomers, labelled C_{2v}, C_s, D_{2d}, D_2, D_{3d} oblate and D_{3d} prolate, the metal atoms are differentiated by their coordination, as $M(\sigma\text{-}C_2)_3$ red, $M(\pi\text{-}C_2)_3$ blue, $M(\sigma\text{-}C_2)_2(\pi\text{-}C_2)$ magenta, $M(\sigma\text{-}C_2)(\pi\text{-}C_2)_2$ yellow.

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Table 1. Calculated (nonlocal BLYP functional) energies [kcal mol^{-1}] for isomers of uncharged $\{M_8(C_2)_6\}$, relative to that of **3**.

$\{M_8(C_2)_6\}^0$	**3**	C_{2v}	C_s	D_{2d}	D_2	D_{3d} oblate	D_{3d} prolate
$\{Ti_8(C_2)_6\}$	0	8	27	32	43	47	41
$\{Zr_8(C_2)_6\}$	0	13	37	46	55	59	60
$\{V_8(C_2)_6\}$	0	−3	17	32	47	40	15
$\{Nb_8(C_2)_6\}$	0	1	20	42	54	50	23
$\{Cr_8(C_2)_6\}$	0	22	33	77	67	52	50
$\{Mo_8(C_2)_6\}$	0	43	37	96	81	105	66
$\{Fe_8(C_2)_6\}$	0	1	−6	6	0	−2	−10

Terminal ligation: In **3** and some other isomers of $\{M_8(C_2)_6\}$ the M atoms at the peak of the spires are exposed with trigonal pyramidal coordination. The undercoordination of these atoms is reflected in the experimentally observed addition reactions, with gaseous ligands such as water, ammonia, alcohols, ethene, benzene and acetonitrile.[5, 25] These addition reactions have been investigated theoretically:[22, 26] the ligation energies for ligands such as NH_3, η^6-C_6H_6 and CO are calculated to range from 15 to 35 kcal mol^{-1} per ligand, and are larger for ^{0}M than for ^{i}M.

In the context of rational synthesis of metallocarbohedrenes it is assumed that the exposed metal sites will be coordinated by additional ligands, in order to reduce their reactivity and to inhibit the undesirable condensation of the target molecules towards thermodynamically stable nonmolecular metal carbides. This capping ligation is a key component of the investigation reported here.

Redox states: In the metallocarbohedrenes, such as **3**, electron delocalisation is possible, and the electronic structures possess some non-innocence which reduces the value of any formal assignment of atomic oxidation states. For example, alternative extreme formal oxidation states for ^{i}M, ^{o}M, and C_2 in **3** are $(^iM^{III})_4(^oM^0)_4(C_2^{2-})_6$, $(^iM^0)_4(^oM^{III})_4(C_2^{2-})_6$, $(^iM^{III})_4(^oM^{III})_4(C_2^{4-})_6$ or $(^iM^0)_4(^oM^0)_4(C_2^{0})_6$; there are other possibilities with intermediate oxidation states. Nevertheless, it is reasonable to expect that the ^{o}M(σ-C_2)$_3$ coordination (**3s**) would be associated with a more positive oxidation state for ^{o}M and the ^{i}M(π-C_2)$_3$ coordination (**3w**) would be associated with a less positive oxidation state for ^{i}M, and the formal oxidation state assignment $(^iM^0)_4(^oM^{III})_4(C_2^{2-})_6$ is argued in the literature.[18] In isomers other than **3** there is more variable coordination and more variable distribution of formal metal oxidation state. In our calculations we are concerned only with the redox level of the overall complex. The reactants in the proposed reactions do have better defined redox states, and will be discussed. Note that the average metal oxidation state for $[M_8(C_2^{2-})_6]^0$ is +1.5, which is relatively reduced.

Expectations, objectives, strategies and criteria: The components to be assembled to form a metallocarbohedrene of structure **3** are six C_2 units and eight M(L) fragments. An obvious reaction type to form metal acetylides is elimination of Me_3XCl from acetylide reactants $Me_3XC_2XMe_3$ (in which X = Si or Sn) and chlorometal precursors. One component should be able to form three σ bonds with acetylides (outer metal), while the inner metal should be π-coordinated to the alkynes. Hence Equation (1) can be written, in which M and M′ with their terminating ligand systems L and L′ generate the inner (**3w**) and outer (**3s**) moieties of **3**, respectively. Here L and L′ symbolise quite general ligand systems: monodentate, multidentate and multiple ligands. It is also expected that a low-valent precursor LM, especially of a late transition metal, would form strong π bonds that would bring several acetylides into close proximity (**3w**), and hence leading to a template effect that would favour the formation of the metallocarbohedrene.

$$4\,LM + 4\,L'M'Cl_31 + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(LM)_4(C_2)_6(M'L')_4] + 12\,Me_3SiCl \qquad (1)$$

Equation (2) provides a combination of alternative reactant oxidation states. There is a mechanistic correspondence between the number of MCl bonds in each precursor and the number of M(σ-C_2) connections formed by it, and, therefore, Equation (2) would formally lead to a metallocarbohedrene containing four M(σ-C_2)(π-C_2)$_2$ and four M(σ-C_2)$_2$(π-C_2) groups, that is, isomers D_2 or D_{2d}. Further, it is formally possible to combine the precursor types LM, LMCl, $LMCl_2$ and/or $LMCl_3$ in other proportions to yield the other isomers in Figure 1. For example, Equation (3) would target isomers C_s and C_{2v}, Equation (4) would target the D_{3d} prolate isomer, and Equation (5) would target the D_{3d} oblate isomer.

$$4\,LMCl + 4\,L'M'Cl_2 + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(LM)_4(C_2)_6(M'L')_4] + 12\,Me_3SiCl \qquad (2)$$

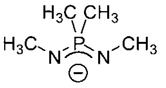
$$2\,LM + 2\,LMCl + 2\,LMCl_2 + 2\,LMCl_3 + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(LM)_8(C_2)_6] + 12\,Me_3SiCl \qquad (3)$$

$$6\,LMCl + 2\,LMCl_3 + 6Me_3SiC_2SiMe_3 \longrightarrow [(LM)_8(C_2)_6] + 12\,Me_3SiCl \qquad (4)$$

$$2\,LM + 6\,LMCl_2 + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(LM)_8(C_2)_6] + 12\,Me_3SiCl \qquad (5)$$

There are many possibilities for M, M′, L and L′ and the scope of these reactions will be discussed in more detail below. At this point there are two general approaches: one is to focus on the reactants and their properties relevant to reactions such as those in Equations (1) and (2); the other approach is to focus on the products and their favourable properties and stabilities. Our strategy is to first survey the possible products according to electronic criteria and geometrical criteria for stability. Pure metallocarbohedrenes in condensed phases are expected to be reactive, and so syntheses should target the least reactive compounds. Undesirable reactivity can arise 1) from the presence of exposed undercoordinated atoms, 2) from the presence of unpaired electrons initiating radical processes, 3) from accessible low-lying excited states or 4) from oxidation or reduction. Therefore, the electronic criteria for stability are that the molecules have 1) closed ground state electronic configurations, 2) relatively large energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and 3) HOMO energies neither too high (and so subject to oxidation) or too low (and subject to reduction). The geometrical criterion is that the metal atoms be coordinatively saturated and protected from reaction, without excessive steric crowding.

The different types of ancillary ligands L considered here are: a) neutral Lewis base σ donors (NR_3, PR_3), b) anionic Lewis base σ donors (Cl^-, O^{2-}), c) neutral π acceptor (CO), d) anionic π acceptor (CN^-), e) alkyl (CR_3^-) and f) π-aryl (η^5-$C_5H_5^-$, η^6-C_6H_6). The ligand types η^2-C_2H_4 and η^1-aryl have not been included in this analysis. We include also some results with the anionic iminophosphanamide ligand **4** with allylic characteristics, for reasons discussed below. The CN^- ligand has bridging ability: it could substitute C_2 in the metallocarbohedrenes, or bridge between them, but these are not necessarily undesirable properties.



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The ligand types a) and e) used in our calculations are relatively small, usually R = H, in order to simplify the calculations, but it is clear that they can be increased in volume through R as may be necessary without significant change in electronic structure, and without affecting the conclusions about ligand influence on electronic structure of the metallocarbohedrenes. In a later section we model and evaluate aspects of the ligand volume required.

All of the calculations reported here are for the metallocarbohedrene structure **3**. This has high symmetry, accelerating the calculations and thereby facilitating exploration of a wide range of M and L. It is not feasible to calculate so many other isomers or other compositions. Structure **3** embodies the principal structural features, and in broad terms the electronic principles relating to M and L in **3** are expected to be transferable to other similar isomers.

First- and second-row transition metals in Groups 4–10 have been considered. Although there are no metallocarbohedrenes yet observed for Group 10, there are for Cu in Group 11, although with different compositions.[27] In recent years intriguing compounds containing C_2 bound to and enclosed by variable numbers of Ag atoms[28] (and to Cu[29]) have been reported. While the structures and formation of these are not directly comparable with standard metallocarbohedrenes, they provide stimulation.

Computational Methods

Density functional calculations with double numerical basis sets including polarisation functions, as implemented in the program DMol,[30, 31] were used with the gradient corrected functional BLYP,[32] which has been successful in other calculations of metallocarbohedrenes.[19–21] The all-electron wave-functions were spin unrestricted. The addition of scalar relativistic corrections for second-row transition metals had negligible influence. Some results validating the density functional procedure are provided below. The calculational strategy involved geometry optimisation of each postulated structure, following the aufbau configuration without specification of the electronic state, to obtain the lowest energy electronic configuration. In addition, smearing techniques allowing partial occupancy of orbitals in the vicinity of the Fermi level[30] were incorporated during optimisation, to enable the energy minimization to access alternative close-lying electronic states and to find the local minimum in geometry-electronic space. Once the lowest energy electronic state had been found, it was optimised with this smearing reduced, in order to define this ground electronic state of the molecule. Each postulated structure was optimised in high symmetry, except where the final gradients indicated a false minimum that could have been caused by excessive symmetry. The behaviour of the gradients in the final stages of optimisation was examined, and, in most cases, indicated a minimum (rather than saddle point) in the potential. Calculations of second derivatives confirmed this for the following species with representative ligands and metals, $[(^{i}Ti{-}CN)_4(C_2)_6(^{o}Cr{-}CN)_4]^{2-}$, $[^{i}Ni_4(C_2)_6(^{o}Ti{-}CH_3)_4]$, $[^{i}Ni_4(C_2)_6(^{o}V{-}O)_4]$, $[^{i}Ni_4(C_2)_6(^{o}Ti{-}Cl)_4]$: the calculated frequencies[33] are valuable for the characterisation of synthesis products. Frequency calculations for some other species—$[(^{i}Ti{-}Cl)_4$-$(C_2)_6(^{o}V{-}Cl)_4]$, $[(^{i}Nb)_4(C_2)_6(^{o}Mo(CO)_3)_4]$ and $[(^{i}Ni{-}Cl)_4(C_2)_6(^{o}Ru{-}PH_3)_4]$—in symmetry T_d yield some imaginary frequencies which indicated that the energy minimum has lower symmetry.

Molecular oxidation states (i.e., net charges) were assessed by the energies of the highest occupied molecular orbitals (HOMO). As calibration of this, our calculational method yielded –3.96 eV for the energy of the HOMO of ferrocene, $[Fe(\eta^5\text{-}C_5H_5)_2]$, and –9.24 eV for the energy of the HOMO of the ferrocenium cation, $[Fe(\eta^5\text{-}C_5H_5)_2]^+$. Thus redox stable species would be expected to have HOMO energies in this range. Since a criterion for electronic stability is a large HOMO–LUMO gap (abbreviated HL gap) together with a suitable HOMO energy, the molecular orbital sequence for each species calculated was inspected for larger energy gaps near the HOMO that could become the HOMO–LUMO separation in new species with different net charge and/or different identities for metals and ligands. Many of the metallocarbohedrene targets identified in this investigation were generated this way.

