Review

Triple-decker transition metal complexes bridged by a single carbocyclic ring

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Abstract

Triple-decker organometallic complexes of transition metals have attracted interest since 1972, when Werner and Salzer prepared the tris(cyclopentadienyl)dinickel cation, the first example of this class of compound. This paper reviews the literature for those triple-decker complexes which contain a single carbocyclic ligand bridging two metal centres.
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1. Introduction

Triple-decker organometallic complexes of transition metals have attracted interest since 1972, when Werner and Salzer [1] prepared the tris(cyclopentadienyl)dinickel cation, the first example of this class of compound. Further development through the 1980s was mainly connected with the use of boron-containing five-membered heterocyclic ligands as bridging moieties, since these readily yield triple-decker as well as multiple-decker complexes [2,3]. More recently, arene ligands and other carbocycles such as naphthalene and the indenyl ring system have been used as middle decks. Triple-decker complexes in which a CH unit of the bridging ligand is substituted by isoelectronic building blocks such as BR^- and P are also known [4]. A plethora of heterocycles such as the substituted boratabenzene $C_5H_5B–Me$ [5] and the phospholyl ligand C_4Me_4P [6], as well as those resulting from complete replacement of CH units

(As_5 [7], P_5 [8–12], Sb_5 [13], P_6 [14,15], $1,2-B_6H_4Cl_2$ [16], etc.) also act as bridging ligands.

This review will be limited to those triple-decker complexes which contain a single carbocyclic bridging ligand. Bimetallic triple-decker and pseudo-triple-decker complexes with polycyclic systems in which the metals bond to the bridge in a π manner and bimetallic complexes in which the bridge cycles are joined by a single carbon–carbon bond (i.e. fulvalene-based systems) have not been reviewed here. There is a profusion of fulvalene-based complexes, and this type of system has already been reviewed [17–20]. Although *trans* coordination of the metal atoms to a common ligand is necessary for a compound to be classified as a true triple-decker complex, mention will be made of the closely related *cis* complexes as appropriate. Likewise, triple-decker complexes in which the middle deck is a heterocycle may be alluded to if such complexes illustrate an interesting aspect of this chemistry. Note, however, that there is a very extensive body of work concerning boron-heterocycle-bridged [21] triple-decker complexes, which have also been reviewed [2,3,22–25]; these systems will not be considered here. Finally, quadruple- and multiple-decker systems will be included where relevant.

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1.1. Nomenclature

The bridging mode and hapticity of the central ligand in a triple-decker complex are denoted by the symbols μ and $\eta^n{:}\eta^m$, respectively, while the prefixes *trans-* and *cis-* signify coordination to opposite faces or to the same face of the ligand, respectively. [1] The superscripts n and m indicate the number of ring atoms to which each metal is bonded. For terminal ring ligands, full hapticity will be assumed unless otherwise noted. These conventions are illustrated for monocyclic bridges.

The complex *trans*-$(CpV)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ (Fig. 1(a)) [26] has two CpV moieties ($Cp = \eta^5$-cyclopentadienyl) coordinated to the opposite faces of a benzene ring. In the $\eta^6{:}\eta^6$ bridging mode, each of the six benzene carbon atoms is equally bonded to both vanadium atoms. However, the bonding to a ligand such as benzene may be unequal, as it is in the cobalt complex *trans*-$(Cp^{\cdot}Co)_2$ $(\mu\text{-}\eta^4{:}\eta^4\text{-}C_6H_6{}^iPr)$ [27]. For this species, each cobalt atom coordinates to four carbon atoms on opposing faces of the benzene ring (Fig. 1(b)). In cases where it is unclear to which members of the bridging ring the bonding occurs, this is indicated by the locations of the bonding carbon atoms in parentheses following the appropriate η designation. Thus, the complex in Fig. 1(c) is accurately described by the formula *trans*-$(CpRh)_2[\mu\text{-}\eta^4(1,2,5,6){:}\eta^4(3,4,7,8)\text{-COT}]$ (COT = cyclooctatetraene) [28].

Most *cis*-coordinated bimetallic complexes closely related to triple-deckers are characterised by some degree of metal–metal bonding. This is indicated by the notation $(M{-}M')$ at the end of the structural formula for these species.

The classification of triple-decker complexes and the terminology used therein are straightforward, as they are derived from the monometallic sandwich descriptors (Fig. 2(a) and (b)). Thus, a triple-decker complex in which the two metal atoms are coordinated to opposing sides of the same ring ligand are termed "straight" triple-decker complexes (Fig. 2(c); e.g. *trans*-$\{(CpNi)_2 (\mu\text{-}\eta^5{:}\eta^5\text{-}Cp)\}^+)$ [1]. The term "slipped" is applied to triple-decker complexes in which the central ligand is monocyclic but the metal coordination sites are not coaxial due to asymmetric ligation.

Just as there are monometallic half-sandwich (or open-faced sandwich) complexes, such as $Cp^*Mn(CO)_3$, there exist a number of triple-decker complexes in which the terminal ligand(s) is/are not cyclic. Such complexes
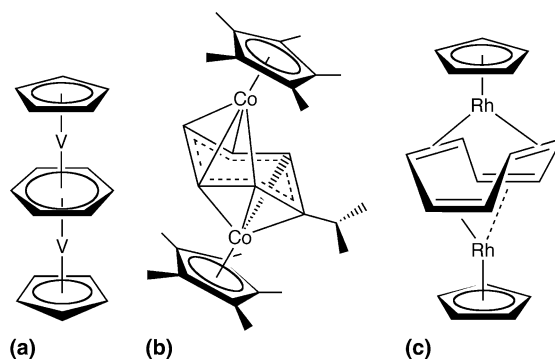

Fig. 1. Different bridging modes of various single carbocyclic ring ligands illustrating the nomenclature of triple-decker complexes. (a) *trans*-$(CpV)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$; (b) *trans*-$(Cp^*Co)_2(\mu\text{-}\eta^4{:}\ \eta^4\text{-}C_6H_5{}^iPr)$; (c) *trans*-$(CpRh)_2[\mu\text{-}\eta^4(1,2,5,6){:}\eta^4(3,4,7,8)\text{-COT}]$.

are considered to be closely related to triple-decker complexes. A suitable naming protocol is required to describe them, but to the best of our knowledge, no such terminology has been generally agreed upon. The terms "singly" and "doubly open-faced triple-decker complexes" have therefore been coined (Fig. 2(e) and (f); e.g. *trans*-$[(COD)Ir][\mu\text{-}\eta^5{:}\eta^5\text{-}(COT)][Mn(CO)_3]$ is a singly open-faced triple-decker complex) [29]. The descriptor "open-faced" was chosen in favour of "half-sandwich" because of the confusing mixture of numerical adjectives that would result in the latter case.

1.2. Theoretical studies

Extended Hückel molecular orbital (EHMO) calculations by Hoffmann et al. in 1976 predicted two series of stable triple-decker complexes [30]. Based on a fragmentation analysis of the structure CpM–Cp–MCp, a "30- and 34-electron rule" was formulated to predict the stability of triple-decker complexes, in analogy to the 18-electron rule for metallocenes. The molecular orbitals of the six highest orbitals of the MCp fragments are considered. The energy level pattern for the 34-valence electron (VE) compound $\{Cp_3Ni_2\}^+$ is shown in Fig. 3(a). Calculation of the interaction between the two CpM fragments and the central ring indicates that the e''_1 orbital is antibonding, and the e'_1 orbital is slightly bonding; for $\{Cp_3Ni_2\}^+$, e'_1 and all lower-lying orbitals are filled. In 30VE complexes, the e'_1 orbitals are not occupied but since these were found not to be essential for binding, 30VE complexes as well as 34VE species are predicted to be thermodynamically and kinetically stable.

Fig. 3(b) shows the more recently derived MO scheme for the 26VE complex *trans*-$(CpV)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$, which is not predicted to be stable by Hoffmann's Rule. With the aid of photoelectron spectra, this new order for the frontier orbitals was established; it is more consistent with the experimental data [32].

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[1] There are several conventions for describing to which face or faces of the bridging ligand the metal atoms are coordinated. Throughout the literature, one finds the prefix pairs "*cis-*" and "*trans-*"; "*cisoid-*" and "*transoid-*"; and "*syn-*" and "*anti-*", as well as descriptors such as "synfacial" and "antifacial" bonding. To avoid confusion, the prefixes "*cis-*" and "*trans-*" will be used predominantly in this work, although the other terms are interchangeable.
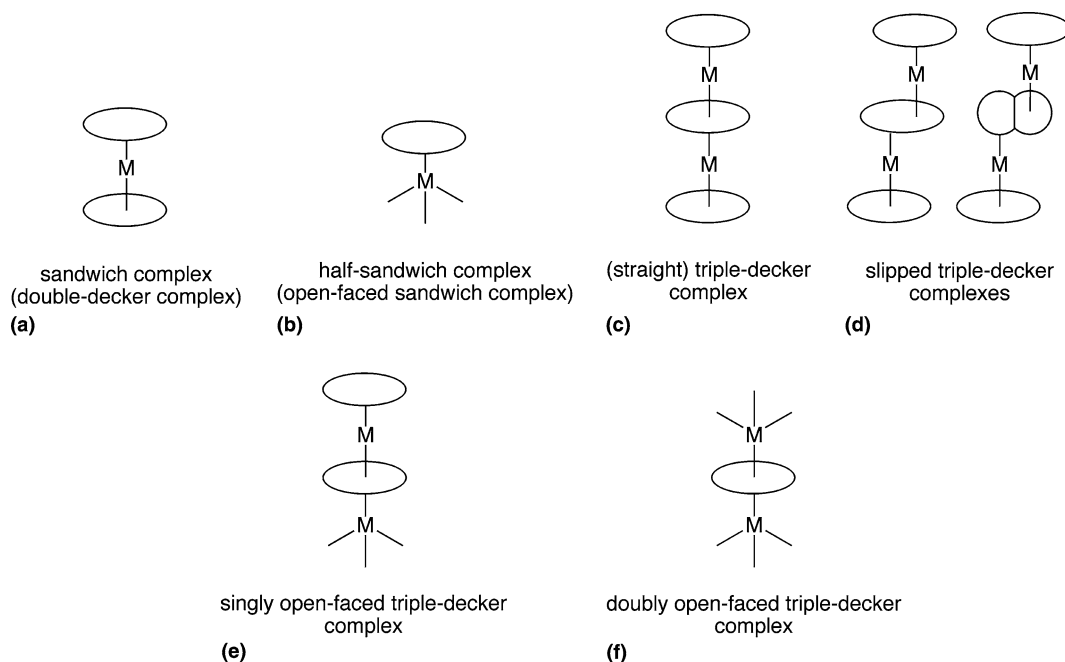
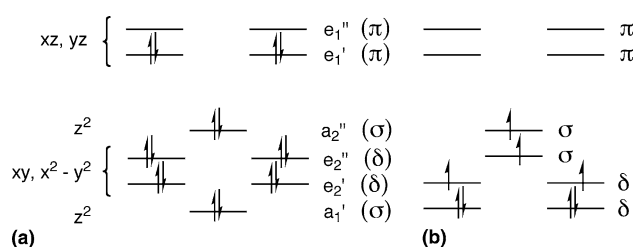Fig. 2. Nomenclature for the common types of sandwich and triple-decker complexes.

Fig. 3. Molecular orbital schemes for (a) $\{Cp_3Ni_2\}^+$ [30]; (b) *trans*-$(CpV)_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)$ [31]. Vertical energy scales are arbitrary; not drawn to scale.

Fig. 4. (a) The cyclobutadiene slipped triple-decker complex *trans*–$\{[Cp(CO)_2Fe]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_4H_4)\}^{2+}$ (**1**). (b) The alternate dicarbenium structure for **1**.

In straight triple-decker complexes, the stable electronic configuration characteristic of the metal in the corresponding mononuclear compounds usually dictates the number of valence electrons found. For example, bridging six-π-electron ligands (C_6H_6, $C_5H_5^-$, etc.) share all six of their π-electrons with both metal centres; in such complexes, therefore, the valence electron count should be $2x - 6$, where x is the valence electron count in the corresponding mononuclear complexes. Straight *n*-decker complexes should have $(n-1)x - (n-2)6$ valence electrons, assuming six-π-electron bridging ligands.

