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Slipped μ-Indenyl Triple-Decker Complexes Containing $(C_4Me_4)Co$ and $(C_5R_5)Ru$ Fragments[‡]

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Slipped triple-decker complexes with a bridging indenyl ligand, namely $[Cb^*Co(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]^+$ (**2**, $Cb^* = C_4Me_4$) and $[Cb^*Co(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)Ru(C_5R_5)]^+$ (R = H, **5a**; Me, **5b**), have been synthesised by electrophilic stacking of $[Cb^*Co(\eta^5\text{-}C_9H_7)]$ (**1**) with $[Cb^*Co(MeCN)_3]^+$ or $[(C_5R_5)Ru(MeCN)_3]^+$ (R = H, Me), respectively. A similar reaction of $[(C_5R_5)Ru(\eta^5\text{-}C_9H_7)]$ (R = H, **3a**; Me, **3b**) with $[Cb^*Co(MeCN)_3]^+$ affords the cations $[(C_5R_5)Ru(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]^+$ (R = H, **4a**; Me, **4b**), which are isomeric with **5a**,**b**. Stacking of $[Ru(\eta^5\text{-}C_9H_7)_2]$ (**7**) with $[Cb^*Co(MeCN)_3]^+$ or $[Cb^*CoI]_x/TlBF_4$ gives the triple-decker complex $[(\eta^5\text{-}C_9H_7)Ru(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]^+$ (**8**). Further reaction of **8** with $[Cp^*RuCl]_4/TlBF_4$ unexpectedly affords the slipped tetradecker ruthenium complex $[Cp^*Ru(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)Ru(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)RuCp^*]^{2+}$ (**11**). The structures of $[\mathbf{4b}][Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]$ and $[Cp^*Ru(\eta^6\text{-}C_9H_7)]$ (**6**) have been determined by X-ray diffraction, and the electrochemical behaviour of the complexes prepared has been studied.

Introduction

The presence of two fused π-systems in pentalene, indenyl and naphthalene makes them able to form slipped triple-decker complexes with an *anti* coordination of the metal atoms.[2] The first example of such compounds, $[(\eta^3\text{-allyl})Ni(\mu{:}\eta^5{:}\eta^5\text{-}C_8H_6)Ni(\eta^3\text{-allyl})]$, was described by Miyake and Kanai in 1971.[3] Manriquez et al. have synthesised a series of fused metallocenes with the formula $[Cp^*M(\mu{:}\eta^5{:}\eta^5\text{-}C_8H_6)M'Cp^*]$ (M, M′ = Fe, Co, Ni, Ru) along with other related compounds.[4] Their most interesting feature is a strong electronic interaction between the metal centres, as established by electrochemical and spectroscopic studies. A few μ-naphthalene triple-decker complexes are known: $[(\eta^6\text{-}C_6H_6)Cr(\mu{:}\eta^6{:}\eta^6\text{-}C_{10}H_8)Cr(\eta^6\text{-}C_6H_6)]$,[5] $[(C_5R_5)M(\mu{:}\eta^6{:}\eta^6\text{-}C_{10}H_8)M(C_5R_5)]$ (M = V, Fe[6]), and $[(cod)Ru(\mu{:}\eta^6{:}\eta^6\text{-}C_{10}H_8)Ru(cod)]$.[7] μ-Indenyl derivatives are the least studied, and the first examples, the ruthenium complexes $[(C_5R_5)Ru(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)Ru(C_5R_5)]^+$,[8] were prepared by electrophilic stacking of $[(C_5R_5)Ru(\eta^5\text{-}C_9H_7)]$ with $[(C_5R_5)Ru]^+$ fragments.[9]

Recently we have developed convenient methods for the preparation of (tetramethylcyclobutadiene)cobalt complexes.[10–13] The acetonitrile complex $[Cb^*Co(MeCN)_3]^+$ ($Cb^* = C_4Me_4$) has been shown to be the most useful synthon of the Cb*Co fragment. In particular, its reaction with the indenide anion gives the η^5-indenyl derivative $[Cb^*Co(\eta^5\text{-}C_9H_7)]$ (**1**).[12] Herein we describe the synthesis and electrochemical behaviour of dicobalt and cobalt-ruthenium triple-decker complexes with a bridging indenyl ligand.[14]

Results and Discussion

Synthesis

Electrophilic stacking of **1** with $[Cb^*Co(MeCN)_3]^+$ in nitromethane affords the slipped dicobalt triple-decker complex $[Cb^*Co(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]^+$ (**2**) in 54% yield (Scheme 1). Similar reactions of the (η^5-indenyl)ruthenium derivatives $[(C_5R_5)Ru(\eta^5\text{-}C_9H_7)]$ (R = H, **3a**; Me, **3b**) give the cobalt-ruthenium complexes $[CpRu(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]^+$ (**4a**, 23%) and $[Cp^*Ru(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]^+$ (**4b**, 54%; Scheme 2). Both reactions are reversible, with nucleophilic degradation of the products by acetonitrile being the back reaction. The low yield of **4a** suggests it degrades easier than **4b**, which is apparently connected with the poorer donor ability of the CpRu fragment. Nevertheless, we were able to increase the yield up to 78% by using a fivefold excess of **3a** and removing acetonitrile from the reaction mixture.

[‡] (Tetramethylcyclobutadiene)cobalt Complexes, 6. For part 5 see ref.[1]

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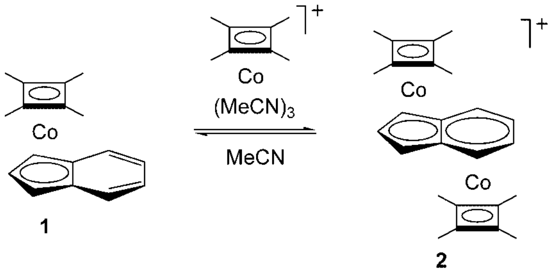
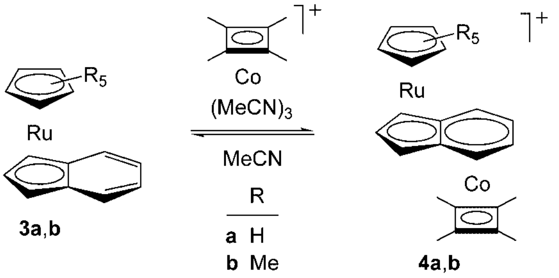
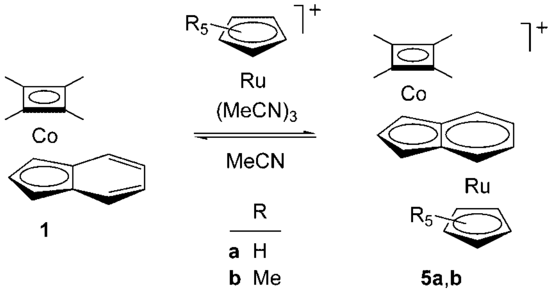


Scheme 1. Synthesis of the Co_2 complex **2**.