As an assessment of the accuracy of our calculation procedure, Table 2 contains dimensions for the related known molecule $[(\eta^5\text{-}C_5H_5)_4Fe_4(HCCH)_2]$ (**5**), which contains acetylene coordinated between four iron atoms.[34] In general the BLYP functional slightly underbinds, and the VWN functional slightly overbinds.

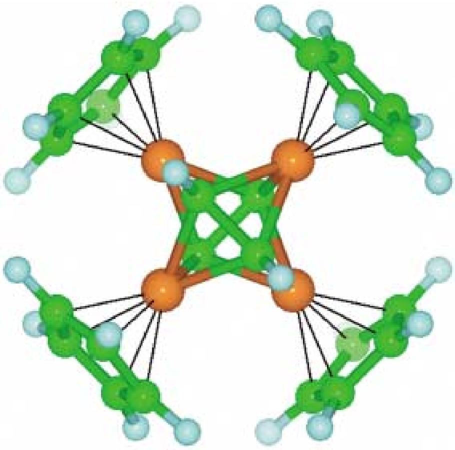

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Table 2. Experimental and calculated distances [Å] for **5** (symmetry D_2).

Dimension	Experimental	BLYP	VWN
Fe–Fe	2.49, 2.49	2.55, 2.55	2.45, 2.45
Fe–C (σ-CHCH)	1.93	1.95	1.88
Fe–C (π-CHCH)	1.98, 1.98	2.02, 2.02	1.95, 1.95
Fe–C (η^5-C_5H_5)	2.06, 2.02, 2.04, 2.07, 2.08	2.17, 2.16, 2.15, 2.16, 2.19	2.06, 2.05, 2.05, 2.06, 2.08
C–C (C_2H_2)	1.50	1.52	1.51

Results

The first objective was to survey M and L in structure **3** to identify species meeting all or most of the electronic criteria. Table 3 summarises the electronic structures calculated for the variety of combinations of M and L in structure **3**. Our

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Table 3. Summary of the electronic properties of molecules with structure **3**. Different molecules that are electronically similar are grouped together. Identifiers in the first column are comprised of the periodic Group number of the inner metal followed by the Group number of the outer metal, and a distinguishing letter. The metals are sorted by increasing periodic group, inner then outer.

	inner metal	inner ligand	outer metal	outer ligand	total charge	closed shell ground state	high-spin [eV]	HL gap [eV]	HOMO energy
44A	4(Ti, Zr)	void	4(Ti, Zr)	void or neutral NH_3	2+	$S=0$		1.4 to 2.0	−9 to −12
44B	4(Ti)	void	4(Ti)	anion Cp^-	0	$S=0$		0.27	−4.5
44C	4(Ti)	neutral NH_3	4(Ti)	neutral NH_3	2+	$S=0$		1.4	−8.3
44D	4(Ti)	anion, Cl^-, CN^-, CH_3^-	4(Ti, Zr)	void or neutral NH_3	0	$S=0$		0.5 to 1.5	−2.8 to −5.6
44E	4(Ti)	anion, CN^-, CH_3^-	4(Ti)	anion, CN^-, CH_3^-	0		$S=1$	0.19	−4.5 to −7.2
44F	4(Ti)	void	4(Ti)	anion Cl^-	0		$S=1$	1.14	−6.0
44G	4(Ti)	void	4(Ti)	anion Cl^-	2−	$S=0$		1.3	0.7
45A	4(Ti, Zr)	void or neutral NH_3	5(V, Nb)	void or neutral NH_3	0	$S=0$		0.5 to 1.0	−2.4 to −3.8
45B	4(Ti)	void	5(V)	carbonyl $(CO)_3$	0		$S=3$	0.11	−4.5
45C	4(Ti)	void	5(V)	anion, Cl^-, Cp^-	2+	$S=0$		1.4 to 1.7	−10.9 to −13.2
45D	4(Ti)	void	5(V)	anion Cp^-	0		$S=1$	0.12	−3.1
45E	4(Ti, Zr)	anion, Cl^-, CH_3^-	5(V, Nb)	anion, Cl^-, CH_3^-, Cp^-	0	$S=0$		0.6 to 1.4	−4.3 to −6.3
45F	4(Ti)	anion, CN^-	5(V)	anion, CN^-	0	$S=0$		1.0	−7.9
45G	4(Ti)	anion CH_3^-	5(V)	neutral NH_3	0		$S=1$	0.22	−2.5
46A	4(Ti)	void	6(Mo)	anion Cl^-	0		$S=3$	0.15	−4.6
46B	4(Ti)	void	6(Cr, Mo)	anion $(CN^-)_3$	0	$S=0$		0.68 to 0.80	−9.2 to −9.5
46C	4(Ti)	anion, CH_3^-	6(Cr)	anion, CH_3^-	2−	$S=0$		0.73	+1.3
46D	4(Ti)	anion, CH_3^-	6(Cr)	anion, CH_3^-	0		$S=1$	0.65	−4.6
46E	4(Ti)	anion, CN^-	6(Cr)	anion, CN^-	2−	$S=0$		0.47	−1.6
46F	4(Ti)	void	6(Cr)	carbonyl $(CO)_3$	0		$S=1$	0.45	−5.0
46G	4(Ti)	anion CN^-	6(Cr)	neutral NH_3	0		$S=3$	0.47	−4.5
47A	4(Ti)	anion CH_3^-	7(Mn)	anion CH_3^-	0		$S=4$	0.14	−4.8
48A	4(Ti)	void	8(Fe)	Cp^-	0		$S=3$	0.26	−3.1
48B	4(Ti)	void	8(Ru)	Cp^-	0	$S=0$		0.72	−2.6
48C	4(Ti)	anion, Cl^-	8(Ru)	Cp^-	0		$S=2$	0.09	−3.8
49A	4(Zr)	void	9(Rh)	neutral, NH_3, PH_3	0	$S=0$		0.30 to 0.53	−3.0 to −3.9
54A	5(V)	void	4(Ti)	Cp^-	0		$S=1$	0.12	−4.6
54B	5(V)	CH_3^-	4(Ti)	CH_3^-	0	$S=0$		0.60	−5.2
55A	5(V)	void	5(V)	Cp^-	0		$S=2$	0.14	−3.1
55B	5(Nb)	void	5(Nb)	Cp^-	0	$S=0$		0.92	−3.5
55C	5(V)	anion CH_3	5(V)	anion CH_3	0		$S=2$	0.19	−4.4
55D	5(Nb)	anion, CH_3^-, CN^-	5(Nb)	neutral, NH_3	0	$S=0$		0.79 to 0.83	−2.8 to −4.6
56A	5(Nb)	void	6(Mo)	neutral $(CO)_3$	0	$S=0$		0.68	−5.2
56B	5(Nb)	void	6(Mo)	trianion $(CN^-)_3$	0		$S=1$	0.26	−8.3
56C	5(Nb)	anion, CH_3^-	6(Mo)	anion, CH_3^-	0	$S=0$		0.43	−4.3
58A	5(Nb)	void	8(Ru)	neutral, NH_3, PH_3	0	$S=0$		0.23 to 0.29	−2.9 to −4.0
64A	6(Cr)	carbonyl $(CO)_3$	4(Ti)	void	0		$S=2$	0.20	−4.6
64B	6(Cr, Mo)	carbonyl $(CO)_3$	4(Ti, Zr)	anion, Cl^-, CH_3^-	0	$S=0$		0.51 to 0.71	−5.4 to −5.9
64C	6(Mo)	carbonyl $(CO)_3$	4(Zr)	anion Cp^-	0	$S=0$		0.68	−5.2
64D	6(Cr)	carbonyl $(CO)_3$	4(Ti)	neutral, NH_3	0		$S=2$	0.18	−3.9
64E	6(Mo)	carbonyl $(CO)_3$	4(Zr)	neutral, NH_3	0	$S=0$		0.31	−3.6
65A	6(Cr)	carbonyl $(CO)_3$	5(V)	neutral, NH_3	0		$S=4$	0.49	−4.4
65B	6(Cr)	carbonyl $(CO)_3$	5(V)	dianion, O^{2-}	0	$S=0$		0.39	−6.6
66A	6(Mo)	void	6(Mo)	anion Cp^-	0		$S=2$	0.47	−3.1
66B	6(Cr)	anion, CH_3^-, CN^-	6(Cr)	anion, CH_3^-, CN^-	0		$S=6$	0.04 to 0.17	−4.7 to −7.7
66C	6(Cr)	carbonyl $(CO)_3$	6(Cr)	neutral, NH_3	0		$S=2$	0.11	−4.5
67A	6(Cr)	void	7(Mn)	neutral, NH_3	0		$S=7$	0.25	−2.7
67B	6(Cr)	carbonyl $(CO)_3$	7(Mn)	neutral, NH_3	0	$S=0$		1.12	−4.8
68A	6(Cr)	void	8(Fe)	neutral, NH_3	0		$S=7$	0.08	−2.7
69A	6(Mo)	void	9(Rh)	neutral, PH_3	0		$S=4$	0.17	−3.9
75A	7(Mn)	carbonyl $(CO)_3$	5(V)	anion Cl^-	0		$S=2$	0.49	−5.6
75B	7(Mn)	carbonyl $(CO)_3$	5(V)	dianion, O^{2-}	0	$S=0$		1.07	−6.3
76A	7(Mn)	carbonyl $(CO)_3$	6(Cr)	neutral, NH_3	0	$S=0$		1.11	−3.9
77A	7(Mn)	anion, CH_3^-	7(Mn)	anion, CH_3^-	0		$S=7$	0.79	−5.0
85A	8(Ru)	void	5(Nb)	dianion, O^{2-}	0		$S=3$	0.54	−3.7
85B	8(Ru)	carbonyl $(CO)_3$	5(Nb)	neutral, NH_3	0	$S=0$		0.10	−3.2
87A	8(Ru)	carbonyl $(CO)_3$	7(Rh)	neutral, NH_3	0	$S=0$		0.24	−3.7
87B	8(Ru)	carbonyl $(CO)_3$	7(Rh)	anion Cl^-	0	$S=0$		0.62	−5.6
88A	8(Fe)	void	8(Fe)	anion Cp^-	0		$S=8$	0.42	−3.5
88B	8(Fe)	anion, CH_3^-	8(Fe)	anion, CH_3^-	0		$S=3$	0.35	−4.9
88C	8(Fe)	anion, CN^-	8(Fe)	anion, CN^-	0		$S=9$	0.02	−7.7
89A	8(Fe)	anion, Cl^-	9(Co)	anion, Cl^-	0		$S=7$	0.41	−6.8
89B	8(Ru)	anion, Cl^-	9(Rh)	anion, Cl^-	0		$S=3$	0.54	−3.7
89C	8(Ru)	anion, Cl^-	9(Ir)	anion, Cl^-	0	$S=0$		0.19	−5.8
95A	9(Rh)	void	5(Nb)	dianion, O^{2-}	0		$S=1$	0.56	−5.3