2. Triple-decker complexes with bridging C_3 or C_4 carbocyclic rings

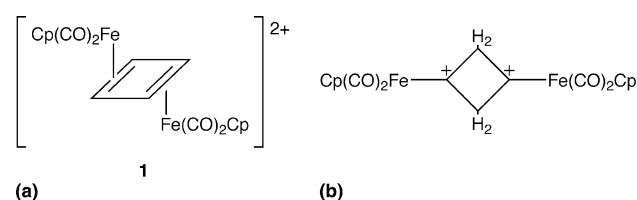To date no triple-decker complex in which a cyclopropenyl ring bridges two metal moieties is known. However, metallocenes containing this ligand have been prepared (e.g. $CpNi(\pi\text{-}C_3Ph_3)$ [33]; $(\pi\text{-}C_3H_3)_2Be$ [34]), and *cyclo*-E_3 (E = P, As) acts as a bridge in several bimetallic complexes (e.g. *trans*-$\{[(triphos)Pd]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}E_3)\}^+$; triphos = 1,1,1-tris[(diphenylphosphino)methyl]ethane) [35–39].

The first example of a bimetallic triple-decker complex bridged by a cyclobutadiene ring is *trans*-$\{[Cp(CO)_2Fe]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_4H_4)\}^{2+}$ (**1**) which has the slipped structure shown in Fig. 4 [40]. The structure in which a symmetrical $\eta^4\text{:}\eta^4$ coordination mode is adopted is likely to be Jahn–Teller unstable [30]. Although a crystal structure has not been obtained for this complex, its coordination geometry has been clearly established by consideration of its spectroscopic and chemical properties. The alternate dicarbenium structure shown in Fig. 4(b) has been ruled out based on the observation of a doublet for the carbon atoms of the cyclobutadiene ring in the proton-coupled ^{13}C NMR spectrum of **1**; only one hydrogen is bonded to each carbon in the ring. The chemistry of **1** demonstrates that the four-membered ring remains intact during reactions such as
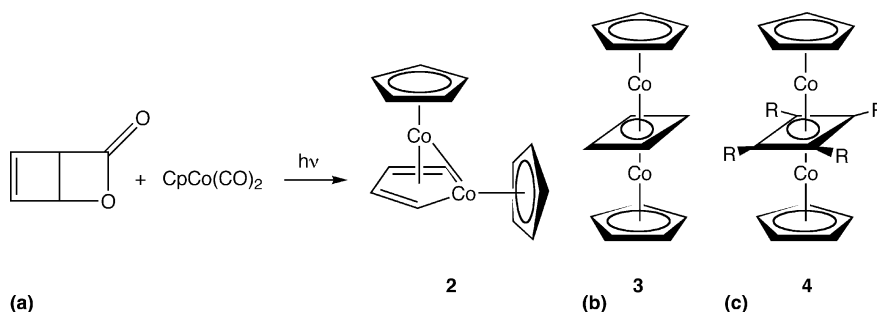
Fig. 5. (a) The formation of $Cp_2Co_2C_4H_4$, **2**. (b) The μ-η^4:$\eta^4(C_4H_4)$ triple-decker structure **3** (not observed). (c) *trans*-$(CpCo)_2(\mu$-η^4:η^4-1,2,3,4-$C_4R_4)$ (**4**, R = Et, ^nPr).

hydride reduction, also supporting the bridging cyclobutadiene structure.

Photolysis of photo-α-pyrone (Fig. 5(a)) in the presence of $CpCo(CO)_2$ yields the monometallic complex $CpCo(\eta^4$-$C_4H_4)$ in moderate yield [41]. A bimetallic complex of composition $(CpCo)_2(C_4H_4)$ is also formed, but it is not the desired cyclobutadiene-bridged species **3**. Rather, it has been shown by NMR spectroscopy and an X-ray crystallographic study to have the structure **2** (Fig. 5(a)) [41]. Although it was proposed that the intramolecular exchange of the Cp rings observed for **2** at high temperatures by ^1H NMR spectroscopy may proceed via **3** (Fig. 5(b)), this possibility was ruled out on the basis that the cyclobutadiene protons retain their identity during the exchange process. This agrees with the fact that two additional electrons are required for **3** to be a stabilised closed-shell structure [30].

The only other examples of this type of triple-decker are the complexes *trans*-$(CpCo)_2(\mu$-η^4:η^4-1,2,3,4-$C_4R_4)$ (**4**, R = Et, ^nPr) [42]. The compounds **4** (Fig. 5(c)) are produced by the reaction of the Jonas reagent $CpCo(C_2H_4)_2$ [43,44] with 2-hexyne or 3-hexyne in equimolar amounts at room temperature. When R = Et, the triple-decker isomerises upon reaction with 3-hexyne at room temperature to a final product structurally related to **2**.

3. Triple-decker complexes with bridging C_5 carbocyclic rings

The first triple-decker complex to be isolated, the tris(cyclopentadienyl)dinickel cation *trans*-{$(CpNi)_2(\mu$-η^5:η^5-Cp)$\}^+$ (**5**), is also the first example of a triple-decker complex bridged by a cyclopentadienyl ring [1]. The synthesis of this complex is shown in Fig. 6. The preparation of the substituted complexes *trans*-{$[(C_5H_4R)Ni]_2(\mu$-η^5:η^5-$C_5H_4R)$}$^+$ (R = Me, ^tBu) provided NMR data that helped confirm the presence of three symmetrically η^5-π-bonded cyclopentadienyl ligands, of which two were equivalent [1]. However, it was mainly the results of the reaction of **5** with various Lewis
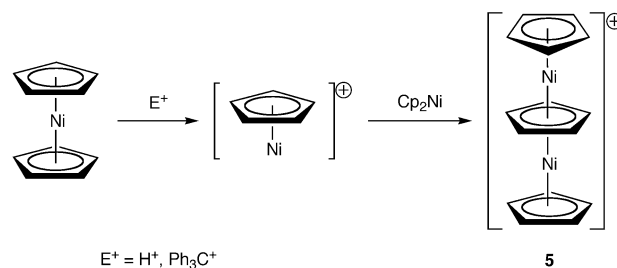

Fig. 6. The preparation of the first triple-decker complex, *trans*-{$(CpNi)_2(\mu$-η^5:η^5-Cp)$\}^+$(**5**) [30].

bases L that increased the confidence in the structural assignment [45]. In nearly all cases, the quantitative formation of Cp_2Ni and {$CpNiL_2\}^+$ (L = PPh_3, $P(OMe)_3$, etc.) was observed. The proposed structure was eventually confirmed by a crystal structure analysis of **5** [46].

Triple-decker complexes with bridging cyclopentadienyl ligands are rare; for over a decade the highly reactive 34VE complex **5** was the only known triple-decker with an unsubstituted bridging Cp ligand [1]. This is surprising, since Hoffmann's EHMO calculations predicted the series of 30-electron complexes (with bridging cyclopentadienyl-based ligands) to be more stable than the 34-electron complexes [30].

The idea that triple-decker sandwiches of general composition $[M_2(C_nH_n)_3]$ could exist and be isolable under ordinary conditions was first put forward on the strength of mass spectral data [47]. The iron complex analogous to **5**, {$Cp_3Fe_2\}^+$ (**6**) had been detected in the high pressure single source electron-impact mass spectra of ferrocene [48]. First reported by Schumacher and Taubnest [47], **6** was presumed to be an ion-neutral reaction product and to have a triple-decker sandwich structure, but there was no concrete evidence. A subsequent study supported this hypothesis, showing that it is unlikely that {$Cp_3Fe_2\}^+$ originates from a neutral ferrocene dimer, since no such species had ever been detected [48]. Similar mass spectrometry experiments also suggest that ions of the type {$Cp_3MM'\}^+$ (M = M' = Cr,

Fe, Ni; M = Fe, M′ = Ni) are formed by electron impact from the corresponding metallocenes [47,49] or from [CpFe(μ_3-CO)]$_4$ [50]. However, not all polynuclear cyclopentadienyl-metal derivatives generate triple-decker sandwich ions upon electron impact, as evidenced by the lack of abundant $\{Cp_3M_2\}^+$ species in the mass spectra of [CpCo(CO)]$_3$ [51] or $Cp_3Ni_3(CO)_2$ [52]. The structures of the triple-decker species remain unconfirmed crystallographically.

Many attempts to prepare other members of this class of compound with a central cyclopentadienyl ligand were largely unsuccessful [45,53,54]. The use of harsh electrophiles (e.g. HBF$_4$) fails in the case of decamethylnickelocene and other substituted nickelocenes, which give stable ring-protonation products under these conditions [54], and in the case of decamethylferrocene, oxidation simply leads to the formation of the decamethylferrocenium radical cation. The reaction of nickelocene with the 12-electron species $\{(COD)Rh$-$(solv)_x\}BF_4$ (or $\{(C_3H_5)Pd(solv)_y\}BF_4$) only yields $\{Cp_3Ni_2\}BF_4$ (5) and (COD)RhCp (or (C$_3$H$_5$)PdCp), and not the desired heterobimetallic triple-decker complexes trans-$\{[(COD)Rh](\mu$-η^5:η^5-Cp)(NiCp)\}^+$ or trans-$\{[(C_3H_5)Pd](\mu$-η^5:η^5-Cp)(NiCp)\}^+$, respectively [45,53]. Several other novel synthetic routes to 5 were discovered as a result of efforts by Werner et al. to prepare new triple-decker sandwich complexes [45].

Why should 5 prove so easy to synthesise, while $\{Cp_3M_2\}^+$ for other metals are so elusive? The answer lies in Hoffmann's Rule. It has been shown that $\{CpNiCpH\}^+$ can be generated by protonating Cp$_2$Ni with HX; under the influence of electrophilic reagents, this species loses CpH to give the stable 14-electron fragment $\{CpNi\}^+$ [55]. This latter can be isolated as a BF$_4^-$ or SbF$_6^-$ salt. Reaction of the fragment with Cp$_2$Ni gives 5, a stable 34VE complex, but reaction with Cp$_2$Fe does not yield the heterobimetallic dinuclear species $\{Cp_3FeNi\}^+$, which would be a 32VE species and thus should act as a diradical. Oddly, the triple-decker $\{Cp_3Fe_2\}^+$ (6) has a stable 30VE configuration but could not be isolated until recently. The exceptional stability of Cp$_2$Fe probably hinders the preparation of 6. In contrast to Cp$_2$Ni, Cp$_2$Fe reacts with electrophiles E to give substitution products CpFeC$_5$H$_4$E. Rybinskaya et al. [56] finally prepared 6 in 1999 by the stacking reaction of ferrocene with the cationic fragment $\{CpFe\}^+$ generated by the visible light irradiation of $\{CpFe(C_6H_6)\}PF_6$ in CH$_2$Cl$_2$ at 0 °C. The permethylated version $\{Cp^*_3Fe_2\}^+$ can be obtained by a similar route, at room temperature due to its higher stability [12].

In 1987, Rybinskaya and co-workers prepared the Cp*-bridged complexes trans-$\{(C_5R_5)M(\mu$-η^5:η^5-Cp*) M′Cp$^*\}^+$ (7) by the reaction of the $\{(C_5R_5)M\}^+$ moiety (M = Fe, R = H; M = Ru, R = H, Me) with the highly nucleophilic decamethyl metallocenes Cp$^*_2$M′ (M′ = Fe, Ru, Os), under the same conditions used for the synthesis of the arene complexes of $\{(C_5R_5)M\}^+$ (Fig. 7) [57–59]. These straight 30-electron triple-decker complexes are formed by the interaction of a 12-electron fragment (e.g. $\{CpFe(\eta^6$-$C_6H_6)\}^+$ or $\{Cp^*M(solv)_3\}^+$, M = Fe, Ru; solv = MeCN or other nucleophilic solvent) with an 18-electron metallocene system in a manner similar to the interaction of a 12-electron cation with a six-electron arene. The composition and structure of the complexes 7 were confirmed by ^{1}H NMR studies and by an X-ray diffraction study of trans-$\{(CpRu)(\mu$-η^5:η^5-Cp*)(RuCp*)\}PF$_6$ [57]. The crystal structures of trans-$\{(Cp^*Ru)_2(\mu$-η^5:η^5-Cp*)\}PF$_6$ and trans-$\{(Cp-Ru)$-$(\mu$-η^5:η^5-Cp*)(OsCp*)\}PF$_6$ were also reported [60], showing the μ-η^5:η^5 bridging nature of the Cp* ring. The intramolecular Ru–Ru and Ru–Os distances (3.679(7) and 3.622(4) Å, respectively) are such that interactions between the metal centres are likely to be very weak or absent.