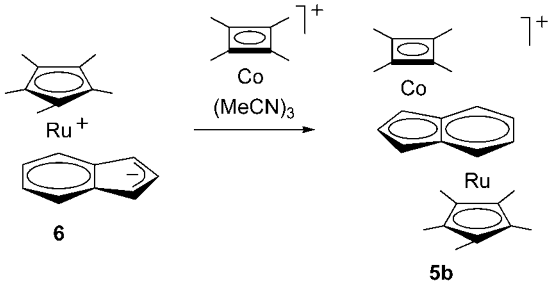


Scheme 2. Synthesis of the CoRu complexes **4a**,**b**.

The cobalt atom in complexes **4a**,**b** is coordinated at the six-membered ring of the indenyl ligand. The isomeric cations [Cb*Co(μ:η^5:η^6-C_9H_7)Ru(C_5R_5)]$^+$ (R = H, **5a**; Me, **5b**) with the cobalt atom at the five-membered ring were prepared by stacking of **1** with [(C_5R_5)Ru(MeCN)$_3$]$^+$ (R = H, Me; Scheme 3). Alternatively, complex **5b** was obtained by treatment of the η^6-indenyl derivative [Cp*Ru(η^6-C_9H_7)] (**6**) with [Cb*Co(MeCN)$_3$]$^+$ (Scheme 4).

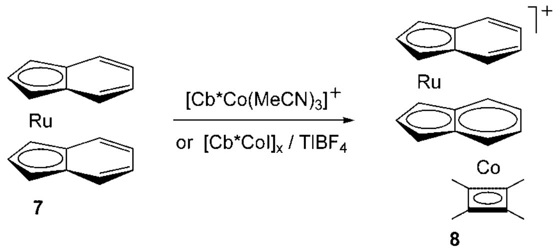


Scheme 3. Synthesis of the CoRu complexes **5a**,**b**.



Scheme 4. Synthesis of **5b** from the η^6-indenyl complex **6**.

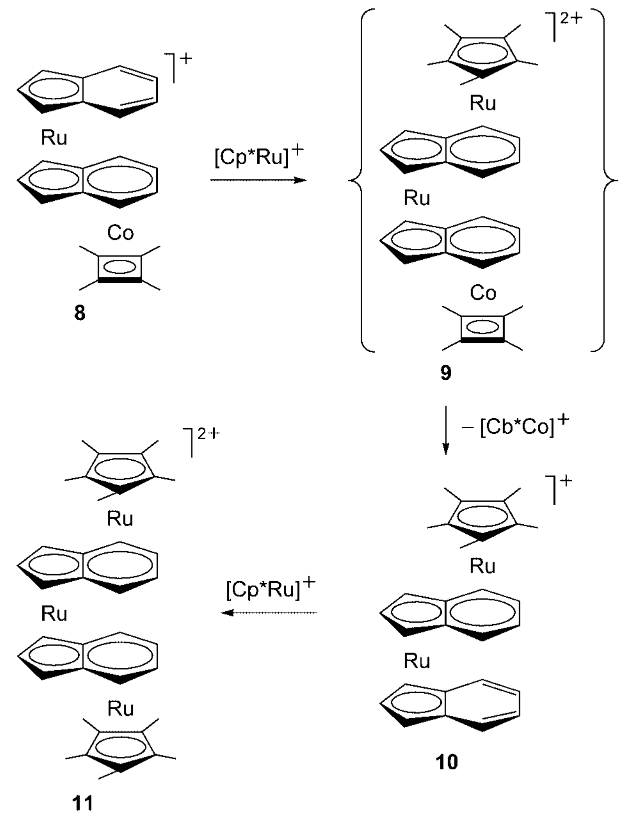
It has been shown previously that stacking of bis(indenyl)ruthenium [Ru(η^5-C_9H_7)$_2$] (**7**) with [(C_5R_5)Ru(MeCN)$_3$]$^+$ affords either triple- or tetra-decker complexes such as [(C_5R_5)Ru(μ:η^5:η^6-C_9H_7)Ru(η^5-C_9H_7)]$^+$ and [(C_5R_5)Ru(μ:η^5:η^6-C_9H_7)Ru(μ:η^5:η^6-C_9H_7)Ru(C_5R_5)]$^{2+}$ as a result of addition of one or two fragments, respectively.[8a] However, a similar reaction of **7** with [Cb*Co(MeCN)$_3$]$^+$ gives only the slipped triple-decker complex [(η^5-C_9H_7)Ru(μ:η^5:η^6-C_9H_7)CoCb*]$^+$ (**8**, 15–20%), irrespective of the reagent ratio (Scheme 5). The yield was greatly increased (up to 65%) by using a new method for the generation of the [Cb*Co]$^+$ fragment. This utilizes halide abstraction from the iodide complex [Cb*CoI]$_x$ by treatment with $TlBF_4$ in thf. The advantage of this method is the absence of strongly coordinating acetonitrile. In particular, it has proved to be very effective for the preparation of arene complexes [Cb*Co(arene)]$^+$ containing acceptor ligands (dichlorobenzene, acetophenone and anthracene).[15]



Scheme 5. Synthesis of the CoRu complex **8**.

However, the reaction of **7** with two equivalents of [Cb*CoI]$_x$/$TlBF_4$ does not give the expected tetra-decker complex [Cb*Co(μ:η^5:η^6-C_9H_7)Ru(μ:η^5:η^6-C_9H_7)CoCb*]$^{2+}$. We propose that the insolubility of the primary product **8**·BF_4 in thf precludes its further stacking reaction.[16] However, the salt [**8**][Co(η-7,8-$C_2B_9H_{11}$)$_2$], which is well soluble in thf, also proved to be unreactive towards [Cb*CoI]$_x$/Tl[Co(η-7,8-$C_2B_9H_{11}$)$_2$].

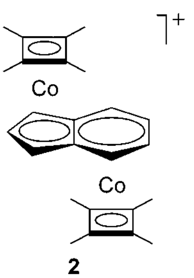
The reaction of the triple-decker cation **8** with the [Cp*Ru]$^+$ fragment, generated as a labile solvate from [Cp*RuCl]$_4$/$TlBF_4$ in $MeNO_2$ (Scheme 6), proved to be very intriguing. A 1:1 molar ratio resulted in a mixture of the slipped triple-decker complexes **8** (25%) and [Cp*Ru(μ:η^5:η^6-C_9H_7)Ru(η^5-C_9H_7)]$^+$ (**10**, 15%) along with the slipped tetra-decker complex [Cp*Ru(μ:η^5:η^6-C_9H_7)Ru(μ:η^5:η^6-C_9H_7)RuCp*]$^{2+}$ (**11**, 60%), whereas with a 1:2 ratio only complex **11** (59%) was isolated. The unstable cobalt-ruthenium tetra-decker cation [Cb*Co(μ:η^5:η^6-C_9H_7)Ru(μ:η^5:η^6-C_9H_7)RuCp*]$^{2+}$ (**9**) is believed to be an intermediate. Its further degradation leads to the diruthenium cation **10** by elimination of the [Cb*Co]$^+$ fragment. Subsequent reaction of **10** with a second equivalent of [Cp*Ru]$^+$ gives the stable Ru_3 tetra-decker cation **11**.