Table 3. (Continued)

	inner metal	inner ligand	outer metal	outer ligand	total charge	closed shell ground state	high-spin [eV]	HL gap [eV]	HOMO energy
98 A	9 (Co)	anion, Cl^-	8 (Fe)	anion, Cl^-	0		$S=7$	0.18	−6.7
98 B	9 (Rh, Ir)	anion, Cl^-	8 (Ru)	anion, Cl^-	0		$S=1$	0.20 to 0.22	−6.3 to −6.6
99 A	9 (Co)	anion, CN^-	9 (Co)	anion, CN^-	0		$S=3$	0.20	−8.1
99 B	9 (Rh)	carbonyl $(CO)_3$	9 (Rh)	neutral, NH_3	0		$S=1$	0.20	−3.9
104 A	10 (Ni)	void	4 (Ti, Zr)	anion, Cl^-, CH_3^-, Cp^-, ligand **4**	0	$S=0$		0.85 to 1.00	−2.7 to −5.5
104 B	10 (Ni)	void	4 (Ti)	trianion $(Cl^-)_3$	0		$S=1$	0.05	−7.2
105 A	10 (Ni)	void	5 (V)	neutral, NH_3	0		$S=4$	0.59	−1.0
105 B	10 (Ni)	void	5 (V)	neutral, PH_3	0		$S=2$	0.27	−2.5
105 C	10 (Ni)	void	5 (V, Nb)	anion, Cl^-	0		$S=2$	0.07 to 0.29	−3.6 to −5.1
105 D	10 (Ni)	void	5 (V, Nb)	dianion, O^{2-}	0	$S=0$		0.55 to 0.63	−5.7 to −6.0
106 A	10 (Ni)	void	6 (Cr)	neutral, NH_3, PH_3	0	$S=0$		0.31 to 0.38	−2.8 to −3.9
106 B	10 (Ni)	void	6 (Cr, Mo)	neutral $(CO)_3$	0		$S=6$	0.16 to 0.21	−5.1 to −5.2
106 C	10 (Ni)	void	6 (Cr, Mo)	anion, Cl^-	0		$S=4$	0.38 to 0.53	−4.5 to −5.7
106 D	10 (Ni)	void	6 (Cr)	anion Cp^-	0		$S=4$	0.07	−3.8
107 A	10 (Ni)	void	7 (Mn)	anion, Cl^-	0	$S=0$		0.33	−6.1
108 A	10 (Ni)	void	8 (Fe)	neutral, NH_3	0		$S=7$	0.12	−2.2
108 B	10 (Ni)	void	8 (Fe)	anion, Cl^-	0	$S=0$		0.44	−6.0
108 C	10 (Ni)	void	8 (Fe)	anion, Cp^-	0		$S=8$	0.06	−3.7
108 D	10 (Ni)	void	8 (Ru)	anion, Cp^-	0		$S=4$	0.53	−4.0
108 E	10 (Ni)	anion, Cl^-, CH_3^-	8 (Fe, Ru)	neutral, NH_3	0	$S=0$		0.26 to 0.45	−3.0 to −4.8
109 A	10 (Ni)	void	9 (Co)	neutral, CO	0		$S=8$	0.31	−5.3
109 B	10 (Ni)	void	9 (Rh)	neutral, CO	0		$S=4$	0.14	−5.5
109 C	10 (Ni)	void	9 (Ir)	neutral, CO	0		$S=3$	0.17	−5.2
109 D	10 (Ni)	void	9 (Co, Ir)	anion, Cl^-	0		$S=1$	0.10 to 0.37	−3.6 to −6.0
109 E	10 (Ni)	void	9 (Rh)	anion, Cl^-	0		$S=2$	0.27	−5.0
1010 A	10 (Ni)	anion, Cl^-	10 (Ni)	neutral, PH_3	0		$S=3$	0.15	−5.2
116 A	11 (Ag)	void	6 (Mo)	anion, Cl^-	0		$S=1$	0.21	−5.0
118 A	11 (Ag)	void	8 (Fe)	neutral, NH_3	0		$S=4$	0.38	−3.0
118 B	11 (Ag)	void	8 (Ru)	neutral, NH_3	0		$S=3$	0.03	−2.3
118 C	11 (Ag)	void	8 (Ru)	neutral, NH_3	+		$S=7/2$	0.26	−5.9
118 D	11 (Ag)	void	8 (Ru)	anion, Cl^-	0		$S=1$	0.52	−5.2
119 A	11 (Ag)	void	9 (Rh)	anion, Cl^-	0	$S=0$		0.70	−5.8
119 B	11 (Ag)	void	9 (Rh)	neutral, CO	0		$S=1$	0.23	−4.4
1110 A	11 (Ag)	void	10 (Ni)	neutral, NH_3	0		$S=4$	0.66	−3.7
1111 A	11 (Ag)	void	11 (Cu)	anion, Cl^-	0		$S=1$	0.14	−6.5
1111 B	11 (Cu)	neutral, NH_3	11 (Cu)	neutral, NH_3	0		$S=1$	0.17	−3.0
1111 C	11 (Cu)	anion, Cl^-	11 (Cu)	anion, Cl^-	0		$S=2$	0.24	−7.1

survey was not exhaustive, but we have sought to identify all favourable species. Compounds and entries in Table 3 are identified by a symbol comprised of the periodic group number of the inner metal followed by the group number of the outer metal, and a distinguishing letter.

General outcomes, and reaction planning: Before we identify specific favourable metallocarbohedrenes in Table 3, and discuss reactions that could be used to synthesise them, we draw attention to some other general results about electronic structure. One general result, evident in Table 3, is that uncharged complexes possess a HOMO energy which indicates that they are redox stable, and, with few exceptions, are not strongly oxidised or strongly reduced. This generalisation applies for metals ranging from Group 4 to 11 and for ligands that are neutral, monoanionic or dianionic.

In general, anionic ligation leads to higher HL gap when the coordination occurs on ^{o}M rather than ^{i}M. Second-row transition metals lead to larger HL gaps than do their first-row counterparts. Global electron counting is not useful, and a number of isovalence-electronic complexes have different electronic structures and ground spin states: two of a number of instances in Table 3 are a) $[(^{i}Fe{-}Cl)_4(C_2)_6(^{o}Co{-}Cl)_4]^0$, which has $S=7$, while $[(^{i}Ru{-}Cl)_4(C_2)_6(^{o}Rh{-}Cl)_4]^0$ has $S=3$, and b) the Group 9 homologues $[(^{i}Ni)_4(C_2)_6(^{o}M{-}CO)_4]^0$, which have $S=8$ for M = Co, $S=4$ for M = Rh and $S=3$ for M = Ir. Some molecules with high-spin ground states have relatively large HL gaps, and could therefore be chemically unreactive.

The effects of ligand elaboration from the simplified ligand substituent H used generally were tested in a few cases. The elaborated molecule $[(^{i}Nb{-}CMe_3)_4(C_2)_6(^{o}Nb{-}NMe_3)_4]^0$ has a very similar electronic and metric structure to $[(^{i}Nb{-}CH_3)_4(C_2)_6(^{o}Nb{-}NH_3)_4]^0$ and manifests the small changes expected for H → Me substitution; the same similarity was found for $[(^{i}Ni)_4(C_2)_6(^{o}Cr{-}NH_3)_4]^0$ and $[(^{i}Ni)_4(C_2)_6(^{o}Cr{-}NMe_3)_4]^0$. We know of one instance in which H → Me substitution changes the electronic structure: $[(^{i}Nb{-}CMe_3)_4(C_2)_6(^{o}Fe{-}NMe_3)_4]^0$ has a $S=3$ spin state, while $[(^{i}Ni{-}CH_3)_4(C_2)_6(^{o}Fe{-}NH_3)_4]^0$ is $S=0$.

Equation (1) combines formally reduced (^{i}M) and oxidised (^{o}M) precursor complexes; this could lead to alternative redox reactions between the precursors, disfavouring the formation of the cluster of T_d symmetry (**3**). One synthetic strategy to avoid this potential problem could be to assemble the $\{(L^{o}M)_4(C_2)_6\}$ frame first, by reaction of $4\,L^{o}M^{III}Cl_3$ with $6\,Me_3SiC_2SiMe_3$, and to add subsequently ^{i}M with very labile ligands in order to close the cluster by coordination to the tris(alkynyl) triangles. This approach is supported by the results of the theoretical investigation. Calculations yield short M−C distances (ca. 2 Å, as is normal) for $^{o}M(\sigma\text{-}C_2)$, considerably longer (ca. 2.4 Å) M−C distances for $^{i}M(\pi\text{-}C_2)$ and, in some cases, for instance with $^{i}M(CO)_3$, the $^{i}M-(\pi\text{-}C_2)$ distances are up to 2.6 Å. This geometry implies that the $M(\sigma\text{-}C_2)$ interactions are the primary contribution to thermodynamic stability and that the $M(\pi\text{-}C_2)$ bonding is secondary; therefore, initial assembly of the tetrahedral $M(\sigma\text{-}C_2)$ scaffolding should be possible: similar reactions have been described.[35] Equation (2) uses oxidation states that are less likely to have redox interference with each other or with the acetylide reagents.

Much of the preceding discussion of reaction planning has been mechanistic, linking the presence of MCl moieties in the precursors with the formation of $M(\sigma\text{-}C_2)$ functions in the products through the elimination of Me_3SiCl, with the $M(\pi\text{-}C_2)$ bonding assembling around low oxidation state metal atoms in the mixture. We also recognise the possibility that the reactions could be under thermodynamic rather than kinetic control, and that, with delocalised bonding and ill-defined metal oxidation states in the products, the nexus between M coordination in precursor and in product be broken. Formally there is an oxidation state crossover in such reactions; in the instances we suggest below these are labelled as "crossover" or redox reactions.

Stable spin singlet metallocarbohedrenes: In Table 3, more than 38 combinations of metals and ligand types satisfy all of the electronic criteria, meaning closure of the electronic configuration and an $S = 0$ ground state, with a relatively large HL gap (> ca. 0.5 eV) and with the HOMO at an appropriate energy (−10 to −3 eV). In the following we list these electronically favourable combinations, and suggest precursors and reactions to form them, usually according to Equations (1) or (2). We suggest suitable reactant complexes that closely match the computed systems. Generally the higher-valent halide precursors [Eqs. (1) and (2)] are more readily accessible for Group 4–6 metals, while the lower-valent precursors with metals more likely to form the inner π bonds are available with metals from Groups 6–11, but some examples with more reactive titanium(0), zirconium(0) and niobium(0) are also given.

In each of the following numbered sections we first summarise the electronically favourable metallocarbohedrenes **3**, and then suggest reactions. Entries in Table 3 are referenced by the symbol in the first column.[36,37]

1. Group 4 metals Ti or Zr as unligated ^{i}M, together with Ti or Zr as ^{o}M, either unligated or ligated with neutral Lewis base with net charge 2+ (**44A**). Amine coordination at both ^{i}Ti and ^{o}Ti is also favourable with charge 2+ (**44C**). The species $[(^{i}Ti)_4(C_2)_6(^{o}Ti-Cp)_4]^0$ (**44B**) is favourable, but with a smaller HL gap. A possible preparation following Equation (1) for a species related to **44C** is Equation (6):[37]

$$4\,[Ti(\eta^4\text{-}C_4H_6)_2(dmpe)] + 4\,[TiCl_3(NH_3)_3] + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti\text{-}dmpe)_4(C_2)_6(^{o}Ti\text{-}NH_3)_4]^{2+} + 12\,Me_3SiCl + 8\,C_4H_6 + 8\,NH_3 + 2\,e^- \tag{6}$$

44B could be prepared as follows [Eq. (7)]:

$$4\,[Ti(\eta^6\text{-}C_6H_5Me)_2] + 4[TiCp^*Cl_3] + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti)_4(C_2)_6(^{o}Ti-Cp^*)_4] + 12\,Me_3SiCl + 8\,C_6H_5Me \tag{7}$$

Another reaction that could lead to **44B** involves a crossover of formal oxidation states [Eq. (8)], driven by the fact that the ligand Cp*[36] is too large to be located on the inner metal (see steric criteria, below):

$$4\,[TiCp^*(CO)_4]^- + 4\,TiCl_4 + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti)_4(C_2)_6(^{o}Ti-Cp^*)_4] + 12\,Me_3SiCl + 16\,CO + 4\,Cl^- \tag{8}$$