The acidity of the α-protons of the Cp* rings in 7 is enhanced by the positive charge of the triple-decker complex, enabling the deprotonation of a terminal Cp* ring in trans-$\{(Cp^*Ru)_2(\mu$-η^5:η^5-Cp*)\}^+$ with a strong base (e.g. ^{n}BuLi–^{t}BuOK) to give the deprotonated form [62]. This can then be trapped by a suitable electrophile, yielding substituted versions of 7. Deprotonation does not occur at the central ligand because the principal resonance form for the deprotonated species is most

M = Fe, Ru, Os

M′ = Fe, L = C$_6$H$_6$
M′ = Ru, L = (MeCN)$_3$

L = C$_6$H$_6$: hν, CH$_2$Cl$_2$
L = (MeCN)$_3$: Δ, MeNO$_2$

7

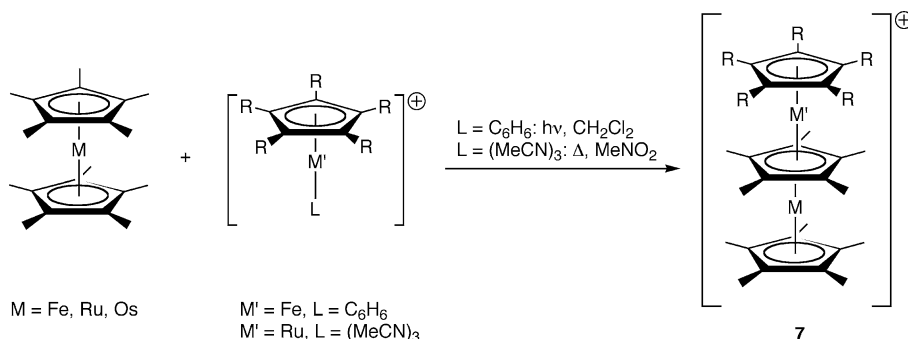Fig. 7. The synthesis of the first 30VE triple-decker sandwich complexes of the Group 8 metals (7) [59,61].
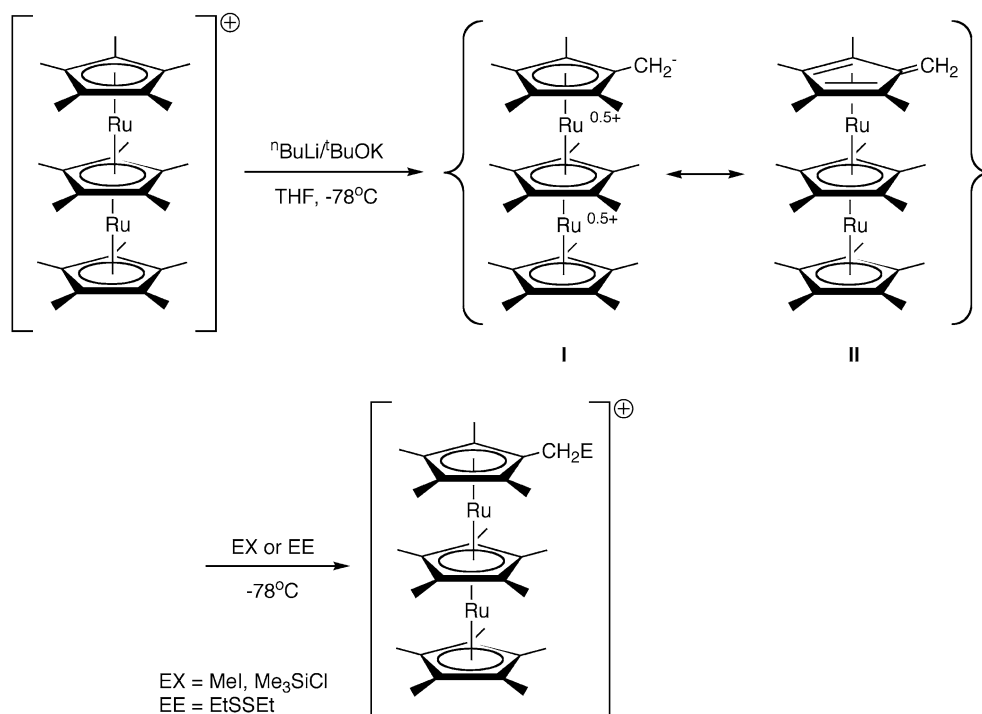
Fig. 8. Deprotonation and functionalisation of trans-{(Cp*Ru)$_2$(μ-η^5:η^5-Cp*)}$^+$ [62].

probably **II** (Fig. 8); an η^4-tetramethylfulvene ligand in the bridging position is unlikely.

Building on the results and insights gained in the pioneering work, new triple-decker complexes bridged by an unsubstituted cyclopentadienyl ligand have been prepared. Herberich et al. have shown that a remarkable regioselectivity takes place in the reaction of [CpML]$^+$ with CpCp*M: the bridging ligand is always the unsubstituted Cp ligand [63]. These reactions are summarised in Fig. 9. In addition, in the related Cp transfer reactions (vide infra), the migrating ring ligand is again always the unsubstituted Cp ligand. The structure of trans-{(Cp*Ru)$_2$(μ-η^5:η^5-Cp)}OTf has been reported [63]; the isolation of this complex demonstrates the stability of these species. In general, ruthenium compounds of this kind are much more stable than their iron counterparts [64].

The chemistry of straight triple-decker complexes with bridging cyclopentadienyl ligands is characterised by various competing equilibrium processes (Fig. 10). The synthesis of these complexes relies on the forward direction of reaction (1) (electrophilic stacking), but their stability is limited by the reverse reaction (nucleophilic degradation). For heterobimetallic triple-decker complexes, two regiochemistries are possible for the reverse reaction and equilibrium (2) becomes relevant. When both equilibria operate, a ring ligand transfer may occur. The reaction of {(COD)Rh(solv)$_x$}$^+$ with

two equivalents of Cp$_2$Ni to give (COD)RhCp and {Cp$_3$Ni$_2$}$^+$ (**5**) discussed above is a closely related example of such a Cp transfer reaction. A key intermediate in this reaction may be postulated to be the short-lived species trans-{[(COD)Rh](μ-η^5:η^5-Cp)(NiCp)}$^+$ [63]. In a detailed study, Herberich et al. [65] provide evidence that the transfer of Cp ligands (Fig. 10) takes place via triple-decker intermediates with a bridging Cp ligand, using the reaction between Cp*Ru(Idcp) and {Cp*Rh-(Me$_2$CO)$_3$}$^+$ as a model system (Idcp = tricyclo [5.2.1.0$^{2.6}$]deca-3,5-dien-2-yl; see below).
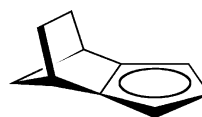
Idcp,
tricyclo[5.2.1.0$^{2.6}$]deca-3,5-dien-2-yl

The only examples of singly open-faced triple-decker sandwich complexes with a strictly carbocyclic bridging ligand are the bimetallic manganese tricarbonyl-capped metallocenes trans-{(Cp*M)(μ-η^5:η^5-Cp*)[Mn(CO)$_3$]}$^+$ (M = Fe, Ru, Os) [66]. All other complexes of this type are bridged by a heterocycle, usually a borole-based system. The manganese tricarbonyl transfer reagent {(η^6-naphthalene)Mn(CO)$_3$}$^+$ is reacted with Cp*$_2$M to yield
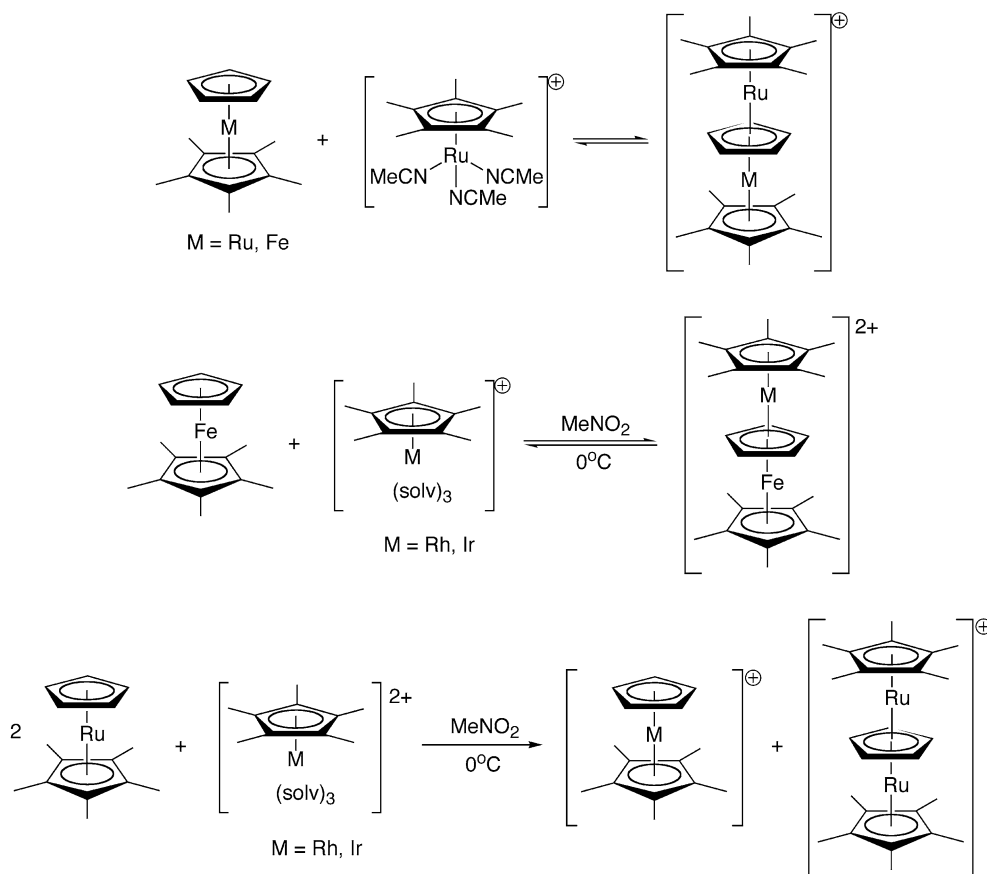
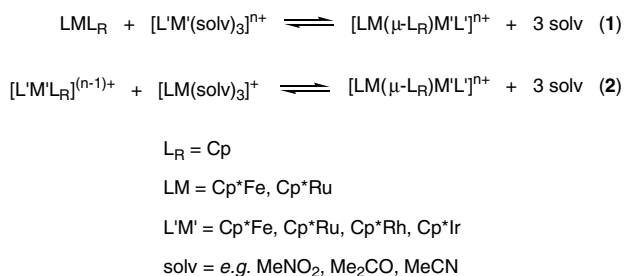Fig. 9. The formation of unsubstituted-Cp-bridged triple-decker complexes [63].

$$LML_R + [L'M'(solv)_3]^{n+} \rightleftharpoons [LM(\mu-L_R)M'L']^{n+} + 3\,solv \quad (1)$$

$$[L'M'L_R]^{(n-1)+} + [LM(solv)_3]^+ \rightleftharpoons [LM(\mu-L_R)M'L']^{n+} + 3\,solv \quad (2)$$

$L_R = Cp$

$LM = Cp^*Fe, Cp^*Ru$

$L'M' = Cp^*Fe, Cp^*Ru, Cp^*Rh, Cp^*Ir$

$solv = e.g.\ MeNO_2, Me_2CO, MeCN$

Fig. 10. The chemistry of triple-decker complexes with bridging cyclopentadienyl ligands.
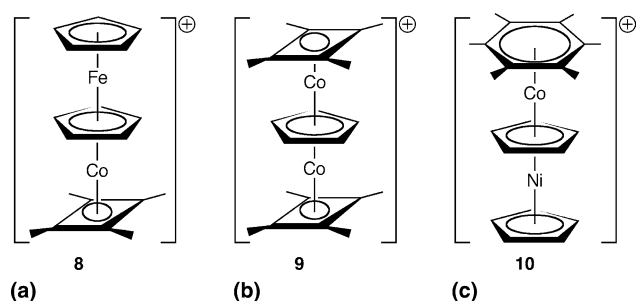
Fig. 12. (a) trans-$\{(CpFe)(\mu-\eta^5:\eta^5-Cp)[Co(C_4H_4)]\}^+$ (8); (b) trans-$\{[(C_4H_4)Co]_2(\mu-\eta^5:\eta^5-Cp)\}^+$ (9); (c) trans-$\{[(C_6Me_6)Co](\mu-\eta^5:\eta^5-Cp)(NiCp)\}^+$ (10).
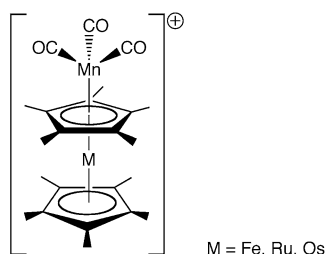
Fig. 11. Heterobimetallic singly open-faced triple-decker complexes.

the triple-deckers trans-$\{(Cp^*M)(\mu-\eta^5:\eta^5-Cp^*)[Mn(CO)_3]\}^+$ (Fig. 11).