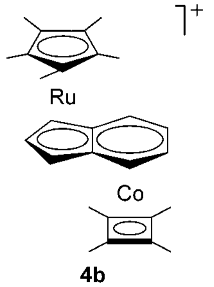
Scheme 6. Formation of the Ru_3 complex **11**.

Nucleophilic Degradation

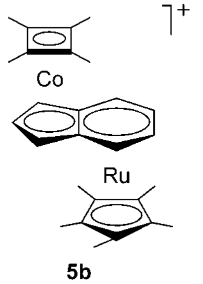
Nucleophilic degradation of triple-decker complexes by solvent molecules is the back reaction to electrophilic stacking.[17] As shown above, this process complicates the preparation of μ-indenyl triple-decker complexes, stimulating us to study degradation of the permethylated cations **2**, **4b** and **5b** by acetone and acetonitrile.



2



4b



5b

In accordance with the ^1H NMR spectroscopic data, all the cations slowly decompose in [D_6]acetone with the formation of a mononuclear η^5-indenyl complex (**1** or **3b**) and a solvate cationic complex ($[Cb^*Co(Me_2CO)_3]^+$ or $[Cp^*Ru(Me_2CO)_3]^+$). After one day, the 30% conversion of **4b** was observed. Further standing for one week did not cause any further changes. The behaviour of complexes **2** and **5b** is slightly different: the initially formed mononuclear cobalt compound **1** decomposes within several days, apparently owing to its oxidation by cationic solvate complexes. The absence of secondary processes for **4b** is in agreement with the higher oxidation potential of **3b** (+0.50 V, vide supra) compared with **1** (+0.33 V).[12]

The nucleophilic degradation rate increases in the order **5b** < **2** < **4b**. Cations **2** and **4b** differ by the fragment coordinated at the five-membered ring of the indenyl ligand. The Cp*Ru fragment accepts electron density of this ring to a greater extent than Cb*Co (due to the more covalent bonding of the ruthenium atom), which results in a higher positive charge at the η^6-coordinated cobalt atom and, as a consequence, to easier degradation of **4b**. Comparing **2** and **5b**, the $[Cp^*Ru]^+$ fragment is more strongly bonded with the six-membered ring than $[Cb^*Co]^+$, which explains the lower reactivity of **5b**.

Dissolution of complexes **2**, **4b** and **5b** in acetonitrile results in immediate decomposition. In the case of **4b**, a yellow solution was formed. ^1H NMR spectroscopy detected the starting compounds, **3b** and $[Cb^*Co(MeCN)_3]^+$ resulting from nucleophilic degradation. The decomposition of **2** and **5b** leads to green solutions that show only very broad signals indicative of paramagnetic species. This behaviour contradicts with the preparation of triple-decker cations from acetonitrile complexes. However, we have shown that **5b** decomposes only slowly in the presence of two equivalents of MeCN in CD_2Cl_2, thus resolving the contradiction. As in the case of degradation by acetone, the more complex behaviour of derivatives **2** and **5b** with the cobalt atom coordinated at the five-membered ring may be explained by the easier oxidation of **1** compared with **3b**.

X-ray Diffraction Study

The structures of complexes **6** and [**4b**][Co(η-7,8-$C_2B_9H_{11})_2$][18] were investigated by X-ray diffraction (Figures 1 and 2, respectively). Selected bond lengths are given in Tables 1 and 2, respectively.

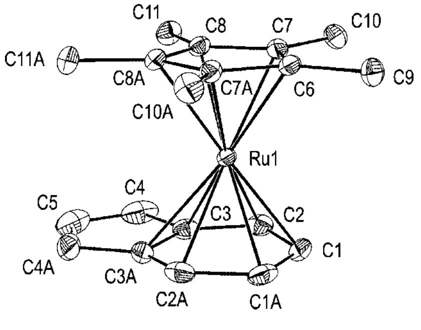


Figure 1. Structure of complex **6**. Ellipsoids are shown at the 50% level.

The structure of **6** is the first example of a mononuclear complex with an η^6-coordinated indenyl ligand. The structure has a symmetry plane. The ruthenium atom is not quite symmetrically coordinated with the six-membered ring, the distances from the Ru atom to the bridgehead C3 and C3A atoms (2.367 Å) being noticeably longer than other Ru–C distances (2.202 and 2.228 Å). This elongation (0.139–0.165 Å) is much greater than that for the isomeric η^5-indenyl complex **3b** (0.02–0.06 Å).[19] The six-membered ring

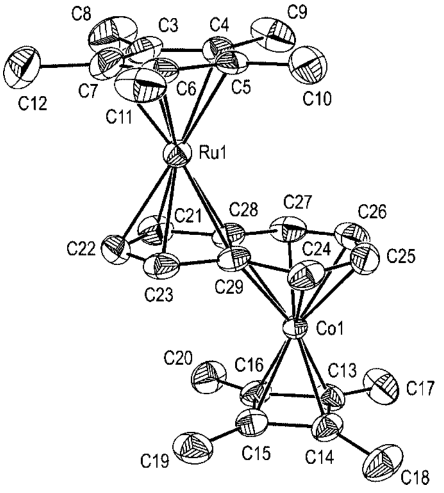


Figure 2. Structure of cation **4b**. Ellipsoids are shown at the 50% level.

Table 1. Selected bond lengths [Å] for complex **6**.

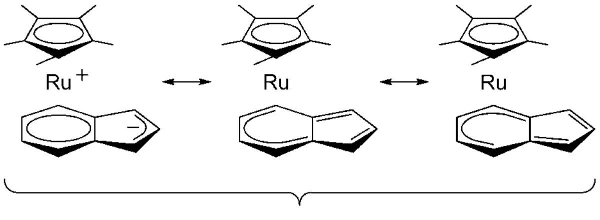
Ru1–C1	2.202(1)	C1–C1A	1.422(3)
Ru1–C2	2.228(1)	C1–C2	1.415(2)
Ru1–C3	2.367(1)	C2–C3	1.427(2)
Ru1–C6	2.165(2)	C3–C3A	1.473(2)
Ru1–C7	2.169(1)	C3–C4	1.411(2)
Ru1–C8	2.169(1)	C4–C5	1.400(3)

Table 2. Selected bond lengths [Å] for complex **4b**.

Ru1–C4	2.125(4)	Co1–C13	2.006(4)
Ru1–C5	2.146(4)	Co1–C14	2.011(4)
Ru1–C7	2.147(5)	Co1–C16	2.014(5)
Ru1–C3	2.149(5)	Co1–C15	2.014(5)
Ru1–C6	2.153(4)	Co1–C24	2.098(4)
Ru1–C21	2.176(4)	Co1–C25	2.099(5)
Ru1–C22	2.176(5)	Co1–C26	2.099(5)
Ru1–C23	2.186(4)	Co1–C27	2.102(5)
Ru1–C28	2.217(4)	Co1–C28	2.185(4)
Ru1–C29	2.218(4)	Co1–C29	2.202(4)
C3–C7	1.394(7)	C13–C14	1.447(6)
C3–C4	1.406(7)	C13–C16	1.480(7)
C4–C5	1.455(6)	C14–C15	1.443(6)
C5–C6	1.427(6)	C15–C16	1.469(7)
C6–C7	1.412(7)	C24–C25	1.409(7)
C21–C22	1.417(7)	C24–C29	1.444(7)
C21–C28	1.454(7)	C25–C26	1.386(8)
C22–C23	1.408(7)	C26–C27	1.374(8)
C23–C29	1.414(6)	C27–C28	1.421(6)
C28–C29	1.477(6)		

is folded along the line C2–C2a (by 6.4°). For comparison, the distances from the metal atom to the non-bonded carbon atoms of the η^4-coordinated arene ligand in the ruthenium compound [(η^6-C_6Me_6)Ru(η^4-C_6Me_6)] (av. 3.028 Å) are 0.838–0.950 Å longer than the other Ru–C distances (av. 2.148 Å); the folding angle is 43°.[20] The much shorter elongation for **6**, along with the requirement of an 18-electron configuration, confirms the η^6-bonding mode of the indenyl ligand.