2. ^{i}Ti ligated with anions (Cl^-, CN^-, CH_3^-) and ^{o}Ti either unligated or with neutral Lewis base (**44D**). A reaction based on disproportionation of a Ti^{II} complex could lead to a member of this class [Eq. (9)]:

$$8\,[TiCl_2(py)_4] + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti-Cl)_4(C_2)_6(^{o}Ti-py)_4] + 12\,Me_3SiCl + 28\,py \tag{9}$$

3. ^{i}Ti (void) with $^{o}Ti-Cl$, charge 2− (**44G**). Reaction proposed [Eq. (10)]:[37]

$$4\,[Ti(\eta^4\text{-}C_4H_6)_2(dmpe)] + 4\,TiCl_4 + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti)_4(C_2)_6(^{o}Ti-Cl)_4]^{2-} + 12\,Me_3SiCl + 8\,C_4H_6 + 4\,dmpe - 2\,e^- \tag{10}$$

4. Group 4 (Ti or Zr) inner, unligated or with amine coordination, combined with Group 5 (V or Nb) outer, unligated or with amine coordination (**45A**) [Eq. (11)].[38]

$$4\,[Ti(\eta^6\text{-}C_6H_5Me)_2] + 4\,[VCl_3(NMe_3)_2] + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti_4)(C_2)_6(^{o}V-NMe_3)_4] + 12\,Me_3SiCl + 4\,NMe_3 + 8\,C_6H_5Me \tag{11}$$

5. ^{i}Ti (unligated) with ^{o}V ligated with anions Cl^- or Cp^-, and net charge 2+ (**45C**) [Eq. (12)].[37]

$$4\,[Ti(\eta^4\text{-}C_4H_6)_2(dmpe)] + 4\,[VCp^*Cl_3] + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti)_4(C_2)_6(^{o}V-Cp^*)_4]^{2+} + 12\,Me_3SiCl + 8\,C_4H_6 + 4\,dmpe + 2\,e^- \tag{12}$$

Alternatively, an unligated ^{i}Ti could be obtained by use of the more reactive $[Ti(\eta^6\text{-}C_6H_5Me)_2]$ as in Equation (11).

6. Inner Group 4 (Ti or Zr), coordinated with anions Cl^-, CN^-, CH_3^-, with outer Group 5 (V or Nb), coordinated with anions Cl^-, CH_3^-, Cp^- (**45E**) or CN^- (**45F**). These compounds could be accessed by treating the cationic species $[(^{i}Ti)_4(C_2)_6(^{o}V-Cp)_4]^{2+}$ (**45C**) with the desired anion.
7. ^{i}Ti with $^{o}Cr(CN)_3$ or $^{o}Mo(CN)_3$ (**46B**). In addition, ^{i}Ti and ^{o}Cr, both coordinated with the anions CN^- or CH_3^-, as overall dianionic complexes (**46B**, **46D**) are electronically favourable but less redox stable.
8. ^{i}Ti with $^{o}Ru-Cp$ (**48B**). The ruthenium(IV) species $[RuCp^*Cl_3]$ is available, but it is a very strong oxidising agent that would not be compatible with an alkyne or a Ti^0 species. Therefore the following crossover reaction is suggested [Eq (13)]:

$$4\,[TiCl_3(thf)_3] + 2\,[Ru_2Cp_2(CO)_4] + 6\,Me_3SiC_2SiMe_3 \longrightarrow [(^{i}Ti_4)(C_2)_6(^{o}Ru-Cp)_4] + 12\,Me_3SiCl + 12\,THF + 8\,CO \tag{13}$$

Mechanistically this could be expected to lead to $[({}^{i}\mathrm{Ru{-}Cp})_4(\mathrm{C_2})_6({}^{o}\mathrm{Ti})_4]$, but ^{i}M–Cp coordination has steric conflict with the π-$\mathrm{C_2}$ groups (see below) and therefore $[({}^{i}\mathrm{Ti}_4)(\mathrm{C_2})_6({}^{o}\mathrm{Ru{-}Cp})_4]$ could form.

9. ^{i}Zr with ^{o}Rh ligated with amine or phosphine (**49A**). Zirconium(0) species are best prepared with dmpe as stabilising ligand [Eq. (14)], leading to:

$$\begin{gathered}4[\mathrm{Zr}(\eta^4\text{-}\mathrm{C_4H_6})_2(\mathrm{dmpe})] + 4[\mathrm{RhCl_3(PPh_3)_3}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Zr{-}dmpe})_4(\mathrm{C_2})_6({}^{o}\mathrm{Rh{-}PPh_3})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{C_4H_6} + 8\,\mathrm{PPh_3}\end{gathered}\tag{14}$$

10. ${}^{i}\mathrm{V{-}CH_3}$, with ${}^{o}\mathrm{Ti{-}CH_3}$ (**54B**).
11. ^{i}Nb with ^{o}Nb–Cp (**55B**). A possible reaction according to Equation (1) is that given in Equation (15):

$$\begin{gathered}4[\mathrm{Nb}(\eta^6\text{-mesitylene})_2] + 4[\mathrm{NbCp^*Cl_3(dmpe)}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Nb})_4(\mathrm{C_2})_6({}^{o}\mathrm{Nb{-}Cp^*})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{C_6H_3Me_3} + 4\,\mathrm{dmpe}\end{gathered}\tag{15}$$

A possible crossover reaction with Cp in the sterically favoured outer position is Equation (16):

$$\begin{gathered}4[\mathrm{NbCp(CO)_4}] + 4[\mathrm{NbCl_3(glyme)}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Nb{-}glyme})_4(\mathrm{C_2})_6({}^{o}\mathrm{Nb{-}Cp})_4] + 12\,\mathrm{Me_3SiCl} + 16\,\mathrm{CO}\end{gathered}\tag{16}$$

12. ^{i}Nb with $\mathrm{CN^-}$ or $\mathrm{CH_3}^-$ ligation plus ^{o}Nb with amine ligation (**55D**). Simple niobium(I) species are usually stabilised by a chelating phosphine and CO that may not be readily removed. One possibility is the disproportionation of a readily available $\mathrm{Nb^{II}}$ chloro-bridged dimer in the presence of an amine [Eq. (17)]:

$$\begin{gathered}4[\{\mathrm{Nb}(\eta^6\text{-arene})\mathrm{Cl_2}\}_2] + 6\,\mathrm{Me_3SiC_2SiMe_3} + 4\,\mathrm{NMe_3} \longrightarrow \\ [({}^{i}\mathrm{Nb{-}Cl})_4(\mathrm{C_2})_6({}^{o}\mathrm{Nb{-}NMe_3})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{arene}\end{gathered}\tag{17}$$

13. ^{i}Nb plus ${}^{o}\mathrm{Mo(CO)_3}$ (**56A**). To access this product, the following reaction under CO is proposed [Eq. (18); carbonylation of Nb may also occur]:

$$\begin{gathered}4[\mathrm{Nb}(\eta^6\text{-mesitylene})_2] + 4\,\mathrm{MoCl_3} + 12\,\mathrm{CO} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Nb})_4(\mathrm{C_2})_6({}^{o}\mathrm{Mo(CO)_3})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{C_6H_3Me_3}\end{gathered}\tag{18}$$

14. ${}^{i}\mathrm{Nb{-}CH_3}$ plus ${}^{o}\mathrm{Mo{-}CH_3}$ (**56C**). Organometallic compounds of $\mathrm{Mo^{IV}}$ are scarce, as are those of $\mathrm{Nb^{I}}$, and so an approach following Equation (1) has low feasibility. Oxidation state crossover could be induced by the preference of Cp to be located on the outer metal, to form related species as in Equation (19):

$$\begin{gathered}4[\mathrm{MoCpCl(CO)_2}] + 4[\mathrm{NbCl_3(glyme)}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Nb{-}Cl})_4(\mathrm{C_2})_6({}^{o}\mathrm{Mo{-}Cp})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{CO} + 4\,\mathrm{glyme}\end{gathered}\tag{19}$$

15. ^{i}Nb plus ^{o}Ru with amine or phosphine coordination (**58A**). Proposed reaction [Eq. (20)]:

$$\begin{gathered}4[\mathrm{Nb}(\eta^6\text{-mesitylene})_2] + 4[\mathrm{RuCl_3(Ph_2SO)_3}] + 4\,\mathrm{PPh_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Nb})_4(\mathrm{C_2})_6({}^{o}\mathrm{Ru{-}PPh_3})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{C_6H_3Me_3} + 12\,\mathrm{Ph_2SO}\end{gathered}\tag{20}$$

16. ${}^{i}\mathrm{Cr(CO)_3}$ or ${}^{i}\mathrm{Mo(CO)_3}$ with Ti or Zr as outer metal, either with anionic ligands such as $\mathrm{Cl^-}$ or $\mathrm{CH_3}^-$ (**64B**), or Cp (**64C**). Reactions with $[\mathrm{Cr(CO)_3(NCMe)_3}]$ or $[\mathrm{Mo(CO)_3(NCMe)_3}]$ [Eq. (21)]:

$$\begin{gathered}4[\mathrm{Cr(CO)_3(NCMe)_3}] + 4[\mathrm{ZrCl_4(thf)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [\{{}^{i}\mathrm{Cr(CO)_3}\}_4(\mathrm{C_2})_6({}^{o}\mathrm{Zr{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{NCMe} + 8\,\mathrm{THF}\end{gathered}\tag{21}$$

17. ${}^{i}\mathrm{Mo(CO)_3}$ with ${}^{o}\mathrm{Zr{-}NH_3}$ (**64E**). Suggested reaction, to form a related phosphine complex [Eq. (22)]:

$$\begin{gathered}4[\mathrm{Mo(CO)_3(NCMe)_3}] + 2[\mathrm{Zr_2Cl_6(PBu_3)_4}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [\{{}^{i}\mathrm{Mo(CO)_3}\}_4(\mathrm{C_2})_6({}^{o}\mathrm{Zr{-}PBu_3})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{NCMe} + 4\,\mathrm{PBu_3}\end{gathered}\tag{22}$$

18. ${}^{i}\mathrm{Cr(CO)_3}$ plus ^{o}V with oxide coordination (**65B**). Proposed reaction [Eq. (23)]:

$$\begin{gathered}4[\mathrm{Cr(CO)_3(NCMe)_3}] + 4\,\mathrm{VOCl_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [\{{}^{i}\mathrm{Cr(CO)_3}\}_4(\mathrm{C_2})_6({}^{o}\mathrm{V{-}O})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{NCMe}\end{gathered}\tag{23}$$

19. ${}^{i}\mathrm{Cr(CO)_3}$ plus ^{o}Mn with amine coordination (**67B**). Note the large HL gap. Proposed reaction [Eq. (24)]:

$$\begin{gathered}4[\mathrm{Cr(CO)_3(NCMe)_3}] + 4/n[\mathrm{MnCl_3(bipy)}]_n + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Cr(CO)_3})_4(\mathrm{C_2})_6({}^{o}\mathrm{Mn{-}bipy})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{NCMe}\end{gathered}\tag{24}$$

20. ${}^{i}\mathrm{Mn(CO)_3}$ with V=O as outer metal (**75B**), or Cr coordinated by amine (**76A**), both of which have large (> 1eV) HL gaps. Proposed reactions [Eqs. (25) and (26)]:

$$\begin{gathered}2[\mathrm{Mn_2(CO)_{10}}] + 4[\mathrm{CrCl_3(NMe_3)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Mn(CO)_3})_4(\mathrm{C_2})_6({}^{o}\mathrm{Cr{-}NMe_3})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{NMe_3} + 8\,\mathrm{CO}\end{gathered}\tag{25}$$

$$\begin{gathered}2[\mathrm{Mn_2(CO)_{10}}] + 4\,\mathrm{VOCl_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Mn(CO)_3})_4(\mathrm{C_2})_6({}^{o}\mathrm{V{-}O})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{CO}\end{gathered}\tag{26}$$