Recently, the stacking reactions of cationic metallofragments with sandwich compounds have been further exploited by Rybinskaya et al. [12]. The mixed-metal 30VE triple-decker trans-$\{(CpFe)(\mu-\eta^5:\eta^5-Cp)[Co(C_4H_4)]\}^+$ (8) results from the reaction of $\{CpFe\}^+$ with $CpCo(\eta^4-C_4H_4)$ at 0 °C (Fig. 12(a)) [12]. Complex 8 is labile and at 20 °C loses ferrocene, leaving a $\{Co(C_4H_4)\}^+$ fragment that reacts with

$CpCo(\eta^4\text{-}C_4H_4)$ present in the reaction mixture. This provides $trans\text{-}\{[(C_4H_4)Co]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}Cp)\}^+$ (**9**, Fig. 12(b)), which can also be synthesised in pure form from $CpCo(\eta^4\text{-}C_4H_4)$ and $\{CpFe(C_6H_6)\}PF_6$ in a molar ratio $\geqslant 2\text{:}1$ [56].

These stacking reactions have been adapted for the preparation of 34VE triple-decker complexes with bridging cyclopentadienyl ligands. The reactions of 14-electron species (isolobal to $\{CpNi\}^+$) with 20-electron nickelocene provide the desired products. Thus, $\{(C_6Me_6)Co\}^+$ generated in situ from $\{(C_6Me_6)_2Co\}PF_6$ in acetone stacks with nickelocene, giving $trans\text{-}\{[(C_6Me_6)Co](\mu\text{-}\eta^5\text{:}\eta^5\text{-}Cp)(NiCp)\}^+$ (**10**), the first example of an unsymmetrical 34VE triple-decker compound with a central cyclopentadienyl ligand [67].

The stacking reactions of cyclopentadienyl-metallacarboranes and cationic metallacarboranes have been used to access 34VE triple-deckers with carboranes as the terminal ligands. Thus, complexes **11** and **12**

(Fig. 13) incorporating the anion $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$ are known, as well as the 30VE ruthenium complexes **13a**, **b** [68].

The most prevalent of metal π-ligands, Cp [4], had been identified as a middle deck in only two cases by the mid-nineties. All other confirmed triple-decker sandwiches were complexes of transition metals, or were mixed transition metal/main group metal multi-decker sandwiches usually containing heterocyclic middle decks (e.g. the multi-decker $[CpCo(\mu\text{-}1,3,4,5\text{-}tetramethyl\text{-}2,3\text{-}dihydro\text{-}1H\text{-}1,3\text{-}diboroyl)]_2Tl)$ [69]. The first example of a homometallic main-group metal triple-decker complex is the $trans\text{-}\{(CpTl)_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}Cp)\}^-$ anion (**14**), prepared from $[CpTl]_\infty$ and CpLi in the presence of 12-crown-4 in THF [70]. The crystal structure of this species shows it to possess a strongly bent structure (Fig. 14). The structure of the anionic cesocene triple-decker, $trans\text{-}\{(CpCs)_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}Cp)\}^-$ (**15**), is very similar [71].
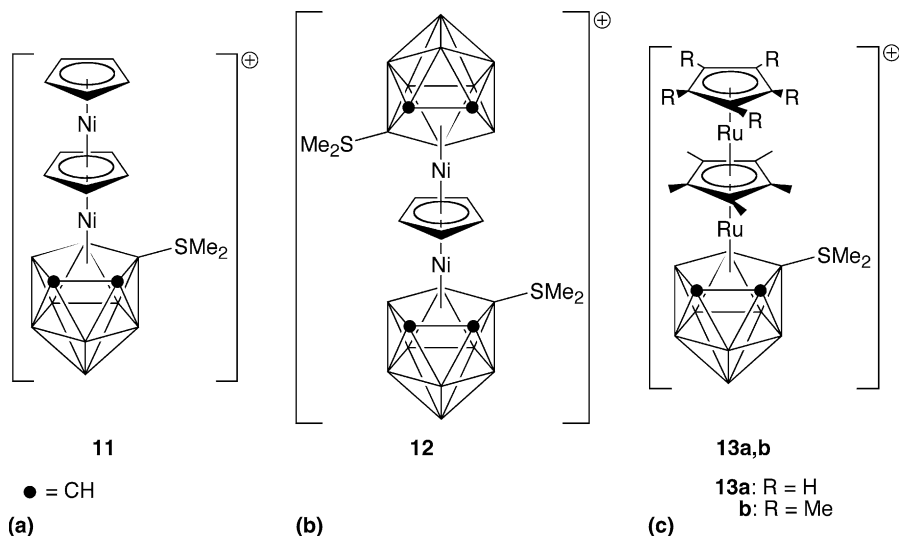

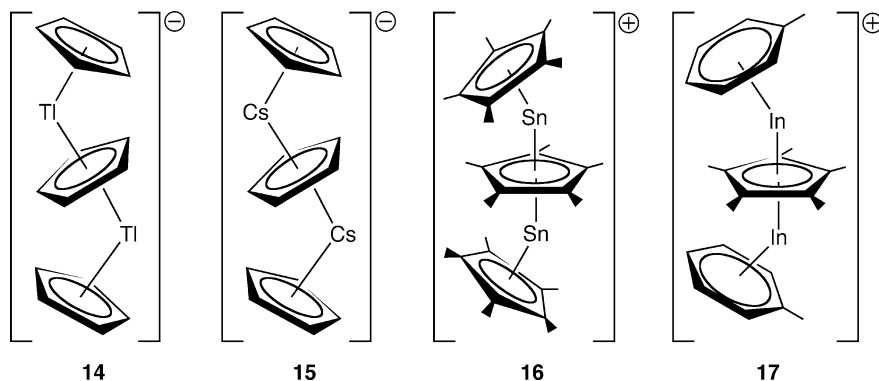Fig. 13. Metallacarborane triple-decker complexes. (a) **11**; (b) **12**; (c) **13a,b**.

Fig. 14. Main-group metal triple-decker sandwich complexes $trans\text{-}[Cp_3M_2]^-$ (**14**, M = Tl; **15**, M = Cs), $trans\text{-}\{(Cp^*Sn)_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}Cp^*)\}^+$ (**16**) and $trans\text{-}\{[(C_6H_5Me)In]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}Cp^*)\}^+$ (**17**).

Table 1
μ-η^6:η^6-Arene-bridged triple-decker complexes

Complex	Formula	Bridging ligand(s)	Ref.
19a–d	*trans*-(CpV)$_2$(μ-arene)	**a**: C$_6$H$_6$; **b**: C$_6$H$_5$Me; **c**: 1,3,5-C$_6$H$_3$Me$_3$; **d**: C$_6$H$_5$^{n}Pr	[26]
20	*trans*-[(C$_6$H$_3$Me$_3$)Cr]$_2$(μ-C$_6$H$_3$Me$_3$)	1,3,5-C$_6$H$_3$Me$_3$	[76,77]
21	*trans*-[(C$_6$H$_3$^{t}Bu$_3$)Cr]$_2$(μ-C$_6$H$_3$^{t}Bu$_3$)	1,3,5-C$_6$H$_3$^{t}Bu$_3$	[78]
22	*trans*-(CpCo)$_2$[μ-C$_6$(COOMe)$_6$]	C$_6$(COOMe)$_6$	[75]
23	*trans*-{(CpNi)$_2$(μ-C$_6$H$_6$)}$^{2+}$	C$_6$H$_6$	[79]

In the case of the cesocene, the bent structure was found to be due to packing forces in the solid state, on the basis of electronic structure studies [72]. The complexes of Tl and Cs are examples of stable triple-decker sandwiches containing only 18 and 22 valence electrons, respectively.

Cationic triple-deckers of main group elements have recently been prepared. The reaction of Cp*$_2$Sn with Ga(C$_6$F$_5$)$_3$ gives *trans*-{(Cp*Sn)$_2$(μ-η^5:η^5-Cp*)}$^+${Ga-(C$_6$F$_5$)$_4$}$^-$ (**16**), while *trans*-{[(C$_6$H$_5$Me)In]$_2$(μ-η^5:η^5-Cp*)}$^+${(C$_6$F$_5$)$_3$BO·(H)B(C$_6$F$_5$)$_3$}$^-$ (**17**) results from the treatment of [Cp*In]$_6$ in toluene with an equimolar mixture of B(C$_6$F$_5$)$_3$ and H$_2$O·B(C$_6$F$_5$)$_3$ [73]. The solvent acts as the source of the terminal ligands. A triple-decker complex with a bridging cyclopentadienyl ligand also exists for lithium. The benzene adduct of dimeric Li(η^5-C$_5$Bz$_5$) (Bz = benzyl) has a triple-decker-like structure, *trans*-[(C$_5$Bz$_5$)Li](μ-η^5:η^5-C$_5$Bz$_5$)[Li(η^2-C$_6$H$_6$)] (**18**) [74].

It is clear from the preceding discussion that monocyclic cyclopentadienyl-based ligands do not provide variety in bridging geometries, the μ-η^5:η^5 mode being found exclusively. This is a result of the small size and anionic nature of the Cp ring.

Despite the interest in the study of metal–metal interactions in organometallic systems generated by the reports of {Cp$_3$Ni$_2$}$^+$ (**5**) and {Cp$_3$Fe$_2$}$^+$ (**6**), no detailed investigations into such interactions have been carried out for bimetallic systems bridged by a single cyclopentadienyl ligand.

4. Triple-decker complexes with bridging C$_6$ carbocyclic rings

The overwhelming majority of arene complexes, which exist for almost all transition metals, have η^6-bound arenes, but complexes are known with η^1, η^2, η^3 and η^4 coordination. A considerable number of multinuclear complexes exist with bridging arene ligands, with various coordination and bridging modes found. Some of these are important model compounds for intermediate steps in arene-exchange reactions and for adsorbates on metal surfaces [75].

Binuclear complexes with *trans*-coordinated arene bridges include both "true" triple-deckers with μ-η^6:η^6 coordination and less symmetrical molecules in which the metals do not bind to all of the ring carbon atoms. *Cis*-bridged complexes are obviously not triple-decker complexes at all, but due to their close relationship with the latter they too merit discussion.