Compound **6** can be represented by three limiting structures (Scheme 7). The elongation of the Ru–C3(3A) distances and folding of the six-membered ring can be explained by a considerable contribution of the neutral structures with an η^5-coordinated indenyl ligand. Following the same reasoning, in the case of the related η^6-fluorenyliron[21] and -manganese[22] complexes the six-membered ring is also folded, with considerable elongation of the distance from the metal atom to one of the bridgehead carbon atoms.



6

Scheme 7. Limiting structures of **6**.

Cation **4b** has a slipped triple-decker structure with a central η^5:η^6-indenyl ligand. This ligand is essentially planar, with maximum deviations of the C(24) and C(27) atoms by 0.060 and 0.046 Å, respectively, towards the cobalt atom. The ligand planes are essentially coplanar, the dihedral angles Cp*/C_9H_7 and Cb*/C_9H_7 being 3.4° and 0.6°, respectively.

A more detailed consideration of the structure revealed a folding of the five- and six-membered rings along the axes C(21)–C(23) (2.5°) and C(24)–C(27) (7.4°). Likewise, the metal atoms are not quite symmetrically coordinated with the rings. For instance, the distances from the Ru atom to the bridgehead C(28) and C(29) atoms (2.217 and 2.218 Å, respectively) are longer than the other Ru–C distances (2.176, 2.176 and 2.186 Å). However, this elongation (0.03–0.04 Å) is rather small and comparable with that for the mononuclear complex **3b** (0.02–0.06 Å),[19] thus confirming the η^5-bonding mode of the indenyl ligand.[23] The Ru···(η^5-C_9H_7) distance (1.835 Å) in cation **4b** is slightly shorter than that in **3b** (1.840 Å),[19] which suggests stronger bonding in the case of **4b**. The Ru···Cp* distance (1.772 Å) in **4b** is also shorter than that in **3b** (1.792 Å).[19]

The bonding of the cobalt atom with the six-membered ring is even more asymmetrical. The Co–C(28) and Co–C(29) distances (2.185 and 2.202 Å, respectively) are longer than the other Co–C distances (2.098, 2.099, 2.099 and 2.102 Å) by 0.09–0.10 Å. This elongation is practically the same as that for the M(η^6-C_9H_7) fragment in [CpRu(μ:η^5:η^6-C_9H_7)RuCp*]$^+$ (**12a**; 0.08–0.10 Å)[8a] and [(cod)Rh(μ:η^5:η^6-C_9H_7)Cr(CO)$_3$] (0.09–0.12 Å),[24] slightly longer than that in the naphthalene complex [Cb*Co($C_{10}H_8$)]$^+$ (0.04–0.06 Å)[15] but smaller than in **6** (0.14–0.17 Å), the η^6-coordination mode in which is clear.

The triple-decker cation **4b** could be considered as an arene complex in which the sandwich compound **3b** acts as a six-electron ligand towards the [Cb*Co]$^+$ fragment. The Co···Cb* distance in **4b** (1.726 Å) is significantly longer than that for cations [Cb*Co(C_6H_6)]$^+$ (1.702 Å) and [Cb*Co($C_{10}H_8$)]$^+$ (1.707 Å),[15] thus suggesting the greater acceptor ability of **3b** compared with benzene and naphthalene.

The C–C bonds within the five-membered ring of the indenyl ligand in **4b** are generally longer than those in **3b**. The bond between the bridgehead carbon atoms is the most elongated (1.477 Å in **4b** and 1.446 Å in **3b**), in accordance with a greater loosening of the π bond upon bifacial coordination. A similar elongation has been observed for the triple-decker complex **12a** (av. 1.481 Å).[8a]

Electrochemistry

In this section we describe the redox properties of the μ-indenyl triple-decker complexes **2**, **4b** and **5a**,**b** and their diruthenium analogues **12a**–**c**. Let us start with the homometallic Ru_2 derivatives. In order to understand their electron-transfer ability, Figure 3 compares the cyclic voltammetric response of the building unit **3b** (Figure 3, a) with that of the dinuclear monocation **12b** (Figure 3, b).

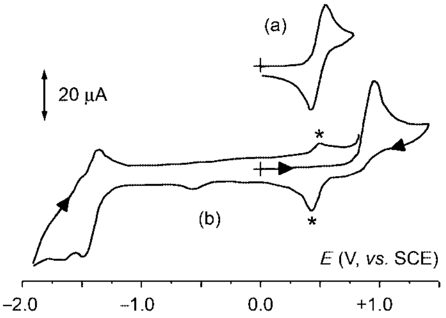
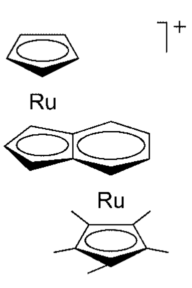
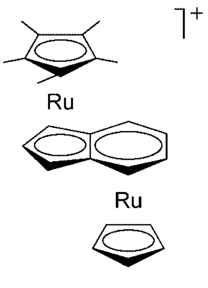


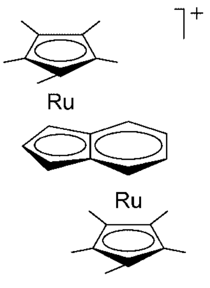
Figure 3. Cyclic voltammetric responses recorded at a platinum electrode for CH_2Cl_2 solutions of: a) **3b** (0.9×10^{-3} M) and b) **12b** (1.0×10^{-3} M). $[NBu_4]PF_6$ (0.2 M) as supporting electrolyte. Scan rate: 0.5 V s^{-1}.



12a



12b



12c

Complex **3b** undergoes a coulometrically measured one-electron oxidation that exhibits features of chemical reversibility on the cyclic voltammetric timescale. In fact, analysis of the responses with progressively increasing scan rates from 0.2 to 1.0 V s^{-1} shows that: (i) the current ratio i_{pc}/i_{pa} is constantly equal to 1; (ii) the current function $i_{pa} \cdot v^{-1/2}$ decreases by about 10% with a tenfold increase of the scan rate; and (iii) the peak-to-peak separation increases progressively from 98 to 130 mV. These parameters are diagnostic of a chemically reversible, but electrochemically quasi-reversible, one-electron process.[25] In reality, cyclic voltammetric tests carried out on the exhaustively oxidised solution (E_w = +0.7 V) show partial decomposition of the electrogenerated monocation. A similar behaviour is exhibited by the parent compound **3a** except for the fact that the corresponding monocation is unstable even on the cyclic voltammetric timescale (the i_{pc}/i_{pa} ratio reaches unity only at 5.0 V s^{-1}).