21. ${}^{i}\mathrm{Ru(CO)_3}$ with ^{o}Nb–amine (**85B**) has a small HL gap and poor HOMO energy, as does ${}^{i}\mathrm{Ru(CO)_3}$ with ^{o}Rh – amine (**87A**), but ${}^{i}\mathrm{Ru(CO)_3}$ with ^{o}Rh – Cl (**87B**) has a good electronic structure. A proposed reaction requires oxidation of the rhodium centre [Eq. (27)]:[37]

$$\begin{gathered}4/3[\mathrm{Ru_3(CO)_{12}}] + 4[\mathrm{RhCl_4(py)_2}]^- + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Ru(CO)_3})_4(\mathrm{C_2})_6({}^{o}\mathrm{Rh{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{CO} + 8\,\mathrm{py} + 4\,\mathrm{e^-}\end{gathered}\tag{27}$$

22. The combination of ^{i}RuCl and ^{o}IrCl (**89C**) meets the criteria, but has a smaller HL gap, and other combinations of Group 8 inner and Group 9 outer, both with $\mathrm{Cl^-}$ coordination, have high spin ground states (see below).
23. ^{i}Ni combined with outer Group 4 (Ti, Zr) ligated by any of the anions $\mathrm{Cl^-}$, $\mathrm{CH_3}^-$, $\mathrm{Cp^-}$, $\mathrm{NPN^-}$ (**4**) (**104A**) has very good electronic structure, with large HL gaps. A representative reaction to form these compounds is given in Equation (28):

$$\begin{gathered}4[\mathrm{Ni(cod)_2}] + 4[\mathrm{ZrCp^*Cl_3}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Ni})_4(\mathrm{C_2})_6({}^{o}\mathrm{ZrCp^*})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{cod}\end{gathered}\tag{28}$$

24. ^{i}Ni with ^{o}VO or ^{o}NbO (**105D**). Possible reaction [Eq. (29)]:

$$\begin{gathered}4[\mathrm{Ni(cod)_2}] + 4\,\mathrm{VOCl_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Ni})_4(\mathrm{C_2})_6({}^{o}\mathrm{V{-}O})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{cod}\end{gathered}\tag{29}$$

25. ^{i}Ni with ^{o}Cr coordinated by amine or phosphine (**106A**). Possible reaction [Eq. (30)]:

$$\begin{gathered}4[\mathrm{Ni(cod)_2}] + 4[\mathrm{CrCl_3(NH_3)_3}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow \\ [({}^{i}\mathrm{Ni})_4(\mathrm{C_2})_6({}^{o}\mathrm{Cr{-}NH_3})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{NH_3} + 8\,\mathrm{cod}\end{gathered}\tag{30}$$

26. ^{i}Ni with ^{o}Mn–Cl (**107A**). $\mathrm{Mn^{III}}$ and $\mathrm{Mn^{IV}}$ compounds are powerful oxidising agents, thwarting reactions according

to Equation (1). However, the affinity of Ni for alkyne may drive the following redox reaction [Eq. (31)]:

$$4\,[\mathrm{NiCl_2(PPh_3)_2}] + 4\,[\mathrm{MnCl_2(py)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Mn{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{PPh_3} + 8\,\mathrm{py} \tag{31}$$

27. ^{i}Ni, with ^{o}Fe–Cl (**108B**). The complex is likely to be oxidised in the following reaction [Eq. (32)]:[37]

$$4\,[\mathrm{Ni(cod)_2}] + 4\,[\mathrm{FeCl_4}]^- + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Fe{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{cod} + 4\,\mathrm{e}^- \tag{32}$$

28. ^{i}Ni ligated by Cl$^-$ or CH$_3{}^-$ combined with outer Group 8 (Fe, Ru) coordinated by amine (**108E**). The preparation of **108E** requires oxidation of the nickel in the presence of a halide source here provided by the Ru^{III} precursor [Eq. (33)]:[37]

$$4\,[\mathrm{Ni(cod)_2}] + 4\,[\mathrm{RuCl_4(NCMe)_2}]^- + 4\,\mathrm{NMe_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ni{-}Cl})_4(\mathrm{C_2})_6(^{o}\mathrm{Ru{-}NMe_3})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{NCMe} + 4\,\mathrm{e}^- \tag{33}$$

29. Unligated ^{i}Ag combined with ^{o}Rh–Cl (**119A**). Proposed crossover reaction [Eq. (34)]:

$$4\,\mathrm{AgCl_2}^- + 4\,[\mathrm{RhCl_3(PPh_3)_3}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ag})_4(\mathrm{C_2})_6(^{o}\mathrm{Rh{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{PPh_3} + 4\,\mathrm{Cl}^- \tag{34}$$

High-spin stable metallocarbohedrenes: It is evident from Table 3 that a considerable number of species are electronically favourable with a suitably large HL gap, but do not have a singlet ground state. These are expected to be relatively stable, by analogy with other paramagnetic coordination complexes.[37] These complexes and possible routes to them are listed here.

30. Titanium as inner metal (unligated) combined with ^{o}Ti–Cl with net charge 0 (**44F**) has a large HL gap (1.1eV). This compound could be reducible to a less stable 2 − species with $S = 0$ (**44G**). A possible reaction is given in Equation (35):

$$4\,[\mathrm{Ti}(\eta^6\text{-}\mathrm{C_6H_5Me})_2] + 4\,[\mathrm{TiCl_4(thf)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ti}_4)(\mathrm{C_2})_6(^{o}\mathrm{Ti{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{THF} + 8\,\mathrm{C_6H_5Me} \tag{35}$$

31. The ^{i}Ti plus ^{o}Cr combinations $[(^{i}\mathrm{Ti{-}CH_3})_4(\mathrm{C_2})_6(^{o}\mathrm{Cr{-}CH_3})_4]^0$ (**46D**), $[(^{i}\mathrm{Ti})_4(\mathrm{C_2})_6(^{o}\mathrm{Cr(CO)_3})_4]^0$ (**46F**) and $[(^{i}\mathrm{Ti{-}CN})_4(\mathrm{C_2})_6(^{o}\mathrm{Cr{-}NH_3})_4]^0$ (**46G**). A favourable reaction for **46F** is given in Equation (36):

$$4\,[\mathrm{Ti}(\eta^6\text{-}\mathrm{C_6H_5Me})_2] + 4\,[\mathrm{CrCl_3(thf)_3}] + 12\,\mathrm{CO} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ti})_4(\mathrm{C_2})_6(^{o}\mathrm{Cr(CO)_3})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{C_6H_5Me} + 12\,\mathrm{THF} \tag{36}$$

It is interesting to compare this reaction with the one leading to **64B** [Eq. (21)] in which the Cr(CO)$_3$ fragments are located on the inner positions. In the present case, the high oxidation state of chromium prevents initial formation of carbonyl species and mechanistically it is likely that CO will only be adsorbed once the Cr–C σ bonds have been formed. A crossover of the metals in **46E** leading to the alternate structure $[(^{i}\mathrm{Cr(CO)_3})_4(\mathrm{C_2})_6(^{o}\mathrm{Ti})_4]$ equivalent to **64A** cannot be excluded, although this species has a smaller HL gap and should be disfavoured. However, such a crossover should be induced by oxidation of the cluster in the presence of chlorides forming **64B**.

32. $[(^{i}\mathrm{Mo})_4(\mathrm{C_2})_6(^{o}\mathrm{Mo{-}Cp})_4]^0$ (**66A**). A reaction possibly forming a related species with Cp replaced by Cl is given in Equation (37):

$$4\,[\mathrm{Mo}(\eta^2\text{-}\mathrm{C_6H_6})_2] + 4\,[\mathrm{MoCl_4(NCMe)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Mo})_4(\mathrm{C_2})_6(^{o}\mathrm{Mo{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{C_6H_6} + 8\,\mathrm{MeCN} \tag{37}$$

33. ^{i}Mn(CO)$_3$ with ^{o}V–Cl (**75A**). Proposed reaction [Eq. (38)]:

$$2\,[\mathrm{Mn_2(CO)_{10}}] + 4\,\mathrm{VCl_4} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Mn(CO)_3})_4(\mathrm{C_2})_6(^{o}\mathrm{V{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{CO} \tag{38}$$

34. $[(^{i}\mathrm{Mn{-}CH_3})_4(\mathrm{C_2})_6(^{o}\mathrm{Mn{-}CH_3})_4]^0$ (**77A**) and $[(^{i}\mathrm{FeCH_3})_4(\mathrm{C_2})_6(^{o}\mathrm{FeCH_3})_4]^0$ (**88B**). No stable organometallic species of manganese(IV) have been reported, and even the chloro species is unstable. However, the following redox reaction [Eq. (39)] is possible:

$$4\,[\mathrm{MnCl_2(py)_2}] + 4/n[\mathrm{MnCl_3(bipy)}]_n + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Mn{-}Cl})_4(\mathrm{C_2})_6(^{o}\mathrm{Mn{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{bipy} + 8\,\mathrm{py} \tag{39}$$

35. $[(^{i}\mathrm{Fe})_4(\mathrm{C_2})_6(^{o}\mathrm{Fe{-}Cp})_4]^0$ (**88A**). This product could be accessed by a crossover reaction [Eq. (40)]:

$$4\,[\mathrm{FeCl_2(thf)}] + 4\,[\mathrm{FeCpCl(CO)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Fe})_4(\mathrm{C_2})_6(^{o}\mathrm{Fe{-}Cp})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{CO} + 4\,\mathrm{THF} \tag{40}$$

36. $[(^{i}\mathrm{Ru})_4(\mathrm{C_2})_6(^{o}\mathrm{Nb{-}O})_4]^0$ (**85A**) and $[(^{i}\mathrm{Rh})_4(\mathrm{C_2})_6(^{o}\mathrm{Nb{-}O})_4]^0$ (**95A**). Possible reactions based on Equation (1) are given in Equations (41) and (42):

$$[\mathrm{Rh_4(CO)_{12}}] + 4\,\mathrm{NbOCl_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Rh})_4(\mathrm{C_2})_6(^{o}\mathrm{Nb{-}O})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{CO} \tag{41}$$

$$4\,[\mathrm{Ru}(\eta^6\text{-naphthalene})(\mathrm{cod})] + 4\,\mathrm{NbOCl_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ru})_4(\mathrm{C_2})_6(^{o}\mathrm{Nb{-}O})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{C_{10}H_6} + 4\,\mathrm{cod} \tag{42}$$

37. $[(^{i}\mathrm{Fe{-}Cl})_4(\mathrm{C_2})_6(^{o}\mathrm{Co{-}Cl})_4]^0$ (**89A**) and $[(^{i}\mathrm{Ru{-}Cl})_4(\mathrm{C_2})_6(^{o}\mathrm{Rh{-}Cl})_4]^0$ (**89B**). The proposed preparation of **89B** is a redox reaction [Eq. (43)]:

$$4/n[\mathrm{RuCl_2(cod)}]_n + 4\,\mathrm{RhCl_3} + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ru{-}Cl})_4(\mathrm{C_2})_6(^{o}\mathrm{Rh{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{cod} \tag{43}$$

38. $[(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{V{-}NH_3})_4]^0$ and $[(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{V{-}PH_3})_4]^0$ (**105A**, **105B**). A suggested reaction is given in Equation (44):

$$4\,[\mathrm{Ni(cod)_2}] + 4\,[\mathrm{VCl_3(NMe_3)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{V{-}NMe_3})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{NMe_3} + 8\,\mathrm{cod} \tag{44}$$

39. $[(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Cr{-}Cl})_4]^0$ and $[(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Mo{-}Cl})_4]^0$ (**106C**). The following redox reaction [Eq. (45)] based on Equation (2) is suggested:

$$4\,[\mathrm{NiCl(PPh_3)_3}] + 4\,[\mathrm{CrCl_3(thf)_3}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Cr{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{THF} + 12\,\mathrm{PPh_3} \tag{45}$$