The first triple-decker complex to contain a bridging arene ligand was *trans*-(CpV)$_2$(μ-η^6:η^6-C$_6$H$_6$) (**19a**) [26]. All complexes characterised by this symmetrical bridging mode are summarised in Table 1. The structure of **19a** is given in Fig. 15. The related complexes **19b,c** were prepared by arene exchange of **19a** at high temperatures in the appropriate aromatic solvent (toluene or mesitylene, respectively); **19d** (isopropylbenzene bridge) is a by-product of the synthesis of **19a** [26]. These paramagnetic 26VE complexes do not obey the 30/34VE rule of Hoffmann et al. [30] but it has been shown that this rule does not in fact apply to complexes of the electron-poor early transition metals [31,32].

The diamagnetic 30VE homoleptic, homobimetallic triple-decker complexes of chromium with mesitylene [76,77] and 1,3,5-tri-*tert*-butylbenzene [78] (**20** and **21**, respectively), are closely related structurally and are both prepared by metal–vapour synthesis. However, **21** is obtained in roughly equal proportions to the mononuclear sandwich complex (C$_6$H$_3$Me$_3$)$_2$Cr during co-condensation, whereas **20** is only obtained in ca. 2%

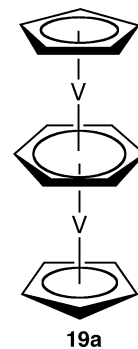Fig. 15. An example of the symmetrical μ-η^6:η^6 bridging mode in arene-bridged triple-decker complexes: *trans*-(CpV)$_2$(μ-η^6:η^6-C$_6$H$_6$) (**19a**).

yield, even at high metal-to-ligand ratios [78]. This difference may result from the ability of 1,3,5-tri-*tert*-butyl-benzene to stabilise the mono(η^6-arene) fragment [Cr(η^6-$C_6H_3{}^t$Bu$_3$)], which is presumed to be an intermediate in the formation of the triple-decker. Attempts were made to prepare the corresponding complexes of Mo and W, without success [78].

Trans-(CpCo)$_2$[μ-η^6:η^6-C_6(COOMe)$_6$] (**22**), a diamagnetic 34VE triple-decker with a bulky middle deck, has not been structurally characterised, but the highly symmetrical NMR spectra exclude other possible structures, such as a *cis* orientation [75].

The first η^6-C_6H_6-Ni(II) sandwich compound to be structurally characterised was prepared recently. The triple-decker dication *trans*-{(CpNi)$_2$(μ-η^6:η^6-C_6H_6)}$^{2+}$ (**23**), in which each nickel atom is formally an 18-electron centre, is obtained by the reaction of Cp$_2$Ni and H$_2$O·B(C_6F_5)$_3$ in CH$_2$Cl$_2$/C_6H_6, and is stabilised by a novel counteranion {(B$_3$O$_3$)(C_6F_5)$_5$}$^-$ [79]. By contrast, the reaction of Cp$_2$Ni with Et$_2$O·HBF$_4$ yields *trans*-{(CpNi)$_2$(μ-η^5:η^5-Cp)}$^+$ (**5**) [1].

In *trans*-[HfI$_2$(PMe$_2$Ph)$_2$]$_2$(μ-η^6:η^6-arene) (arene = benzene, toluene), the arene ring carbon atoms are almost equidistant from one another, but the ring is puckered – unlike the preceding complexes, the ring carbons are not coplanar [80,81].

The μ-η^4:η^4-bridging mode is rare for monocyclic arenes, and only one family of true triple-decker complexes of this type has been reported. The possibility exists for both *cis* and *trans* μ-η^4:η^4 coordination. The *cis*-bonding mode is always accompanied by a metal–metal bond which can be bridged by other ligands. μ-η^4:η^4-Arene-bridged bimetallic complexes are summarised in Table 2.

Although the complexes *cis*-(CpVH)$_2$(μ-C_6H_6)(*V–V*) (**24**) and *cis*-(CpFe)$_2$(μ-C_6R_6)(*Fe–Fe*) (**25**) (Fig. 16(a)) appear to be similar based on their formulae, the only true common feature is the bonding of all the benzene ring carbons to an M$_2$ unit. All the C–C bond distances within the benzene ring of **24** are equal, but the C–C double bonds that are coordinated to only one iron atom are significantly shorter than the other C–C bonds

Table 2
μ-η^4:η^4-Arene-bridged bimetallic complexes

Complex	Formula[a]	Bridging ligand(s)	Ref.
24	*cis*-(CpVH)$_2$(μ-C_6H_6)(*V–V*)	C_6H_6	[82]
25a,b	*cis*-(CpFe)$_2$(μ-C_6R_6)(*Fe–Fe*)	**a**: C_6Me_6; **b**: C_6Et_6	[83]
26a–g	*trans*-(Cp*Co)$_2$(μ-arene)	**a**: C_6H_6; **b**: C_6H_5Me; **c**: *o*-$C_6H_4Me_2$; **d**: *m*-$C_6H_4Me_2$; **e**: *p*-$C_6H_4Me_2$; **f**: $C_6H_5{}^i$Pr; **g**: C_6D_6	[27,84,85]
27a–f	*trans*-(Cp′Co)$_2$(μ-arene)	**a**: C_6H_6; **b**: C_6H_5Me; **c**: *o*-$C_6H_4Me_2$; **d**: *m*-$C_6H_4Me_2$; **e**: *p*$C_6H_4Me_2$; **f**: C_6D_6	[85,86]

[a] Cp′ = 1,2,4-^{t}Bu$_3$Cp.
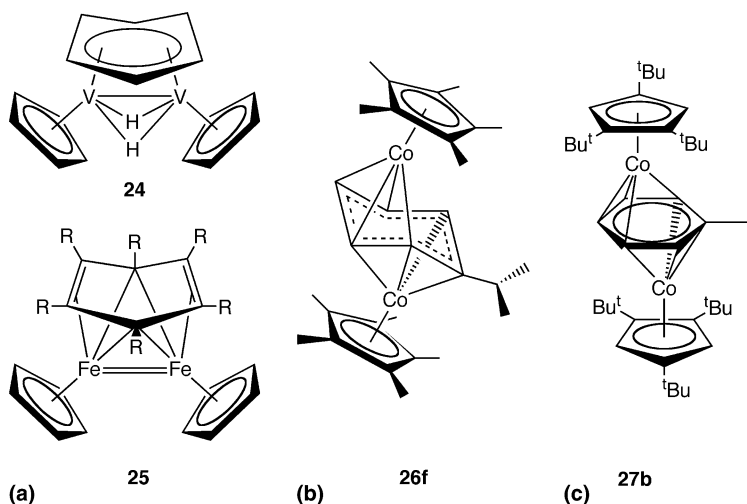
Fig. 16. μ-η^4:η^4-Arene bridged bimetallic complexes. (a) *cis*-(CpVH)$_2$(μ-C_6H_6)(*V–V*) (**24**) and *cis*-(CpFe)$_2$(μ-C_6R_6)(*Fe–Fe*) (**25**); (b) *trans*-(Cp*Co)$_2$(μ-$C_6H_5{}^i$Pr) (**26f**); (c) *trans*-(1,2,4-^{t}Bu$_3$CpCo)$_2$(μ-C_6H_5Me) (**27b**).

in the hexamethylbenzene ring of **25a** [83]. Thus, it is proposed that the vanadium atoms (bridged by two hydride ligands) in **24** are bonded to "aromatic" benzene, while a localised dienediyl structure is postulated for **25** [75]. Both complexes are fluxional in solution.

The families of complexes **26** (*trans*-(Cp*Co)$_2$(μ-arene)) and **27** (*trans*-(Cp′ Co)$_2$(μ-arene)) are useful synthetic precursors to a variety of other triple-decker complexes and have been very well studied. These compounds are fluxional in solution, exhibiting in their NMR spectra splittings and coupling patterns characteristic of time-averaged symmetrical μ-η^6:η^6-coordinate arene ligands [84]. However, a crystal structure obtained for **26f** (Fig. 16(b)) shows that the arene ligand bridges the two Cp*Co fragments in such a way that the antifacial arrangement of the two complex fragments results in a slipped triple-decker, with coordination mode μ-η^4(1,2,3,6):η^4(2,3,4,5)-1-^{i}PrC$_6$H$_5$. [84] The C$_6$ arene system is no longer planar, and a chair conformation results. Two adjacent carbon atoms each bridge the metal atoms (C2 and C3), and each metal atom is coordinated to two other carbon atoms independently, in a novel asymmetrical μ-η^4:η^4 bridging mode for arenes. The incorporation of bulkier terminal ligands such as 1,2,4-^{t}Bu$_3$Cp results in a *symmetrical* coordination mode for the two CpCo fragments. This is illustrated by the crystal structure of complex **27b** (*trans*-(1,2,4-^{t}Bu$_3$Cp-Co)$_2$(μ-η^4(1,2,3,6):η^4(3,4,5,6)-1-MeC$_6$H$_5$), in which two opposite carbon atoms (C3 and C6) of the arene moiety are bonded to both of the Co centres (Fig. 16(c)) [86]. No distortion is seen in the structure of the middle deck (planar ring system) and the coordination symmetry is evident in the ^{1}H NMR data for **27b**. Semiempirical ZINDO calculations were performed and traced the electronic origin of the arene-ring distortion in asymmetrically coordinated **26f** [86].

A shift away from symmetrical (μ-η^6:η^6) coordination has been shown to enhance the metal-arene orbital overlap population for late-transition metal arene-bridged complexes [87]. Increased metal-arene slippage is thus seen for metals such as cobalt (complexes **26** and **27**, η^4:η^4 binding) and nickel (A, Fig. 17, η^3:η^3 binding to the central aromatic ring of decacyclene) [87] compared to vanadium (complex **19**, η^6:η^6 binding). The μ-η^6:η^6 cobalt complex *trans*-(CpCo)$_2$[μ-η^6:η^6-C$_6$(COOMe)$_6$] (**22**) appears to be an exception, but has not been structurally characterised [75]; it may be that the steric bulk of the middle deck forces a more symmetrical arrangement of the coordinated metal fragments. The nickel complex *trans*-{(CpNi)$_2$(μ-η^6:η^6-C$_6$H$_6$)}$^{2+}$ (**23**) also does not display the expected slipped coordination. However, for a given metal, removing electrons from the neutral triple-decker complex of interest has been demonstrated to increase the metal-arene orbital overlap. This can be explained by the fact that the frontier orbitals are largely metal-centred, but also have
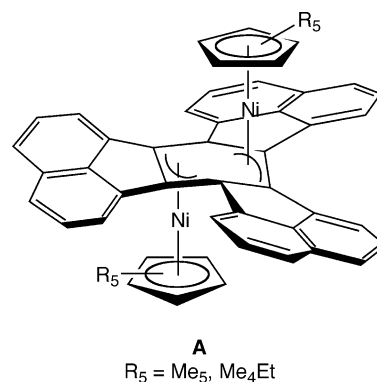

Fig. 17. Nickel triple-decker complexes of decacyclene; *trans*-(Cp^{R}Ni)$_2$(μ-η^3:η^3-C$_{36}$H$_{18}$) (**A**) [87].

metal-to-ligand antibonding combinations. Therefore, the cationic nature of the metal centres leads to an increased orbital overlap, offsetting the drop in overlap population due to symmetrical coordination.

It has been demonstrated by EHMO calculations on μ-η^6:η^6-and μ-η^3:η^3-benzene-bridged complexes of V, Co, and Ni that the orbital overlap population between a given metal and an arene ring, which is used as a measure of arene–metal bond stability, decreases as additional electrons are placed in the frontier orbitals [87]. Therefore, an increased metal–arene lability is expected in the triple-decker arene-bridged complexes of the late transition metals (e.g. cobalt and nickel), due to the increased filling of metal–arene antibonding orbitals. This is in fact observed experimentally for complexes **26** and **A**; recall that arene exchange occurs only at elevated temperatures for **19a**.