The voltammetric pattern exhibited by the triple-decker cation **12b** is more complex. It essentially undergoes an irreversible oxidation and a reduction displaying features of partial chemical reversibility. The rather positive and negative potential values of the two processes prevent a reliable determination of the number of electrons involved by controlled potential coulometry. Nevertheless, the cyclic voltammetric comparison with the one-electron oxidation of *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine ($E°'$ = +0.55 V) (an appropriate calibrant due to its similar molecular weight of 625.5)[25] supports the two-electron nature of the anodic step.[26] Since the cathodic process possesses a peak height similar to the anodic one, we assume that the reduction also involves a two-electron process. As a matter of fact, the minor reduction following the main cathodic step can be assigned to the by-product arising from the primary reduction as it tends to disappear with an increase of the scan rate.

We finally underline that the starred peak system that appears in the back-scans after traversing the anodic peak occurs at potential values coincident with those of **3b**, thus suggesting that the electron transfers trigger decomposition of the triple-decker derivative **12b** and regeneration of the precursor **3b**. A qualitatively similar redox picture holds for complexes **12a** and **12c**. The pertinent electrode potentials are compiled in Table 3.

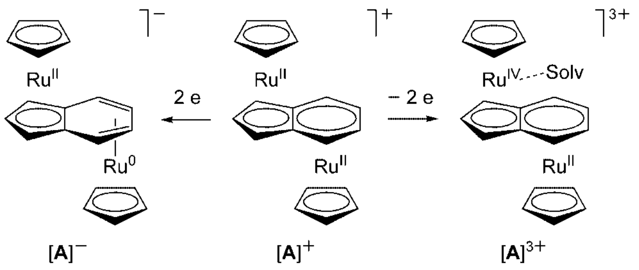
Table 3. Formal electrode potentials [V vs. SCE] and peak-to-peak separations [mV] for the redox processes of the Ru_2 complexes and their mononuclear precursors in CH_2Cl_2 solution.

Complex	$E°'_{Ox}$	ΔE_p[a]	$E°'_{Red}$	ΔE_p[a]
3a	+0.73[b,c]	127	–	–
3b	+0.50[b,d]	96	–	–
12a	+0.92[a,e,f]	–	–1.74[c,e]	120
12b	+0.92[a,e,f]	–	–1.43[c,e]	66
12c	+0.89[a,e,f]	–	–1.73[c,e]	110
$FeCp_2$	+0.39[b]	72		

[a] Measured at 0.2 V s^{-1}. [b] One-electron process. [c] Complicated by chemical reactions. [d] See refs.[19,29] [e] Two-electron process. [f] Peak-potential value for irreversible processes.

In principle, the occurrence of single two-electron processes in binuclear derivatives would imply the lack of any electronic communication between metal centres.[27] We must, however, consider that the two ruthenium centres in cations **12a**–**c** are in different ligand surroundings: one is coordinated to the five-membered ring while the other is coordinated to the six-membered ring, which results in different charges at the metal centres. Therefore, two simultaneous one-electron processes at the two metal centres can be excluded. Most likely, the two-electron reduction occurs at the atom coordinated to the six-membered ring as it has a more positive charge whereas the two-electron oxidation is centred on the ruthenium atom coordinated to the five-membered ring. Such an assumption is supported by a comparison between the redox behaviour of ruthenocene and the benzene complex $[CpRu(C_6H_6)]^+$, which can be considered as the fused parts of the parent triple-decker cation $[CpRu(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)RuCp]^+$ ($[\mathbf{A}]^+$). The arene complex is reduced at –2.02 V but not oxidized up to +2.5 V,[28] whereas ruthenocene is oxidized at +0.8 V,[19] but, to the best of our knowledge, is not reduced up to –2 V.

As shown in Scheme 8, the two-electron reduction would result in anion $[\mathbf{A}]^-$, in which one ruthenium atom is η^4-coordinated to the six-membered ring of the indenyl ligand. Both metal atoms have 18 valence electrons (VE), in accordance with the strong preference of ruthenium for an 18 VE configuration. The two-electron oxidation would give cation $[\mathbf{A}]^{3+}$ with one 16 VE metal centre, which could be stabilized by coordination with a solvent molecule or a counterion (a similar process for mononuclear indenyl complexes is known[29]). Apparently, $[\mathbf{A}]^{3+}$ decomposes to give cation $[\mathbf{3a}]^+$, thereby explaining its appearance in the backscans.



Scheme 8. Reduction and oxidation of $[CpRu(\mu{:}\eta^5{:}\eta^6\text{-}C_9H_7)RuCp]^+$.

Let us now move on to the CoRu complexes **4b** and **5a**,**b**. The pertinent electrode potentials are compiled in Table 4. Cation **4b** obviously represents the simplest comparative connection with the preceding diruthenium derivatives. In fact, as illustrated in Figure 4, it affords a redox profile substantially similar to that of **12b**. The usual comparison with an equimolar amount of *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine supports the two-electron nature of the anodic process (and hence of the cathodic one). Also in this case, the chemical complication accompanying the oxidation process generates the monomeric building block **3b** (starred peak system).

Table 4. Formal electrode potentials [V vs. SCE] and peak-to-peak separations [mV] for the redox processes of the Co_2 complex **2** and CoRu complexes **4** and **5** in CH_2Cl_2 solution.

Complex	$E_{pOx(I)}$	$E_{pOx(II)}$	$E^{\circ\prime}_{Red}$	ΔE_p[a]
2	+0.72[b]	≈ +1.6[b,c,d]	–1.74[e]	74
4b	≈ +0.93[b,e]	≈ +0.93[b,e]	–1.67[c]	102
5a	+1.04[b,e]	[d]	–1.40[b,c]	–
5b	+0.70[b,e]	≈ +1.5[b,e]	–1.81[b,c]	–

[a] Measured at 0.2 V s⁻¹. [b] Peak-potential value for irreversible processes. [c] Two-electron process. [d] Substantially overlapped by the solvent discharge. [e] One-electron process.

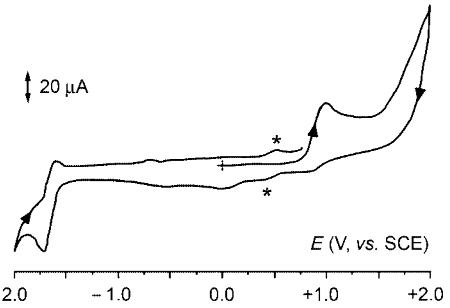


Figure 4. Cyclic voltammetric response recorded at a platinum electrode for a CH_2Cl_2 solution of **4b** (0.8×10^{-3} M). $[NBu_4]PF_6$ (0.2 M) as supporting electrolyte. Scan rate: 0.5 V s⁻¹.