40. $[(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Ru{-}Cp})_4]^0$ (**108D**). Ruthenium(IV) species usually involve solutions in HCl incompatible with

organometallic species. The crossover approach is given in Equation (46):

$$4\,[\mathrm{NiCl_2(PPh_3)_2}] + 4\,[\mathrm{RuCpCl(CO)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Ru{-}Cp})_4] + 12\,\mathrm{Me_3SiCl} + 8\,\mathrm{PPh_3} + 8\,\mathrm{CO} \tag{46}$$

41. $[(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Co{-}CO})_4]^0$ (**109 A**). The following carbonylation after formation of three Co–σ-C_2 bonds from a cobalt(III) amine precursor [Eq. (47), based on Eq. (1)] could work:

$$4\,[\mathrm{Ni(cod)_2}] + 4\,[\mathrm{CoCl_3(NH_3)_3}] + 6\,\mathrm{Me_3SiC_2SiMe_3} + 4\,\mathrm{CO} \longrightarrow [(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Co{-}CO})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{NH_3} + 8\,\mathrm{cod} \tag{47}$$

An alternative is combination of a $\mathrm{Ni^{I}{-}Cl}$ species with $CoCl_2$ under carbonylation conditions [Eq. (48)]:

$$4\,[\mathrm{NiCl(PPh_3)_3}] + 4\,\mathrm{CoCl_2\cdot 1.5\,THF} + 6\,\mathrm{Me_3SiC_2SiMe_3} + 4\,\mathrm{CO} \longrightarrow [(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Co{-}CO})_4] + 12\,\mathrm{Me_3SiCl} + 12\,\mathrm{PPh_3} + 6\,\mathrm{THF} \tag{48}$$

42. $[(^{i}\mathrm{Ag})_4(\mathrm{C_2})_6(^{o}\mathrm{Fe{-}NH_3})_4]^0$ (**118 A**) and $[(^{i}\mathrm{Ag})_4(\mathrm{C_2})_6(^{o}\mathrm{Ni{-}NH_3})_4]^0$ (**1110 A**). The approach outlined in Equation (2) could make use of a strongly coordinating phosphine ligand to drive Fe to the outer position [Eq. (49)]:

$$4\,[\mathrm{AgCl_2}]^- + 4\,[\mathrm{FeCl_2(PPh_3)_2}] + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ag})_4(\mathrm{C_2})_6(^{o}\mathrm{Fe{-}PPh_3})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{PPh_3} + 4\,\mathrm{Cl^-} \tag{49}$$

Another reaction is possible with freshly prepared silver acetylides (Caution: silver acetylides are shock sensitive and explosive when dry!). The phosphine ligand liberated from the Fe reactant should help keep the byproduct AgCl in solution [Eq. (50)]:

$$4\,[\mathrm{FeCl_2(PPh_3)_2}] + 6\,[\mathrm{AgC_2Ag}] \longrightarrow [(^{i}\mathrm{Ag})_4(\mathrm{C_2})_6(^{o}\mathrm{Fe{-}PPh_3})_4] + 8\,\mathrm{AgCl} + 4\,\mathrm{PPh_3} \tag{50}$$

43. $[(^{i}\mathrm{Ag})_4(\mathrm{C_2})_6(^{o}\mathrm{Ru{-}Cl})_4]^0$ (**118 D**). A proposed redox reaction is given in Equation (51):

$$4\,[\mathrm{AgCl_2}]^- + 4\,[\mathrm{RuCl_4(NCMe)_2}]^- + 6\,\mathrm{Me_3SiC_2SiMe_3} \longrightarrow [(^{i}\mathrm{Ag})_4(\mathrm{C_2})_6(^{o}\mathrm{Ru{-}Cl})_4] + 12\,\mathrm{Me_3SiCl} + 4\,\mathrm{Cl^-} + 8\,\mathrm{NCMe} \tag{51}$$

We recognise that the equations presented above hide a number of experimental difficulties, including selection of suitable solvents.

Geometric structure

Phosphine coordination: Our calculations indicate that a number of metallocarbohedrene complexes with early transition metals coordinate normally to amines, but not to phosphines. The M–P bond at the energy minimum is elongated. Weakened and elongated M–P coordination occurs for the species $[(^{i}\mathrm{Ti})(^{o}\mathrm{Ti{-}PR_3})]^{2+}$ (using abbreviated formulas) and $[(^{i}\mathrm{TiX})(^{o}\mathrm{Ti{-}PR_3})]^0$ (X = Cl, CH_3, CN), for which the Ti–P distance is approximately 2.8 Å in contrast to the comparable Ti–N distance of 2.3 Å in $[(^{i}\mathrm{Ti})(^{o}\mathrm{Ti{-}NH_3})]^{2+}$ and $[(^{i}\mathrm{TiX})(^{o}\mathrm{Ti{-}NH_3})]^0$. In $[(^{i}\mathrm{Ti})(^{o}\mathrm{V{-}PH_3})]^{2+}$ the V–P distance, 2.55 Å, is also long: normal M–P distances in other complexes are Rh–P = 2.37 Å in $[(^{i}\mathrm{Zr})(^{o}\mathrm{Rh{-}PH_3})]^0$, Ru–P = 2.38 Å in $[(^{i}\mathrm{Nb})(^{o}\mathrm{Ru{-}PH_3})]^0$, Cr–P = 2.37 Å in $[(^{i}\mathrm{Ni})(^{o}\mathrm{Cr{-}PH_3})]^0$. The elongated coordination of phosphine occurs also for Ti at the inner position: in $[(^{i}\mathrm{Ti{-}NH_3})(^{o}\mathrm{V{-}NH_3})]^0$ Ti–N = 2.31, V–N = 2.27 Å, while in $[(^{i}\mathrm{Ti{-}PH_3})(^{o}\mathrm{V{-}PH_3})]^0$ Ti–P = 2.79, V–P = 2.57 Å. There is a distinct energy minimum at the longer distance. This behaviour is not an artifact of the use of PH_3 in the calculations, because the same result is obtained in calculations with PMe_3. Concepts of softness for the phosphine ligand and hardness for the early transition metals are consistent with this result, but full explanation will require further investigation.

Steric criteria and control via ancillary ligands: The ancillary ligands at ^{i}M and ^{o}M can have variable size. It is necessary to analyse the ability of experimentally feasible ancillary ligands to fit over the surface of the molecule, and their ability to enclose the core. The $\{(^{i}\mathrm{M})_4(\mathrm{C_2})_6(^{o}\mathrm{M})_4\}$ core is relatively small. The simplified ligands NH_3, PH_3 and CH_3 used in the above DF calculations are smaller than the amines, phosphines and alkyl groups that are normally used in syntheses, and so we have assessed the steric effects of substituents on these ancillary ligands. To reduce the further reactivity of the products, it is desirable to control the volume and shape of ancillary ligands so that they envelop the cluster and restrict access to its potential reaction sites. Therefore, in the following we show space-filling pictures of some representative species: all atom surfaces are drawn with the Bondi radii,[39] namely H 1.20, C 1.65, N 1.55, O 1.52, Si 2.10, P 1.85, S 1.80, Cl 1.80, first-row transition metals 1.8, second-row transition metals 2.0, Sn 2.20 Å.

Figure 2 shows $[(^{i}\mathrm{Zr})_4(\mathrm{C_2})_6(^{o}\mathrm{Rh{-}PPh_3})_4]$ (entry **49 A** in Table 3), with the PH_3 ligand elaborated as the common phosphine PPh_3. There are no steric interferences, and indeed there is plenty of access space over the molecular surface. A notable feature of the PPh_3 conformer presented is the occurrence of two Ph groups as perpendicular sentinels at the end of each C_2 group, a property that would influence supramolecular interactions between such molecules and their solvents.

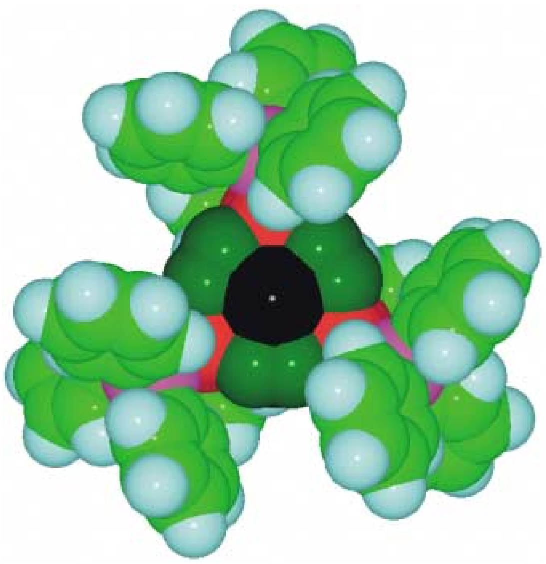


Figure 2. Space-filling representation of $[(^{i}\mathrm{Zr})_4(\mathrm{C_2})_6(^{o}\mathrm{Rh{-}PPh_3})_4]$: Zr black, Rh red, C_2 olive, P magenta, C green, H cyan.

There is no steric problem with π-arene ligands at ^{o}M. The more significant issue is the size of ligands at ^{i}M when there is also π-arene ligation at ^{o}M. Figure 3 shows the space-filling representation of $[(^{i}\text{Ti}{-}t\text{Bu})_4(\text{C}_2)_6(^{o}\text{V}{-}\eta^5\text{-C}_5\text{H}_5)_4]$ (one of group **45E** in Table 3). The *tert*-butyl coordination at the inner metal atoms and Cp ligation of the outer metal atoms generate a very nice compact molecule with no steric interference and with strongly restricted access to the C_2 groups. From a geometrical perspective, as well as the electronic perspective, this is an attractive target.

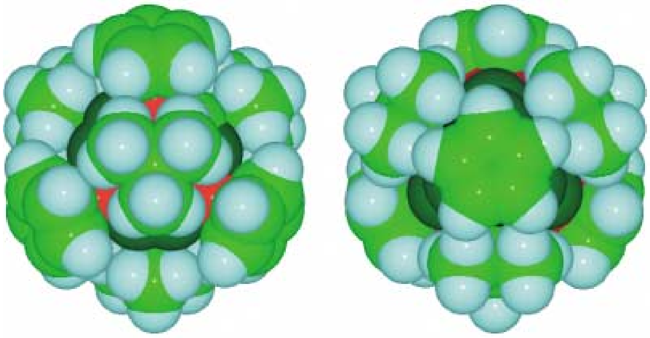


Figure 3. Space-filling representations of $[(^{i}\text{Ti}{-}t\text{Bu})_4(\text{C}_2)_6(^{o}\text{V}{-}\eta^5\text{-C}_5\text{H}_5)_4]$. Colouring as in Figure 2.

Figure 4 shows $[(^{i}\text{Ni}{-}t\text{Bu})_4(\text{C}_2)_6(^{o}\text{Fe}{-}\text{NMe}_3)_4]$ (cf. **108E** in Table 3) with *tert*-butyl coordination at the inner Ni atom and trimethylamine as tertiary amine in the outer position. Again the product is a compact, symmetrical and enclosed molecule. Expansion to higher alkyl tertiary amines is similarly feasible (provided that one of the substituents is not larger than methyl), and heterocyclic amines such as pyridine which would radiate from the outer position similarly present no steric difficulty.

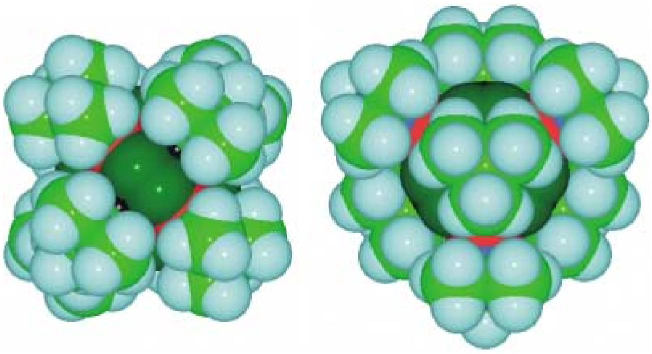


Figure 4. Space-filling representations of $[(^{i}\text{Ni}{-}t\text{Bu})_4(\text{C}_2)_6(\text{Fe}^{o}{-}\text{NMe}_3)_4]$. Atom colouring as in Figure 2.