The toluene ligand in **26b** can easily be substituted at room temperature by a variety of arenes or conjugated olefins, such as C$_6$D$_6$, cycloheptatriene, or COT, exchanging the middle deck with retention of the *trans* stereochemistry to produce **26g**, *trans*-(Cp*Co)$_2$(μ-η^4:η^4-C$_7$H$_8$) (**44**), or *trans*-(Cp*Co)$_2$(μ-η^4:η^4-COT) (**48**), respectively [27]. Similar reactivity studies have been carried out on **27a** and -**b**, showing that the ligand exchange proceeds by a dissociative pathway in which highly reactive 14-electron [Cp′Co]$_{solv}$ or [Cp*Co]$_{solv}$ fragments and heteroleptic CpCo(η^6-arene) sandwich-type complexes are formed [86]. This degree of reactivity in an arene triple-decker complex is unprecedented; only *trans*-(CpV)$_2$(μ-η^6:η^6-C$_6$H$_6$) (**19a**) had previously shown the ability to exchange its middle deck with retention of structure and then only at elevated temperatures [26]. Thus, **26b** can be considered an excellent source of the [Cp*Co] fragment and can be used as a transfer agent for the latter under mild conditions, as an alternative to the widely used Cp*Co(C$_2$H$_4$)$_2$ [88]. This is advantageous, as the nature of a starting material (i.e. whether it is monomeric or dimeric) can greatly influence the regiochemistry of the product it forms.

Table 3
μ-η^3:η^3-Arene-bridged bimetallic complexes

Complex	Formula[a]	Bridging ligand	Ref.
28	trans-[(Cy$_2$PC$_2$H$_4$PCy$_2$)Co]$_2$(μ-p-C$_6$H$_4$Me$_2$)	p-C$_6$H$_4$Me$_2$	[83]
29	trans-[(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Co]$_2$(μ-C$_6$H$_6$)	C$_6$H$_6$	[89]
30	cis-(CpRh)$_2$(μ-C$_6$H$_6$)(Rh–Rh)	C$_6$H$_6$	[90]
31a–c	cis-(CpIr)(μ-C$_6$H$_6$)(LM)(Ir–M)(a: LM = CpCo; b: LM = CpRh; c: LM = Cp*Rh)	C$_6$H$_6$	[91]
32	cis-[(C$_6$H$_5$Me)Fe]$_2$(μ-C$_6$H$_5$Me)(Fe–Fe)	C$_6$H$_5$Me	[92]

[a] Cy = cyclohexyl.

The μ-η^3:η^3-arene coordination mode is less common than the μ-η^4:η^4 bridging geometry, and only two, related, complexes have been found with arenes as bis-(enyl) bridging ligands. Triple-deckers trans-[(R$_2$PC$_2$H$_4$PR$_2$)Co]$_2$[μ-η^3(1–3):η^3(4–6)-C$_6$H$_4$R$'_2$] 28 (R = Cy, R′ = p-Me$_2$) [82] and 29 (R = ^{i}Pr, R′ = H) [89] (Table 3 and Fig. 18) differ only in the substituents on the ancillary ligands and on the middle deck. As in trans-(Cp*Co)$_2$-(μ-arene) (26) or trans-(Cp′Co)(μ-arene) (27), the bridging arene takes on a flattened chair conformation. The geometry in the p-xylene bridge of 28 is typical for an η^3-methallyl group [82] (see Fig. 18).

Each cobalt atom in 28 and 29 has a 16 VE configuration (d^8 Co(I)). A symmetrical (μ-η^6:η^6) triple-decker structure is not formed; such a structure would have 32VE and thus be an unstable diradical.

A cis geometry for the preceding complexes is disfavoured on steric grounds. However, cis μ-η^3:η^3-arene complexes are more common than their trans counterparts. The irradiation of CpRh(C$_2$H$_4$)$_2$ in the presence of benzene gives cis-(CpRh)$_2$[μ-η^3(1–3):η^3(4–6)-C$_6$H$_6$](Rh–Rh) (30) [90]. The thermal reaction of CpIr(η^4-C$_6$H$_6$) with CpCo(C$_2$H$_4$)$_2$ yields cis-(CpIr)(μ-η^3:η^3-C$_6$H$_6$)(CpCo)(Ir–Co) (31a) while a photochemical reaction with Cp(*)Rh(C$_2$H$_4$)$_2$ provides cis-(CpIr)(μ-η^3:η^3-C$_6$H$_6$)(CpRh)(Ir–Rh) (31b) and cis-(CpIr)(μ-η^3:η^3-C$_6$H$_6$)(Cp*Rh)(Ir–Rh) (31c) [91]. The cis-bis(enyl) benzene ring takes a boat conformation in the solid state (Fig. 19); the complexes are fluxional in solution. It is interesting that the lighter homologue of 30, trans-

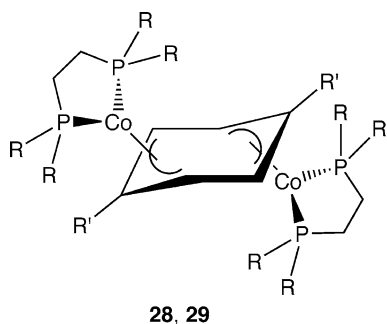(Cp*Co)$_2$(μ-η^4:η^4-C$_6$H$_6$) (26a), forms an antifacially co-ordinated complex with no metal–metal bond.

A cis μ-η^3:η^3 system is also known for iron. The mononuclear complex (η^6-C$_6$H$_5$Me)Fe(η^4-C$_6$H$_5$Me) is formed by co-condensation of metal atoms and toluene, and will react with various nitrogen-containing ligands to form unstable intermediates. These intermediates react with toluene between −80 and −30 °C, yielding cis-[(C$_6$H$_5$Me)Fe]$_2$(μ-η^3:η^3-C$_6$H$_5$Me)(Fe–Fe) (32) [92]. The solid-state structure is similar to that shown in Fig. 19; as expected, the bridging ligand is fluxional in solution.

One of the earliest structurally characterised metal adducts (i.e. not a molecular compound such as 19) of an arene is the silver(I) compound [Ag(C$_6$H$_6$)ClO$_4$]. [93] The benzene molecules are only weakly bound, rendering this complex unstable in the absence of a benzene atmosphere. Zigzag chains of [Ag–(C$_6$H$_6$)–Ag–(C$_6$H$_6$)]$_n$ characterise the structure. The metal atoms are bound to the arenes in a trans-μ-η^2(1,2):η^2(4,5) coordination mode.

All of the molecular species with a μ-η^2:η^2-bridging arene ligand are triple-decker complexes (Table 4); to the best of our knowledge, no cis-μ-η^2:η^2-arene structures have been reported.

The complex trans-[Cp*Re(CO)$_2$]$_2$[μ-η^2(1,2):η^2(3,4)-C$_6$H$_6$] (33) is formed in poor yield during the photolysis of Cp*Re(CO)$_3$ in benzene [94]. The bridging ligand can be described as η^2:η^2-coordinated cyclohexatriene (Fig. 20(a)), with the free C–C bond being considerably shorter than the rhenium-coordinated C–C bonds. A trans-[μ-η^2(1,2):η^2(3,4)] structure has also been proposed for the complexes trans-(NiL$_2$)$_2$[μ-η^2:η^2-C$_6$(CF$_3$)$_6$] (36) on the basis of ^{31}P and ^{19}F NMR data.

Fig. 18. μ-η^3:η^3-Arene bridged triple-decker complexes: trans-(R$_2$PC$_2$H$_4$PR$_2$)Co]$_2$[μ-η^3(1–3):η^3(4–6)-C$_6$H$_4$R$'_2$] (28 and 29).
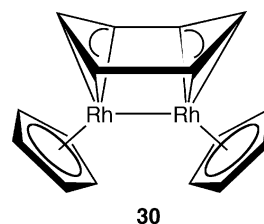
Fig. 19. An example of a cis-μ-η^3:η^3-arene-bridged triple-decker complex: cis-(CpRh)$_2$[μ-η^3(1–3):η^3(4–6)-C$_6$H$_6$](Rh–Rh) (30).

Table 4
μ-$η^2$:$η^2$-Arene-bridged triple-decker complexes

Complex	Formula[a]	Bridging ligand	Ref.
33	*trans*-[Cp*Re(CO)$_2$]$_2$(μ-C$_6$H$_6$)	C$_6$H$_6$	[94]
34	*trans*-[Ta(silox)$_3$]$_2$(μ-C$_6$H$_6$)	C$_6$H$_6$	[95]
35a,b	*trans*-{[Os(NH$_3$)$_5$](μ-C$_6$H$_6$)[M(NH$_3$)$_5$]}$^{4+}$	C$_6$H^6	[96–98]
	(**a**: M = Os; **b**: M = Ru)		
36a–c	*trans*-(NiL$_2$)$_2$[μ-C$_6$(CF$_3$)$_6$]	C$_6$(CF$_3$)$_6$	[99,100]
	(**a**: L$_2$ = COD; **b**: L$_2$ = [P(OMe)$_3$]$_2$;		
	c: L$_2$ = P[(OCH$_2$)$_3$CMe])		

[a] silox = OSi^{t}Bu$_3$.
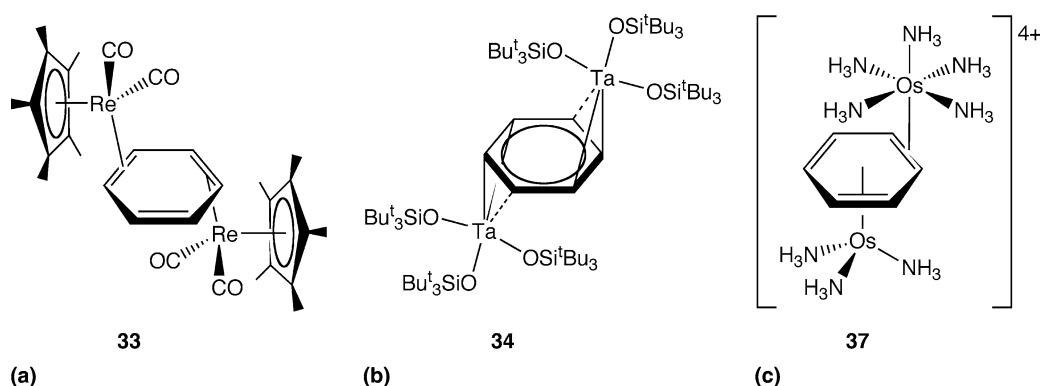
Fig. 20. Different bridging modes in μ-$η^2$:$η^n$-arene-bridged triple-decker complexes. (a) μ-$η^2$(1,2):$η^2$(3,4); (b) μ-$η^2$(1,2):$η^2$(4,5); (c) μ-$η^2$:$η^6$.

Due to the steric bulk of the Ta(silox)$_3$ fragments, the alternative *trans*-[μ-$η^2$(1,2):$η^2$(4,5)] coordination is seen in *trans*-[Ta(silox)$_3$]$_2$(μ-$η^2$:$η^2$-C$_6$H$_6$) (**34**) [95]. The bonding of each Ta atom to one C–C bond of the benzene is very asymmetrical, and because a weaker interaction takes place between each Ta and another benzene C atom, the bridging can also be considered as distorted $η^3$-enyl (Fig. 20(b)). Unfortunately, the geometry of the benzene ring could not be precisely determined.

The complexes *trans*-{[Os(NH$_3$)$_5$][μ-$η^2$(1,2):$η^2$(3,4)-C$_6$H$_6$][M(NH$_3$)$_5$]}$^{4+}$ (**35**) exhibit bridging and ring geometry similar to those of **33** [97]. The free C=C double bond is remarkably chemically inert, probably due to the steric protection of the ammonia groups [75]. Complex **35a** loses two NH$_3$ groups under vacuum to give *trans*-{[Os(NH$_3$)$_5$](μ-$η^2$:$η^6$-C$_6$H$_6$)[Os(NH$_3$)$_3$]}$^{4+}$ (**37**), a complex with a highly unusual, mixed hapticity bridging benzene ligand (Fig. 20(c)) deduced from spectroscopic data [97].

Of those species reviewed, it appears that only the osmium complex *trans*-{[Os(NH$_3$)$_5$]$_2$(μ-$η^2$:$η^2$-C$_6$H$_6$)}$^{4+}$ (**35a**) has been investigated with regard to metal–metal interactions.