In reality, Osteryoung square-wave voltammetry shows a slight inflection of the oxidation process, probably due to a very slight difference between the oxidation potentials of the $Ru^{II/III}$ and the $Ru^{III/IV}$ processes. A difference of about 0.08 V can be estimated from Figure S2 in the Supporting Information, even though the relative peak heights do not seem to support the one-electron nature of both processes. It cannot, however, be ruled out that this apparent discrepancy might be due to the mathematical treatment.

A different redox pattern is exhibited by complexes **5a**,**b**, which have the cobalt atom coordinated to the five-membered ring. As illustrated in Figure 5 for **5b**, they undergo two separate oxidations (the second of which is partially overlapped by the solvent discharge) and one reduction, which are irreversible in character. The peak height of the reduction is about twice that of each oxidation step. Comparison with the response of *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine supports the one-electron nature of the first anodic step.

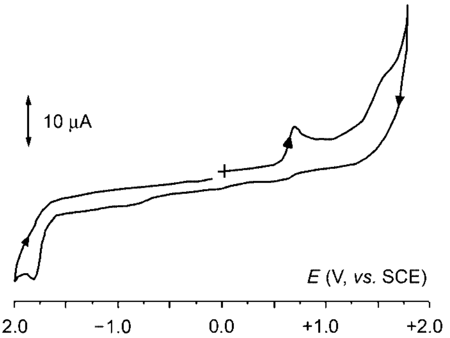


Figure 5. Cyclic voltammetric response recorded at a gold electrode for a CH_2Cl_2 solution of **5b** (1.0×10^{-3} M). $[NBu_4]PF_6$ (0.2 M) as supporting electrolyte. Scan rate: 0.2 V s⁻¹.

As a final consideration, we will briefly mention the redox behaviour of the Co_2 complex **2**. In CH_2Cl_2 solution, it exhibits a cyclic voltammetric profile which is qualitatively reminiscent of that exhibited by complexes **4b** and **5**, even though, as indicated in Table 4, some differences hold in the number of electrons involved either in the cathodic or the most anodic processes.

In view of the preceding discussion on the nucleophilic degradation of the present complexes in MeCN solution, it is interesting to compare the anodic response recorded in

CH_2Cl_2 solution with that recorded in MeCN solution, at low temperature (250 K). As illustrated in Figure 6, in MeCN solution the irreversible oxidation of the complex apparently occurs at notably lower potential values (E_p = –0.09 V) and is followed by a main oxidation process with features of chemical reversibility ($E^{\circ\prime}$ = +0.22 V). It should be noted that an increase of the temperature makes the two oxidation processes disappear (the first oxidation disappearing more quickly than the second one).

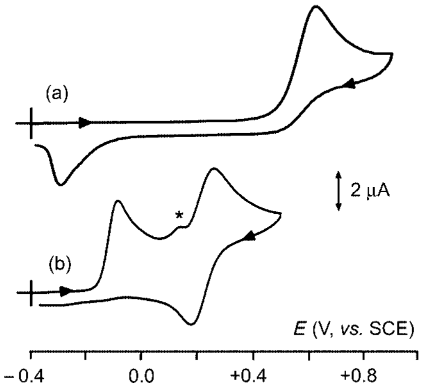


Figure 6. Cyclic voltammetric responses exhibited by **2** at a platinum electrode, under the following experimental conditions: a) CH_2Cl_2 solution (0.7×10^{-3} M), b) MeCN solution (0.8×10^{-3} M). $[NBu_4]PF_6$ (0.2 M) as supporting electrolyte. T = 250 K. Scan rate: 0.2 $V s^{-1}$.

We would like to assign the second reversible oxidation present in MeCN solution to the decomposition product **1** even though the couple **1**/[**1**]$^+$ exhibits a rather congruent potential value ($E^{\circ\prime}$ = +0.33 V) in CH_2Cl_2 solution.[12] The starred peak at +0.13 V could be attributed to the second decomposition product $[Cb^*Co(MeCN)_3]^+$.[30] The assignment of the first irreversible oxidation is, in reality, rather less straightforward. In fact, even though it is conceivable that the low temperature might attenuate the lability of complex **2**, thus allowing us to detect the oxidation of the residual original product, the difference of about 0.7 V in redox potentials on passing from CH_2Cl_2 to MeCN solution makes such a proposal questionable. It is more likely that the first irreversible oxidation is due to the transient product $[Cb^*Co(\mu{:}\eta^5{:}\eta^4\text{-}C_9H_7)Co(MeCN)Cb^*]^+$, which arises from partial solvolysis of **2**.

Conclusions

Electrophilic stacking reactions of indenyl sandwich complexes with the acetonitrile derivatives $[Cb^*Co(MeCN)_3]^+$ and $[(C_5R_5)Ru(MeCN)_3]^+$ have proved to be effective for the preparation of slipped triple-decker cations. However, the acetonitrile eliminated can induce nucleophilic degradation of the product, thereby reducing the yield. The new method using $[Cb^*CoI]_x/TlBF_4$ lacks this limitation and allows to obtain the target compounds in high yield.

Experimental Section

General: All reactions were carried out under argon in anhydrous solvents that were purified and dried using standard procedures. The isolation of products was conducted in air unless otherwise stated. Starting materials were prepared as described in the literature: **1**,[12] **3a**,**b**, **6**,[8a] **7**,[31] $[Cb^*Co(CO)_2I]$,[11,12] $[Cb^*Co(MeCN)_3]PF_6$,[11,12] $[Cp^*RuCl]_4$,[32] $[(C_5R_5)Ru(MeCN)_3]PF_6$[33,34] and $Tl[Co(\eta\text{-}7,8\text{-}C_2B_9H_{11})_2]$.[35] Irradiation was conducted in a Schlenk tube using a high-pressure mercury vapour lamp with phosphor-coated bulb (400 W). Both the tube and the lamp were placed in a vessel of appropriate volume covered inside with aluminium foil; cooling was accomplished with running water. The ^1H and ^{11}B NMR spectra were recorded with a Bruker AMX 400 spectrometer operating at 400.13 and 128.38 MHz, respectively. Materials and apparatus for electrochemistry have been described elsewhere.[36]

Preparation of the Benzene Complex $[Cb^*Co(C_6H_6)]I$: A mixture of $[Cb^*Co(CO)_2I]$ (3.5 g, 10 mmol), anhydrous aluminium chloride (13.3 g, 100 mmol) and benzene (70 mL) was vigorously stirred under reflux for 8 h. After cooling, the reaction mixture was carefully hydrolysed with cold water (ca. 100 mL). The aqueous phase was separated, filtered and stirred with $Me_3NO\cdot 2H_2O$ (ca. 0.2 g, 1.2 mmol) and $NaI\cdot 2H_2O$ (ca. 0.4 g, 2 mmol) for 4 h. The resulting brown precipitate of $[Cb^*Co(CO)_2I]$ was filtered off. The filtrate was stirred with $NaI\cdot 2H_2O$ (2.8 g, 15 mmol) and extracted with CH_2Cl_2 (4 × 50 mL). The organic phase was separated, dried under $MgSO_4$ and eluted through a short layer of silica gel (ca. 5 cm) with CH_2Cl_2. The filtrate was evaporated in vacuo to about 50 mL and diethyl ether (ca. 100 mL) was added. The yellow solid was filtered off and dried in vacuo. Yield: 2.3 g (63%). ^1H NMR ([D$_6$]acetone): δ = 6.72 (s, 6 H, C_6H_6), 1.70 (s, 12 H, Cb*) ppm. $C_{14}H_{18}CoI$ (372.13): calcd. C 45.18, H 4.87; found C 45.01, H 4.93.