In $[(^{i}\text{Ni})_4(\text{C}_2)_6\{^{o}\text{Mo(CO)}_3\}_4]$ (**106B**, Table 3) there is considerable exposure of ^{i}M and of the C_2 groups (see Figure 5). In $[(^{i}\text{Ni})_4(\text{C}_2)_6(^{o}\text{V}{=}\text{O})_4]$ (**105D**, Table 3) there would be even greater exposure of these potentially reactive sites. A benzene molecule will fit in the threefold space over ^{i}Ni in a postulated molecule $[(^{i}\text{Ni}{-}\eta^6\text{C}_6\text{H}_6)_4(\text{C}_2)_6(^{o}\text{V}{=}\text{O})_4]$, but there is close contact between C of C_2 and C of C_6H_6: a π-arene molecule cannot bind at sufficiently close distances to ^{i}M.

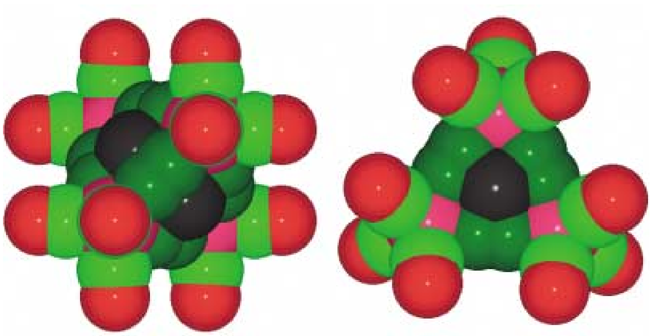


Figure 5. Space-filling representation of $[(^{i}\text{Ni})_4(\text{C}_2)_6\{^{o}\text{Mo(CO)}_3\}_4]$: Mo violet. There is another T_d isomer in which the $(\text{CO})_3$ groups are rotated by 60°.

Tricarbonyl coordination of the inner metal occurs in a number of electronically favourable species. We describe two geometrical consequences of $^{i}\text{M(CO)}_3$ coordination. The first is that the inner metals are drawn away from the centroid of the cluster along the threefold axes of **3**, concomitant with elongated $^{i}\text{M}{-}\text{C}_2$ π bond lengths. For instance, in $[\{^{i}\text{Cr(CO)}_3\}_4(\text{C}_2)_6\{^{o}\text{TiCl}\}_4]$ the $^{i}\text{Cr}{-}\eta^2\text{-C}_2$ distance is 2.59 Å (compared with $^{i}\text{Ti}{-}\eta^2\text{-C}_2 = 2.24$ Å in $[(^{i}\text{Ti})_4(\text{C}_2)_6(^{o}\text{TiCl})_4]^{2-}$) and the Cr_4Ti_4 array is almost exactly cubic. In $[\{^{i}\text{Cr(CO)}_3\}_4(\text{C}_2)_6\{^{o}\text{CrNH}_3\}_4]$ the “outer” Cr atoms are actually closer to the centroid than the “inner” Cr atoms, and this occurs in a number of similar species. In $[\{^{i}\text{Ru(CO)}_3\}_4(\text{C}_2)_6\{^{o}\text{NbNH}_3\}_4]$ the $^{i}\text{Ru}{-}\eta^2\text{-C}_2$ distance has extended to 2.9 Å, which is weak bonding, and for the more electron-rich complex $[\{^{i}\text{Rh(CO)}_3\}_4(\text{C}_2)_6\{^{o}\text{RuNH}_3\}_4]$ energy minimisation caused the $^{i}\text{Rh(CO)}_3$ moiety to dissociate further to $^{i}\text{Rh}{-}\eta^2\text{-C}_2 = 3.2$ Å.

The second geometrical aspect of $^{i}\text{M(CO)}_3$ coordination is that it does not interfere sterically with $^{o}\text{M}{-}\eta^5\text{-Cp}$ coordination, as illustrated in Figure 6 for $[\{^{i}\text{Cr(CO)}_3\}_4(\text{C}_2)_6\{^{o}\text{RuCp}\}_4]$.

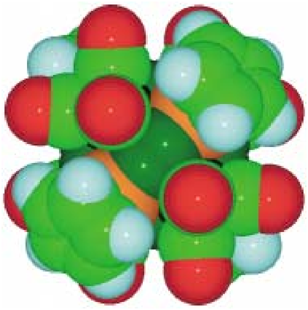
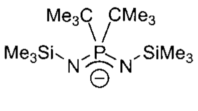
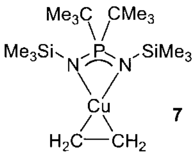


Figure 6. The compatibility of $^{o}\text{M}{-}\eta^5\text{-Cp}$ coordination with $^{i}\text{M(CO)}_3$ coordination, illustrated by a space-filling representation of $[\{^{i}\text{Cr(CO)}_3\}_4(\text{C}_2)_6\{^{o}\text{RuCp}\}_4]$: the ^{i}Cr atoms are obscured by the CO ligands parallel to the view direction.

Steric factors for iminophosphanamide ligands: Some DFT calculations of electronic structure were made for the methylated iminophosphanamide ligand **4** (Table 3, entry **104A**). This is a simplification of the ligand **6**, which has been investigated recently (see also the preliminary experimental results below).[40] Ligand **6** is bulkier than **4**, and here we describe some modelling of **6** as a terminal ligand at ^{o}M of **3**. This modelling is based on the three crystal structures involving **6** and transition metals, deposited in the Cambridge structural database (CSD).[41,42] The three molecules from the CSD, **7**, **8** and **9**, show that the ligand **6** is crowded and slightly twisted to accommodate the crowding, and also encloses much of the space around the coordinated metal. Figure 7 provides relevant space-filling representations of **7** and **9**: complex **8** is very similar to **7**.



6



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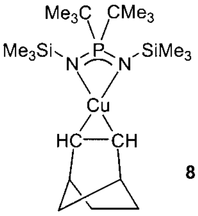
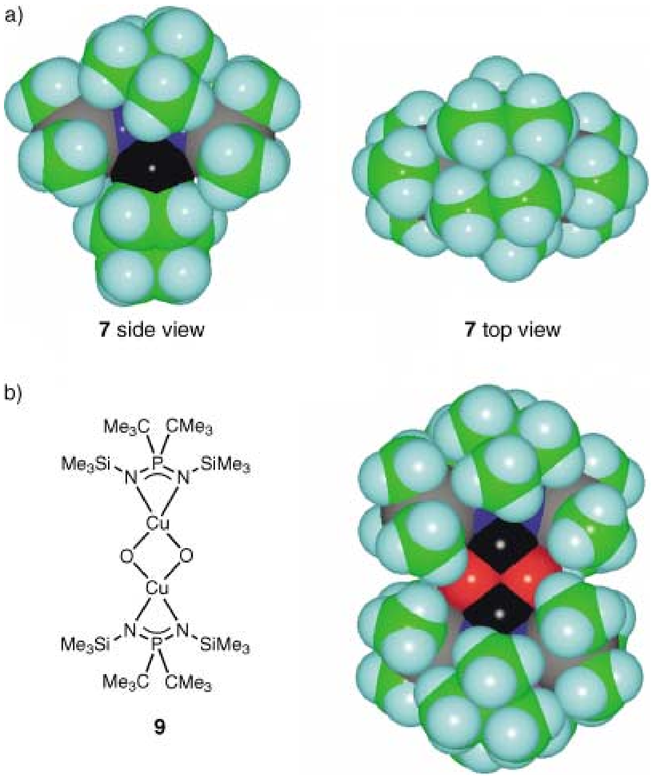


8

These molecular structures demonstrate the distinctive geometrical properties of coordinated **6**. In all three cases ligand **6** is coordinated to a metal with square-planar stereochemistry, and the other ligands do not protrude laterally in the coordination plane. In fact the other ligands associated with planar **6**–Cu coordination could not extend laterally because they would encounter the SiMe$_3$ groups of **6**; these SiMe$_3$ groups extend well down around the coordinated metal (Figure 7). The space-filling pictures show that a bis-**6** metal complex with planar coordination of M is sterically impossible; tetrahedral coordination also appears to be impossible because SiMe$_3$ groups would overlap the CMe$_3$ on the other ligand.

These properties of **6** impede its involvement as a protective terminal ligand in metallocarbohedrenes. Virtually all metallocarbohedrene core structures have M(C$_2$)$_3$ coordination, and the various isomers arise according to the combination of σ or π coordination of the C$_2$ at three-coordinate M atoms. This threefold trigonal coordination of M occurs also in nanocrystal structures in which ligands are C, and in metallocarbohedrenes that mix C$_2$ and C units. The part of a metallocarbohedrene core most geometrically favourable for extra ligation is ^{o}M of a spire with trigonal stereochemistry, **3s**. However, when **6** with distinctly twofold geometry is coordinated to ^{o}M with threefold symmetry, there is conflict between the SiMe$_3$ ends of the ligand and the (C$_2$)$_3$ ligands of the metcar core, as shown in Figure 8. Diminution of the SiMe$_3$ groups to CMe$_3$ does not remove this conflict.



7 side view 7 top view

Figure 7. Space-filling representation of the complexes containing ligand **6**: C green, H cyan, N blue, Si grey, Cu black, O red. a) Complex **7** (CSD refcode GUGBEP). The top view, parallel to the C$_2$CuN$_2$ plane shows how the ligand is twisted to reduce interference between the two CMe$_3$ substituents. The side view shows how the SiMe$_3$ groups extend around the edges of the square planar Cu towards the η^2-C$_2$H$_4$ ligand. b) Complex **9** (CSD refcode WOMVOJ). Note again how the SiMe$_3$ groups extend around the planar Cu and almost meet near the bridging O atoms.

Our modelling also reveals that there would be conflict between ligands **6** coordinated at each of the four ^{o}M of **3**, as detailed in Figure 9. Again this is a direct consequence of the SiMe$_3$ wings of the ligand protruding too far around the metal.

So, we conclude that iminophosphanamide ligands need to be less crowded than **6**. All other ligand types considered in Table 3 are suitable, and can be adjusted, through substitutents, to suitably enclose the target molecules.

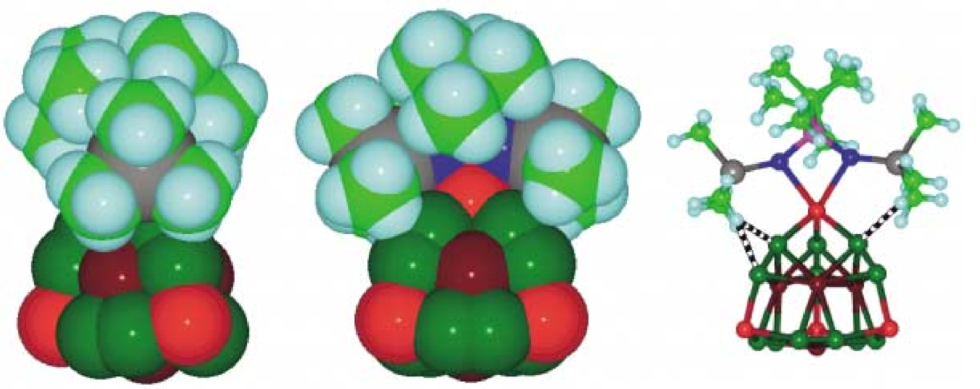


Figure 8. Modelled coordination of ligand **6** at ^{o}M: ^{o}M red, C$_2$ olive, N blue, Si grey, C green, H cyan. Space-filling views along (left) and normal (middle) to the SiNPNSi plane of **6**. Right: Skeletal representation of b) showing the close H···C$_2$ contacts (striped) of 1.87, 2.14, 2.35 Å.