The cyclic voltammogram (CV) for **35a** shows two oxidation waves separated by 0.50 V, and the redox behaviour of this complex confirms that the mixed-valence (MV) complex is stable, at least on the electrochemical time-scale [96]. Chemical oxidation of **35a** with ferroce-

nium provides the mixed-valence pentacation, for which a near-infra-red (NIR) spectrum was obtained. A broad, weak band was seen at 1750 nm, with a half-height width of 1600 cm^{-1}; this value is less than half that calculated by the Hush model for a valence-trapped system [96]. Along with the large ΔE value found in the CV, this suggests that the MV form of **35a** is a fully-delocalised Robin-Day class III MV complex, and that an arene middle deck, at least bound in a μ-$η^2$:$η^2$ manner, can permit or promote metal–metal interactions.

5. Triple-decker complexes with bridging C$_7$ carbocyclic rings

While the use of seven-membered cycloolefins such as cycloheptatriene as ligands in organometallic chemistry is well established, complexes in which two transition metals are attached to the same cycloheptatriene molecule are rare. The bimetallic coordination chemistries of cycloheptatriene (C$_7$H$_8$) and the tropylium ion (C$_7$H$_7^+$) are dominated by the synfacial binding of two metal moieties to the carbocycle. The first homobimetallic complexes of cycloheptatriene were *cis*-[Fe(CO)$_3$]$_2$[μ-$η^3$(1–3):$η^3$(4–6)-C$_7$H$_7$R](*Fe–Fe*) (**38a**, R = H; **38b**, R = OMe), prepared from Fe$_2$(CO)$_9$ and the appropriate cycloheptatriene [101]. The ruthenium analogues of these complexes are also known [102,103]. The structure
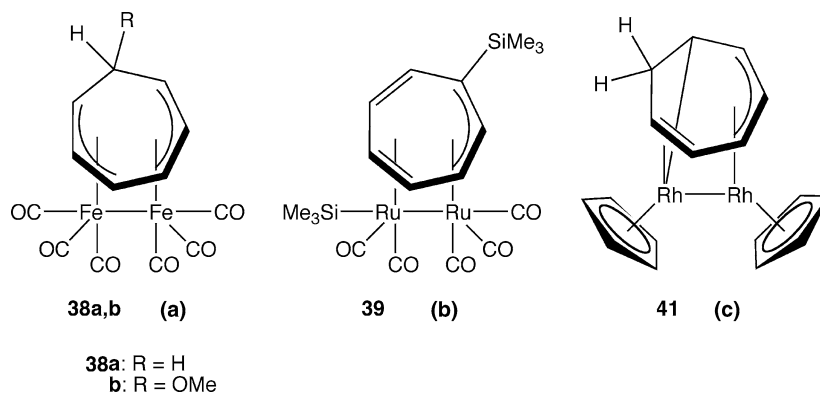
Fig. 21. Examples of bimetallic *cis*-cycloheptatriene and -cycloheptatrienyl complexes displaying a variety of coordination modes. (a) *cis*-[Fe(CO)₃]₂[μ-η³(1–3):η³(4–6)-C₇H₇R](*Fe–Fe*)(**38**); (b) *cis*-[Ru(CO)₃](μ-η³:η⁴-C₇H₆SiMe₃)-[Ru(CO)₂SiMe₃](*Ru–Ru*)(**39**); (c) *cis*-(CpRh)₂(μ-η³:σ,η²-C₇H₈)(*Rh–Rh*) (**41**).

of **38** (Fig. 21(a)) was determined by spectroscopic and X-ray crystallographic methods. Other complexes of this type have also been synthesised from metal–metal bonded and/or dimeric starting materials, including *cis*-[Ru(CO)₃](μ-η³:η⁴-C₇H₇)[Ru(CO)₂SiMe₃](*Ru–Ru*) (**39**; Fig. 21(b)) [104], *cis*-[Ru(CO)₃](μ-η³:η⁴-C₇H₆SiMe₃)[Ru-(CO)₂SiMe₃](*Ru–Ru*) (**40**) [104,105] and *cis*-(CpRh)₂-(μ-η³:σ,η²-C₇H₈)(*Rh–Rh*) (**41**; Fig. 21(c)) [106].

The use of the cycloheptatrienyliron tricarbonyl anion, [(C₇H₇)Fe(CO)₃]⁻ (**42**) [107], as a source of C₇H₇⁻ has provided numerous examples of heterobimetallic complexes. The reaction of **42** with dimeric [M(CO)₂ₓBr(THF)ᵧ]₂ (M = Rh, x = 1, y = 0; M = Mn, x = 2, y = 0; M = Re, x = 3/2, y = 1) yields exclusively *cis* geometries, as expected: *cis*-[Fe(CO)₃](μ-η³:η⁴-C₇H₇)[Rh(CO)₂](*Fe–Rh*), *cis*-[Fe(CO)₃](μ-η³:η⁴-C₇H₇)[Mn-(CO)₃](*Fe–Mn*), and *cis*-[Fe(CO)₃](μ-η³:η⁴-C₇H₇)[Re-(CO)₃](*Fe–Re*)[108]. Further examples of *cis*-coordinated bimetallics include the products of the reactions between **42** and [(COD)RhCl]₂, [(NBD)RhCl]₂ (NBD = norbornadiene) and [(C₃H₅)PdCl]₂ [109].

To the best of our knowledge, the only known examples of *trans* cycloheptatrienyl complexes are the heterobimetallic species *trans*-[Fe(CO)₃][μ-η⁴(1–4):η³(5–7)-C₇H₇][Mn(CO)₂L] (**43a**, L = Cp; **43b**, L = poly-(pyrazolyl)borate) and *trans*-(Cp*Co)₂(μ-η³:η⁴-C₇H₈) (**44**) shown in Fig. 22 [110]. To obtain the first examples of a *trans*-bound cycloheptatriene bridge (**43**), the steric bulk of the ancillary ligands on the metal moieties was exploited: the slipped triple-decker *trans*-(Cp*Co)₂-(μ-η³:η⁴-C₇H₈) (**44**, Fig. 22(b)) is formed exclusively from Cp*Co(C₂H₄)₂ and Cp*Co[η⁴(1–4)-C₇H₈]. In contrast, the *cis*-complex is the sole product of the corresponding unmethylated starting materials [111]. The two bulky Cp* groups prevent the formation of a Co–Co bond, thereby forcing the triple-decker structure. Though the large Co–Co distance in **44** precludes any direct metal–metal interactions, the two metal atoms are
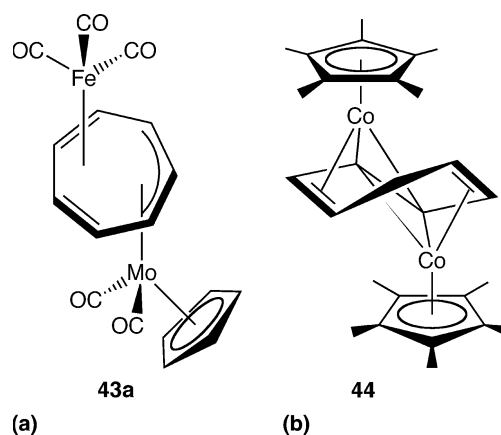

Fig. 22. The *trans* complexes of cycloheptatriene and cycloheptatrienyl. (a) *trans*-[Fe(CO)₃][μ-η⁴(1-4):η³-(5–7)C₇H₇][Mn(CO)₂Cp] (**43a**); (b) *trans*-(Cp*Co)₂(μ-η⁴:η⁴-C₇H₈) (**44**).

electronically coupled *via* the bridging ligand as is usual for triple-decker complexes, giving a closed 34VE shell.

6. Triple-decker complexes with bridging C₈ carbocyclic rings

The known triple-decker complexes of cyclooctatetraene (COT) are summarised in Tables 5–7. The larger ring size of COT compared to cyclopentadienyl and benzene allows for many variations in coordination mode. Therefore, the *cis*-COT-bridged bimetallic complexes, of which there are many, will not be considered here.

A selection of μ-η⁴:η⁴-COT-bridged triple-decker complexes representing the various bonding modes exhibited by this type of compound are shown in Fig. 23. In *trans*-[Fe(CO)₃]₂(μ-η⁴:η⁴-COT) (**45**), each Fe(CO)₃ moiety is bonded to a set of four CH groups, each set forming a planar, butadiene-like moiety. An

Table 5
μ-η^4:η^4-COT-bridged triple-decker complexes

Complex	Formula[a]	Bridging ligand	Ref.
45	*trans*-[Fe(CO)$_3$]$_2$(μ-COT)	C$_8$H$_8$	[112,113]
46	*trans*-[(COT)Ti]$_2$(μ-COT)	C$_8$H$_8$	[115–118]
47	*trans*-(CpCo)$_2$(μ-COT)	C$_8$H$_8$	[114,119]
48	*trans*-(Cp*Co)$_2$(μ-COT)	C$_8$H$_8$	[28,88]
49	*trans*-(CpRh)$_2$(μ-COT)	C$_8$H$_8$	[28,106,120]
50	*trans*-(IndRh)$_2$(μ-COT)	C$_8$H$_8$	[121]
51	*trans*-(CpRh)(μ-COT)(IndRh)	C$_8$H$_8$	[121]
52	*trans*-(CpRh)(μ-COT)[(acac)Rh]	C$_8$H$_8$	[121]
53	*trans*-(CpRh)(μ-COT)(CpCo)	C$_8$H$_8$	[121]
54	*trans*-{(CpRh)(μ-COT)[(HMB)Rh]}$^+$	C$_8$H$_8$	[121]
55	*trans*-{[(HMB)Rh]$_2$(μ-COT)}$^{2+}$	C$_8$H$_8$	[121]
56a,b	*trans*-{(CpCo)(μ-COT)[(C$_3$H$_4$-2-R)Pd]}$^+$ (**a**: R = H; **b**: R = Me)	C$_8$H$_8$	[122]

[a] HMB = hexamethylbenzene.

Table 6
μ-η^5:η^5-COT-bridged triple-decker complexes

Complex	Formula	Bridging ligand	Ref.
57	*trans*-{(CpRh)$_2$(μ-COT)}$^{2+}$	C$_8$H$_8$	[28]
58	*trans*-{(Cp*Co)$_2$(μ-COT)}$^{2+}$	C$_8$H$_8$	[28]
59	*trans*-{(Cp*Co)(μ-COT)(Cp*Rh)}$^{2+}$	C$_8$H$_8$	[121]
60a,b	*trans*-(CpM)$_2$ (μ-COT) (**a**: M = Ru; **b**: M = Fe)	C$_8$H$_8$	[121,123]
61	*trans*-[(COD)Ir](μ-COT)[Mn(CO)$_3$]	C$_8$H$_8$	[29]
62a,b	*trans*-(Cp$'$ Ru)(μ-COT)[Mn(CO)$_3$] (**a**: Cp$'$ = Cp; **b**: Cp$'$ = Cp	C$_8$H$_8$	[29]

Table 7
μ-η^8:η^8-COT-bridged triple-decker complexes

Complex	Formula[a–c]	Bridging ligand	Ref.
63	*trans*-[{(Me$_3$Si)$_2$N}^{2}Sm]$_2$(μ-COT)	C$_8$H$_8$	[128]
64a,b	*trans*-[Cp*(THF)$_x$ Eu]$_2$(μ-COT) (**a**: x = 2; **b**: x = 0)	C$_8$H$_8$	[129,130]
65a,b	*trans*-[Cp*(THF)$_x$Yb]$_2$(μ-COT (**a**: x = 1; **b**: x = 0)	C$_8$H$_8$	[130]
66a,b	*trans*-[Cp*(THF)$_x$Sm]$_2$(μ-COT) (**a**: x = 1; **b**: x = 0)	C$_8$H$_8$	[131]
67	*trans*-[Cp$''$Sm]$_2$(μ-COT)	C$_8$H$_8$	[131]
68	*trans*-[Cp*Yb(THF)](μ-COT)(Cp*Yb)	C$_8$H$_8$	[132]
69a–c	*trans*-[(COT$'$)Ln]$_2$(μ-COT$'$)[d] (**a**: Ln = Ce; **b**: Ln = Nd; **c**: Ln = Sm)	1,4-C$_8$H$_6$(SiMe$_3$)$_2$	[127]
70	*trans*-(^{4}CpBa)$_2$(μ-COT)	C$_8$H$_8$	[126]

[a] COT$'$ = 1,4-C$_8$H$_6$(SiMe$_3$)$_2$; [b] Cp$''$ = C$_5$Me$_4$Et; [c] ^{4}Cp = C$_5$(CHMe$_2$)$_4$H; [d] not structurally characterised.

approximate eight-membered chair conformation is found for COT [112,113].