Preparation of Slipped Triple-Decker Complexes Starting from $[Cb^*Co(MeCN)_3]PF_6$ and $[(C_5R_5)Ru(MeCN)_3]PF_6$. $[Cb^*Co(\mu,\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]PF_6$ (2·PF$_6$): A mixture of $[Cb^*Co(MeCN)_3]PF_6$ (57 mg, 0.13 mmol) and **1** (45 mg, 0.16 mmol) in $MeNO_2$ (3 mL) was stirred overnight. The solvent was then removed in vacuo and the residue was dissolved in CH_2Cl_2 (ca. 1 mL). Addition of diethyl ether (ca. 10 mL) gave a dark pink precipitate which was twice re-precipitated from CH_2Cl_2 by addition of diethyl ether. Yield: 42 mg (54%). ^1H NMR ($CDCl_3$): δ = 6.86 (m, 2 H, 4,7-H), 5.98 (m, 2 H, 5,6-H), 5.32 (t, ^3J = 2.4 Hz, 1 H, 2-H), 5.29 (d, ^3J = 2.4 Hz, 2 H, 1,3-H), 1.27 (s, 12 H, Cb*, η^6), 1.23 (s, 12 H, Cb*, η^5) ppm.[37] $C_{25}H_{31}Co_2F_6P$ (594.34): calcd. C 50.52, H 5.26; found C 50.29, H 5.18.

The following compounds were prepared in a similar way.

$[Cp^*Ru(\mu,\eta^5{:}\eta^6\text{-}C_9H_7)CoCb^*]PF_6$ (4b·PF$_6$): Yellow-orange solid. Yield: 73 mg (79%) from **3b** (56 mg, 0.16 mmol) and $[Cb^*Co(MeCN)_3]PF_6$ (61 mg, 0.14 mmol) in $MeNO_2$ (3 mL). ^1H NMR (CD_2Cl_2): δ = 6.72 (m, 2 H, 4,7-H), 5.80 (m, 2 H, 5,6-H), 5.00 (d, ^3J = 2.4 Hz, 2 H, 1,3-H), 4.86 (t, ^3J = 2.4 Hz, 1 H, 2-H), 1.67 (s, 15 H, Cp*), 1.30 (s, 12 H, Cb*) ppm.[37] $C_{27}H_{34}CoF_6PRu$ (663.52): calcd. C 48.87, H 5.16; found C 48.77, H 5.17.

$[Cb^*Co(\mu,\eta^5{:}\eta^6\text{-}C_9H_7)RuCp]PF_6$ (5a·PF$_6$): All manipulations were carried out under argon. Red solid. Yield: 38 mg (54%) from **1** (37 mg, 0.13 mmol) and $[CpRu(MeCN)_3]PF_6$ (52 mg, 0.12 mmol) in thf (10 mL). ^1H NMR (CD_2Cl_2): δ = 6.93 (m, 2 H, 4,7-H), 5.67 (m, 2 H, 5,6-H), 5.20 (br., 2 H, 1,3-H), 5.13 (br., 1 H, 2-H), 4.89 (s, 5 H, Cp), 1.29 (s, 12 H, Cb*) ppm.[37] $C_{22}H_{24}CoF_6PRu\cdot 0.5CH_2Cl_2$ (635.86): calcd. C 42.50, H 3.96; found C 42.60, H 3.91.

$[Cb^*Co(\mu,\eta^5{:}\eta^6\text{-}C_9H_7)RuCp^*]PF_6$ (5b·PF$_6$): Dark red solid. Yield: 89 mg (79%) from **1** (53 mg, 0.19 mmol) and $[Cp^*Ru(MeCN)_3]PF_6$

(86 mg, 0.17 mmol) in CH_2Cl_2 (10 mL). Alternatively, this complex was prepared by treatment of **6** (77 mg, 0.22 mmol) with [Cb*Co(MeCN)$_3$]PF_6 (83 mg, 0.19 mmol) in thf (10 mL); yield 76 mg (60%). ^{1}H NMR (CD_2Cl_2): δ = 6.27 (m, 2 H, 4,7-H), 5.37 (m, 3 H, 2,5,6-H), 5.04 (d, ^3J = 2.4 Hz, 2 H, 1,3-H), 1.65 (s, 15 H, Cp*), 1.27 (s, 12 H, Cb*) ppm.[37] $C_{27}H_{34}CoF_6PRu$ (663.52): calcd. C 48.87, H 5.16; found C 48.93, H 5.19.

[CpRu(μ,η^5:η^6-C$_9$H$_7$)CoCb*]PF$_6$ (4a·PF$_6$): All manipulations were carried out under argon. A mixture of [Cb*Co(MeCN)$_3$]PF_6 (52 mg, 0.12 mmol) and **3a** (194 mg, 0.6 mmol) in $MeNO_2$ (3 mL) was stirred for 1 h. The solvent was then removed in vacuo, a new portion of $MeNO_2$ (3 mL) was added and stirring was continued for 1 h. This solvent removal-addition cycle followed by stirring for 1 h was repeated twice more. The volume was then reduced in vacuo to about 0.5 mL. Addition of diethyl ether (10 mL) gave a yellow-orange precipitate, which was twice re-precipitated from $MeNO_2$ by addition of diethyl ether. Yield: 55 mg (78%). ^{1}H NMR ($CDCl_3$): δ = 7.04 (m, 2 H, 4,7-H), 5.81 (m, 2 H, 5,6-H), 5.47 (d, ^3J = 2.7 Hz, 2 H, 1,3-H), 5.02 (t, ^3J = 2.6 Hz, 1 H, 2-H), 4.45 (s, 5 H, Cp), 4.29 (s, 2 H, $MeNO_2$), 1.35 (s, 12 H, Cb*) ppm.[37] $C_{22}H_{24}CoF_6PRu\cdot 0.75MeNO_2$ (639.17): calcd. C 42.75, H 4.14; found C 42.86, H 4.26.