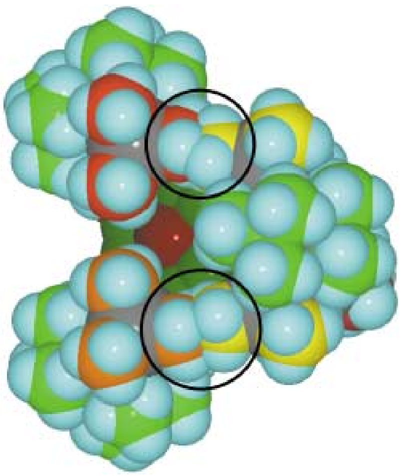


Figure 9. Modelled coordination of three ligands **6** at three °M of **3**. Two ligands (C of the $SiMe_3$ groups red and orange) can be added without mutual interference, but addition of the third ligand is impossible: there is direct overlap (encircled) of the $SiMe_3$ groups.

Preliminary experimental results: Following the ideas presented above, several reactions have been attempted, but the low solubilities of products have hindered their characterisation. For example, the complex [$TiCp^*Cl_3$] has been treated with a stoichiometric amount of $Me_3SnC_2SnMe_3$ in the presence of one equivalent of $Cr(CO)_6$. The reaction was slow and led to an unidentifiable mixture, but did show the formation of the desired Me_3SnCl as a side-product. The reaction was faster when repeated with the more reactive chromium(0) complex [$Cr(CO)_3(NCMe)_3$], but again identification was not successful. Similar treatment of [$CrCl_3(thf)_3$] with $Me_3SnC_2SnMe_3$ in the presence of [$Cr(CO)_3(NCMe)_3$] showed fast formation of a compound that had CO bands in the IR spectrum similar to an [arene−$Cr(CO)_3$] complex, and mass spectrometry showed a signal at $m/z = 713$ consistent with a Cr_8 cluster. Results obtained from the reaction of LiC≡CLi with [$ZrCp^*Cl_3$] in the presence of [$Ni(cod)_2$] were promising with mass spectrometry signals consistent with a cluster of the type [$Zr_4Ni_4Cp^*_4(C_2)_6$], but again the solubility of the final material was very low. To increase the solubility of the products, use of the iminophosphonamide [$t\mathrm{Bu}_2\mathrm{P(NSiMe_3)_2}]^-$ (**6**) as ligand was initiated, although this may be too sterically encumbered to form metallocarbohedrenes of structure **3**: other smaller species, possibly useful as intermediates, may be formed.

Conclusion

We have provided an overview of the electronic structures of a comprehensive range of more than 125 species as potential metallocarbohedrenes, and identified those with particularly favourable or otherwise interesting (highly paramagnetic with large HOMO–LUMO gap) electronic structures. These results provide a guide to the design of synthetic mixtures, and we have suggested a considerable number of specific reactions.

Before proceding to summarise some of the key findings, we take care to recognise what we have not assessed. We have not estimated the thermodynamic stabilities of the molecules evaluated, because these are relevant only in the context of numerous, diverse, alternative products (either molecular or nonmolecular). We have not attempted to calculate reaction energies or pathways (which would be for the gas-phase), because solvation and other solution interactions are crucial in practical synthesis. Other compositions and other geometrical structures for metallocarbohedrenes have not been explicitly evaluated, but their formation in any of the proposed reactions would be considered as success. Of concern in practice are nonmolecular solids that could precipitate from these reactions, and there is no information about the relative depths of their thermodynamic wells. Our initial experimental results show evidence of insoluble products, and the use of solubilising terminal ligands is expected to be crucial in the synthesis of metallocarbohedrenes.

Further, it is conceivable that metallocarbohedrenes will need to be kinetically stabilised, and for this some control of the mechanism of their formation will be required. We have been mindful of the preferences for the more reduced metal precursors to bind C_2 groups through their π orbitals, and the more oxidised metal components to bind to the σ orbitals of C_2. We envisage that the template effect of reduced metal sites forming π bonds with the acetylides will favour the metallocarbohedrenes, via intermediates reminicent of tweezer complexes.[13, 43] We note, however, that differentiation of π- and σ-binding metal sites is variable in isomers of $\{M_8(C_2)_6\}$ (Figure 1).

The average formal oxidation state for the metal atoms in the $\{M_8(C_2)_6\}$ core is +1.5. One formal construct for isomer **3** is a combination of M^0 and M^{III}, that is, $\{(^iM^0)_4(^oM^{III})_4\}$. However, many of the electronically favourable complexes are uncharged, with anionic ligands, with the consequence that the metal oxidation states (and those in the precursor compounds) are raised. For instance, in $[(^i\mathrm{Ti{-}CN})_4(C_2)_6(^o\mathrm{V{-}CN})_4]^0$ (**45F**) or $[(^i\mathrm{Ni})_4(C_2)_6(^o\mathrm{VO})_4]^0$ (**105D**) the average metal oxidation state is +2.5, and then there are questions about the ability of these metals to form π-C_2 bonds and about the redox compatibility of the acetylenediide precursors and the more oxidised metal precursors. We have considered two types of formation reaction [Eqs. (1) and (2)] in which the oxidation states of the metal precursors are strongly [Eq. (1)] or weakly [Eq. (2)] differentiated. With numerous σ and π bonds within the $\{M_8(C_2)_6\}$ core it is probable that there is considerable electron delocalisation, and no sharp differentiation of the effective charges on the geometrically different metal atoms.

Enclosing terminal ligation is expected to provide kinetic stabilisation against condensation of metallocarbohedrenes through ligands bridging the outer metal atoms.

A possible problem for synthesis is the alternative formation of extended oligomers, and the use of solutions under high-pressure, which have been shown to give preferentially metallacycles over linear compounds,[44] could assist.

We summarise our findings about favourable electronic structure. 1) Preparable complexes are expected to be uncharged, with some dications or dianions being favourable. 2) A large number of ligated complexes have large HOMO–

LUMO gaps and suitable HOMO energies, and appear to be excellent targets (Table 3). 3) Combinations of metals in Groups 4 or 5 and of metals in Group 10 with metals in Groups 4 or 5 are generally better than other combinations. 4) We have not identified any generally applicable electron counting rules.

We note that some of these molecules are calculated to have very high-spin ground states, with substantial HOMO–LUMO gaps, and, being otherwise stable, could be relevant to the quest for molecular magnets.[45] Attention is drawn to $[(^{i}\mathrm{Mn{-}CH_3})_4(\mathrm{C_2})_6(^{o}\mathrm{Mn{-}CH_3})]^0$ $S=7$, $[(^{i}\mathrm{Fe})_4(\mathrm{C_2})_6(^{o}\mathrm{Fe{-}Cp})]^0$ $S=8$, $[(^{i}\mathrm{Fe{-}Cl})_4(\mathrm{C_2})_6(^{o}\mathrm{Co{-}Cl})]^0$ $S=7$ and $[(^{i}\mathrm{Ni})_4(\mathrm{C_2})_6(^{o}\mathrm{Co{-}CO})]^0$ $S=8$. There are similarities between these metallocarbohedrene molecules and some recently reported very high-spin polycyanometallate molecular clusters such as $[\mathrm{Mn\{Mn(MeOH)_3\}_8(\mu\text{-}CN)_{30}\{Mo(CN)_3\}_6}]$,[46] $[\mathrm{(Me_3tacn)_8Cr_8Ni_6(CN)_{24}}]^{12+}$,[47] and $[\mathrm{Cr_8Ni_5(CN)_{24}}]$ and $[\mathrm{Cr_{10}Ni_9(CN)_{42}}]$[48] clusters in crystals.

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[33] Calculated vibrational properties, tabulated as frequency ($\mathrm{cm^{-1}}$) (degeneracy, intensity ($\mathrm{km\,mol^{-1}}$, 0 = IR inactive)): $[(^{i}\mathrm{Ti{-}CN})_4(\mathrm{C_2})_6(^{o}\mathrm{Cr{-}CN})_4]^{2-}$: 49 (t, 0). 59 (e, 0), 60 (t, 0.5), 69 (e, 0), 73 (t, 8.3), 96 (t, 0), 146 (t, 0), 176 (a, 0), 190 (e, 0), 197 (t, 7.7), 218 (t, 0), 229 (a, 0), 235 (e, 0), 244 (t, 0.6), 281 (t, 0), 300 (e, 0), 302 (t, 1.8), 303 (t, 0), 323 (t, 26.6), 339 (e, 0), 341 (t, 0), 391 (t, 21.5), 404 (t, 0), 421 (t, 54), 423 (a, 0), 449 (a, 0), 475 (t, 110), 476 (a, 0), 495 (a, 0), 517 (t, 38), 520 (e, 0), 521 (t, 0), 531 (t, 56), 546 (e, 0), 728 (t, 5.1), 731 (t, 0), 1335 (e, 0), 1355 (t, 69), 1395 (a, 0), 2074 (t, 19.3), 2075 (a, 0), 2129 (t, 93), 2129 (a, 0); $[^{i}\mathrm{Ni}_4(\mathrm{C_2})_6(^{o}\mathrm{Ti{-}CH_3})_4]$: 85 (e, 0), 86 (t, 0), 90 (t, 0), 130 (e, 0), 152

(t, 5.1), 154 (t, 0), 190 (t, 17.0), 198 (t, 0), 202 (a, 0), 235 (e, 0), 238 (t, 3.2), 245 (t, 0), 247 (a, 0), 327 (t, 3.3), 328 (t, 0), 368 (a, 0), 373 (e, 0), 381 (t, 5.7), 408 (a, 0), 411 (t, 10.8), 436 (t, 0), 452 (t, 0), 456 (e, 0), 459 (t, 58.7), 481 (e, 0), 496 (t, 144), 520 (a, 0), 628 (t, 0), 664 (t, 156), 1118 (t, 2.4), 1119)a, 0), 1400 (t, 0), 1400 (e, 0), 1401 (t, 21.5), 1662 (e, 0), 1682 (t, 148), 1712 (a, 0), 2945 (t, 7.1), 2945 (a, 0), 3032 (t, 0), 3032 (e, 0), 3032 (t, 16.0); [^{i}Ni$_4$(C$_2$)$_6$(^{o}VO)$_4$]: 100 (t, 0), 114 (e, 0), 115 (t, 1.7), 140 (e, 0), 158 (t, 2.1), 190 (a, 0), 191 (t, 0), 193 (t, 11.1), 237 (e, 0), 242 (t, 3.8), 244 (a, 0), 253 (t, 0), 340 (t, 2.4), 348 (t, 0), 384 (a, 0), 421 (t, 1.7), 436 (a, 0), 449 (t, 2.6), 454 (t, 0), 454 (e, 0), 481 (e, 0), 671 (t, 14.8), 671 (t, 0), 1002 (t, 438), 1010 (a, 0), 1678 (e, 0), 1691 (t, 50.0), 1713 (a, 0); [^{i}Ni$_4$(C$_2$)$_6$(^{o}Ti−Cl)$_4$]: 51 (e, 0), 54 (t, 1.3), 69 (t, 0), 127 (e, 0), 140 (t, 2.7), 143 (t, 0), 183 (t, 3.0), 214 (a, 0), 239 (t, 16.1), 243 (e, 0), 254 (t, 0), 331 (t, 17.6), 343 (t, 0), 373 (a, 0), 377 (t, 76.2), 401 (e, 0), 408 (a, 0), 420 (t, 14.3), 455 (t, 0), 470 (t, 110), 474 (e, 0), 488 (a, 0), 630 (t, 0), 670 (t, 148), 1659 (e, 0), 1678 (t, 111), 1706 (a, 0).

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