The structure of *trans*-[(COT)Ti]$_2$(μ-η^4:η^4-COT) (**46**) displays a less symmetrical coordination of the COT ligand. Each titanium atom is close to four carbon atoms of the boat-shaped middle deck, and two of these are shared by the two titaniums [114,115]. The outer COT rings are regular octagons. Following the reasoning of Hoffmann et al. [30], the complex with an octahapto central COT ring would be characterised by a half-filled degenerate orbital, and therefore does not occur. Although the analogous Cr$_2$(COT)$_3$, W$_2$(COT)$_3$ and Mo$_2$(COT)$_3$ complexes have also been prepared [116], it has been shown that Cr$_2$(COT)$_3$ takes on a completely different structure from **46**, of the *cis* μ-η^5:η^5-type [117]. It has been speculated that the structures of W$_2$(COT)$_3$ and Mo$_2$(COT)$_3$ are similar to that of Cr$_2$(COT)$_3$, since the importance of metal–
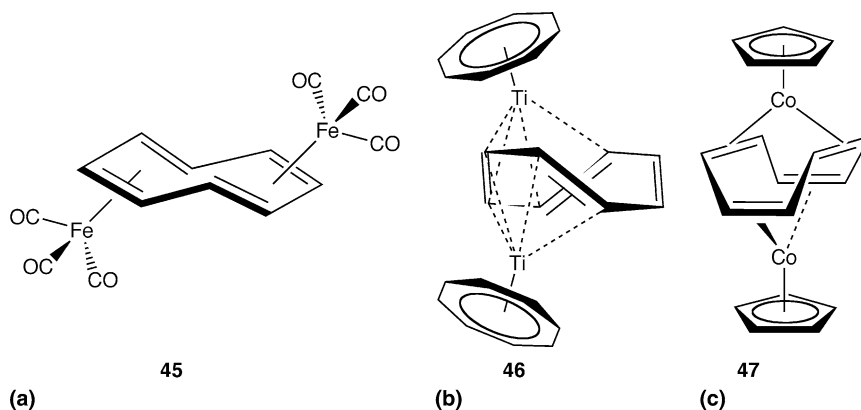
Fig. 23. Representative examples of the types of μ-η^4:η^4-COT-bridged triple-decker complexes. (a) *trans*-[Fe(CO)$_3$]$_2$(μ-η^4:η^4-COT) (**45**); (b) *trans*-[(COT)Ti]$_2$(μ-η^4:η^4-COT) (**46**); (c) *trans*-(CpCo)$_2$(μ-η^4:η^4-COT) (**47**). The Ti–C bonds in structure **46** have been shown as dotted lines for clarity.

metal bonding is believed to increase as one moves down the periodic table [117].

The remaining cobalt and rhodium μ-η^4:η^4-COT complexes in Table 5 display yet another structural type, in which the COT middle deck is folded into a tub-shaped conformation (Fig. 23(c)), allowing the two independent metals in these structures to achieve their favoured chelating coordination [28,119,121]. Complexes **47-56** have been classified as "near-misses" to the triple-decker class due to their 36VE electron-count. Chemical oxidation is possible, leading to the cationic 34VE species (see below), to which genuine triple-decker structures (albeit slipped) have been assigned.

The triple-decker complexes for which μ-η^5:η^5-COT bridges are known are summarised in Table 6. The complexes *trans*-{(CpRh)$_2$(μ-η^5:η^5-COT)}$^{2+}$ (**57**) and *trans*-{(Cp*Co)$_2$(μ-η^5:η^5-COT)}$^{2+}$ (**58**) are the dicationic oxidation products of **49** and **48**, respectively. Complex *trans*-{(Cp*Co)(μ-η^5:η^5-COT)(Cp*Rh)}$^{2+}$ (**59**) is formed by the reaction of Cp*Co(COT) and [Cp*Rh]-(BF$_4$)$_2$ [121]. Meanwhile, *trans*-(CpFe)$_2$(μ-η^5:η^5-COT) (**60a**) and *trans*-(CpRu)$_2$(μ-η^5:η^5-COT) (**60b**) are iso-electronic with **57-59** and so can be expected to display the same structural characteristics.

The structure of μ-η^5:η^5-COT-bridged bimetallic complexes is of the type shown in Fig. 24. Both metals coordinate to an η^5-dienyl portion of COT, sharing two carbon atoms. This type of double coordination of carbons is seen in *trans*-[(COT)Ti]$_2$(μ-η^4:η^4-COT) (**46**; see above).

The effect of the removal of electrons from 36VE complexes such as **48** and **49** has been well studied [123]. The structural preferences of the various electron configurations are summarised in Fig. 25. Upon oxidation of *trans*-(CpRh)$_2$(μ-η^4:η^4-COT) (**49**) or its cobalt analogue (**48**) by removing two electrons, a 34VE complex is formed (**57**) with a concomitant change in COT bridging mode from μ-η^4:η^4 to μ-η^5:η^5. The ruthenium complex *trans*-(CpRu)$_2$(μ-η^5:η^5-COT) (**60b**) was employed in order to obtain and study structures with even
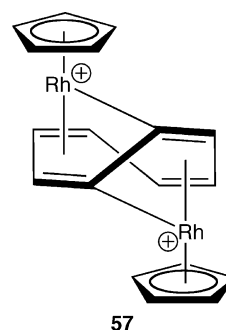
Fig. 24. The μ-η^5:η^5-coordination mode of the COT ligand: *trans*-{(CpRh)$_2$(μ-COT)}$^{2+}$ (**57**).

lower valence electron counts, because **60b** is more ame-nable to oxidation than **57** due to its overall neutral charge. As the VE count is decreased, [2] the structures become more "closed" [29]. The tub form of the bridg-ing ligand undergoes substantial flattening, taking on the "twist" form characteristic of the μ-η^5:η^5 complexes and finally (reversibly) breaking a C–C bond to give the 10-membered metallacycles found in the flyover com-plexes depicted in Fig. 25 [125].

The only structure that is truly in question is that of the 35VE complexes. The formal electron count is based on a constant number of valence electrons for the CpM moieties (14e, M = Co, Rh; 13e, M = Ru) and for the COT ligand (8e) [123]. To retain the stability of the 18e configuration in each even-electron species, the met-als form new bonds after each two-electron transfer. Thus, in the 34VE structure, the bridging C–C bond

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[2] This series is continued by the complexes (CpCr)$_2$(μ-COT) and (CpV)$_2$(μ-COT), which have 28 and 26 VE, respectively; *cis* coordi-nation is seen for both complexes. The missing complexes of Mn and Re in this series are represented by the isoelectronic heterobimetallic complex (CpCr)(μ-COT)(CpFe), which has *cis* η^4:η^4-COT coordina-tion [124]. Both *cis* and *trans* isomers of (CpRh)$_2$(μ-COT) (**49**) are known [121].
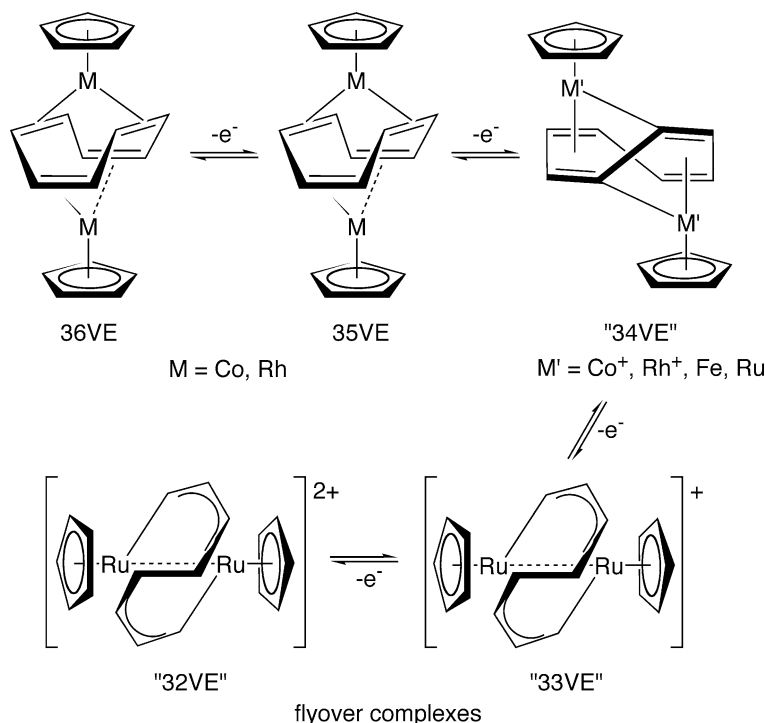
Fig. 25. The series of structures obtained upon oxidation of COT-bridged triple-decker complexes [123].

donates an extra electron to each metal, preserving the electron count. Metal–metal bond formation provides another valence electron to each metal in the 32VE flyover species.

In progressing from C_4H_4 to C_8H_8 there is a dramatic increase in ring size, and small metals cannot coordinate in an η^8 manner as easily as they can η^4 or η^5. In order to achieve full hapticity the metal atoms would have to move closer to the (COT) ring centroid, which then prevents maximum orbital overlap between the ring and the metal. This explains in part the abundance of *cis*-bimetallic COT complexes; metal–metal bonds are the preferred means of achieving the desired electron-count.

It is not surprising, then, that true triple-decker complexes of COT do not occur for the d-block metals and have only been found for the lanthanides and the heavy main group metal barium (Table 7). The μ-η^8:η^8-coordination mode has been proposed for the dianion of *trans*-[(COT)Ti]$_2$(μ-η^4:η^4-COT) (**46**) [118]; however, there is no substantial proof for this claim.

The barium complex **70** is notable, as very few triple-decker complexes exist for the main group metals [126]. In most cases, a "bent" triple-decker structure is found (Fig. 26), with the ancillary ring ligands tilted away from the M–COT(centroid)–M axis to varying degrees. Unfortunately the homoleptic complexes, *trans*-[(COT′)Ln]$_2$-(μ-COT′) (**69**; COT′ = 1,4-C_8H_6(SiMe$_3$)$_2$), have not yet been structurally characterised. The coordination mode of the middle deck has been confirmed by NMR spectroscopy [127], but it would be of interest to determine
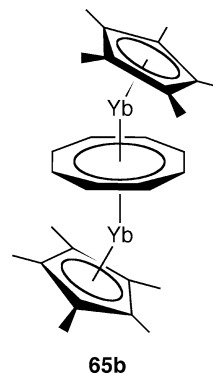

Fig. 26. A bent triple-decker lanthanide complex containing a μ-η^8:η^8-COT ring: *trans*-(Cp*Yb)$_2$(μ-η^8:η^8-COT) (**65b**).

whether the rings are parallel. As of yet, triple-decker sandwich complexes with parallel rings are unknown in organolanthanide chemistry, the bent structures alluded to being preferred.

Of all the COT triple-decker complexes discussed above, only *trans*-(CpCo)$_2$(μ-η^4:η^4-COT) (**47**) has been characterised in order to determine if metal–metal communication takes place [119]. The CV data for this complex indicate that two electrons are removed from the complex in separate steps with $E_2° < E_1°$, and (in a separate experiment) that two one-electron reductions are seen for the neutral complex. The latter observation supports the hypothesis that there is electronic interaction between the cobalt atoms.

7. Triple-decker complexes with bridging C_9 or larger carbocyclic rings

Although the cyclononatetraenyl ($C_9H_9^-$) ring is a planar, aromatic 10π-electron system (unlike cyclodecapentaene, which does not favour a planar geometry) [133], no triple-decker complexes with this carbocycle as bridging ligand are known. Triple-decker complexes are also unknown for larger rings.

8. Conclusion

A great diversity of triple-decker complexes with carbocyclic middle decks exists, spanning a range of monocyclic bridging ligands. These complexes have been reviewed and their structures discussed. Although these bimetallic compounds are potential candidates for exhibiting electronic interaction between the metal centres, they have been relatively poorly studied in this respect.

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