Preparation of Slipped Triple-Decker Complexes Starting from [Cb*CoI]$_x$. [(η^5-C$_9$H$_7$)Ru(μ,η^5:η^6-C$_9$H$_7$)CoCb*]BF$_4$ (8·BF$_4$): All manipulations were carried out under argon. The iodide complex [Cb*CoI]$_x$ was prepared from [Cb*Co(C_6H_6)]I and used without further purification. A solution of [Cb*Co(C_6H_6)]I (100 mg, 0.27 mmol) in acetonitrile (3 mL) was irradiated for 4 h, resulting in a colour change from yellow to red. The solvent was removed in vacuo to give [Cb*Co(MeCN)$_3$]I as a dark-red microcrystalline solid. This was heated in vacuo (ca. 0.01 Torr) at 50–60 °C for 15 min to afford crude [Cb*CoI]$_x$ as a dark-green solid. The latter was dissolved in thf (5 mL) to give a clear, dark-green solution. Complex **7** (106 mg, 0.32 mmol) and $TlBF_4$ (79 mg, 0.27 mmol) were then added and the mixture was stirred overnight. The yellow-orange precipitate was filtered off, washed with diethyl ether and dissolved in CH_2Cl_2 (ca. 5 mL). The orange-red solution obtained was filtered and concentrated in vacuo to about 0.5 mL. Addition of diethyl ether (ca. 10 mL) gave an orange solid, which was re-precipitated from CH_2Cl_2 by addition of diethyl ether. Yield: 103 mg (65%). ^{1}H NMR ($CDCl_3$): δ = 6.87 (m, 4 H, 4–7-H, η^5-C_9H_7), 6.49 (m, 2 H, 4,7-H, μ-C_9H_7), 5.81 (m, 2 H, 5,6-H, μ-C_9H_7), 5.29 (s, 1 H, CH_2Cl_2), 5.12 (m, 4 H, 1,3-H, C_9H_7), 4.98 (t, ^3J = 2.6 Hz, 1 H, 2-H, μ-C_9H_7), 4.75 (t, ^3J = 2.4 Hz, 1 H, 2-H, η^5-C_9H_7), 1.35 (s, 12 H, Cb*) ppm.[37] $C_{26}H_{26}BCoF_4Ru\cdot 0.5CH_2Cl_2$ (627.77): calcd. C 50.70, H 4.34; found C 50.87, H 4.41. In a similar way, complex **8**·PF_6 (69%) was prepared using $TlPF_6$ instead of $TlBF_4$.

[Cp*Ru(μ,η^5:η^6-C$_9$H$_7$)CoCb*][Co(η-7,8-C$_2$B$_9$H$_{11}$)$_2$] ([4b][Co(η-7,8-C$_2$B$_9$H$_{11}$)$_2$]): The title compound was prepared similar to **8**·BF_4 from [Cb*Co(C_6H_6)]I (100 mg, 0.27 mmol), **3b** (112 mg, 0.32 mmol) and Tl[Co(η-7,8-$C_2B_9H_{11}$)$_2$] (143 mg, 0.27 mmol). Yield: 164 mg (72%) of a dark-red solid. ^{1}H NMR (CD_2Cl_2): δ = 6.72 (m, 2 H, 4,7-H), 5.77 (m, 2 H, 5,6-H), 5.00 (d, ^3J = 2.6 Hz, 2 H, 1,3-H), 4.88 (t, ^3J = 2.6 Hz, 1 H, 2-H), 3.95 (br., 4 H, CH), 1.67 (s, 15 H, Cp*), 1.31 (s, 12 H, Cb*) ppm.[37] ^{11}B NMR: δ = 5.8 (d, $J_{B,H}$ = 144 Hz, 1 B), 1.4 (d, $J_{B,H}$ = 141 Hz, 1 B), –5.5 (d, $J_{B,H}$ = 107 Hz, 2 B), –6.8 (d, $J_{B,H}$ = 125 Hz, 2 B), –17.3 (d, $J_{B,H}$ = 154 Hz, 2 B), –22.7 (d, $J_{B,H}$ = 168 Hz, 1 B) ppm.

Formation of the Slipped Tetra-Decker Complex [Cp*Ru(μ,η^5:η^6-C$_9$H$_7$)Ru(μ,η^5:η^6-C$_9$H$_7$)RuCp*][PF$_6$]$_2$ ([11][PF$_6$]$_2$): A mixture of **8**·PF_6 (39 mg, 0.06 mmol), [Cp*RuCl]$_4$ (33 mg, 0.03 mmol) and $TlPF_6$ (42 mg, 0.12 mmol) in $MeNO_2$ (3 mL) was stirred overnight. The solvent was then removed in vacuo. The residue was extracted with CH_2Cl_2/petroleum ether (10:1) and filtered. The filtrate was concentrated in vacuo to about 0.5 mL. Addition of petroleum ether (10 mL) gave an orange-red precipitate, which was twice re-precipitated from CH_2Cl_2 by addition of petroleum ether. Yield: 28 mg (43%). ^{1}H NMR ($CDCl_3$): δ = 6.38 (m, 4 H, 4,7-H), 5.45 (m, 4 H, 5,6-H), 5.20 (br., 6 H, 1–3-H), 1.66 (s, 30 H, Cp*) ppm. According to ^{1}H NMR spectroscopy, a similar reaction with a 4:1 molar ratio of **8**·PF_6 and [Cp*RuCl]$_4$ resulted in a mixture of complexes **8** (25%), **10** (15%) and **11** (60%).

X-ray Crystallography: Crystals of [**4b**][Co(η-7,8-$C_2B_9H_{11}$)$_2$] suitable for X-ray diffraction were grown by slow interdiffusion of a two-phase system containing diethyl ether and a CH_2Cl_2 solution of the complex. Crystals of **6** were obtained by cooling a hexane solution to –15 °C. X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD at 120 K. The adsorption correction was applied semi-empirically using equivalent reflections. Crystallographic data and structure refinement parameters are given in Table 5. All calculations were performed on an IBM PC/AT using the SHELXTL software.[38]

Table 5. Crystallographic data and structure refinement parameters for [**4b**][Co(η-7,8-$C_2B_9H_{11}$)$_2$] and **6**.

Compound	[**4b**][Co(η-7,8-$C_2B_9H_{11}$)$_2$]	**6**
Empirical formula	$C_{31}H_{56}B_{18}Co_2Ru$	$C_{19}H_{21}Ru$
Molecular weight	842.27	350.43
Crystal colour, habit	orange, prism	yellow, prism
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pnma$
a [Å]	12.406(2)	11.4039(6)
b [Å]	13.040(2)	12.4270(7)
c [Å]	24.781(4)	10.6831(6)
β [°]	90.619(4)	90
V [Å^3]	4008.6(12)	1513.97(14)
Z (Z)	4(1)	4(0.5)
$D_{calcd.}$ [g cm^{-3}]	1.214	1.537
2θ max [°]	52	60
Abs. coeff., μ(Mo-K_α) [cm^{-3}]	12.14	10.23
T_{max}/T_{min}	0.7121/0.7932	0.7489/0.8216
Collected reflections	34252	39865
Independent reflections (R_{int})	7669 (0.0417)	2252 (0.0462)
Observed reflections [$I > 2\sigma(I)$]	6127	2129
Parameters	469	114
R_1 (on F for obsd. reflections)[a]	0.0525	0.0218
wR_2 (on F^2 for all reflections)[b]	0.1167	0.0553
F(000)	1720	716
GOF	1.001	1.023
Largest diff. peak and hole [e Å^{-3}]	1.221/–0.742	0.569/–0.662

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$ for observed reflections. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$ for all reflections.

CCDC-602655 (for [**4b**][Co(η-7,8-$C_2B_9H_{11}$)$_2$]) and -602656 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Cyclic voltammetric responses of **12b** after the addition of an equimolar amount of *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine and the OSWV response of **4b**.

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