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# Radial (tetracyclopentadienyl)cyclobutadiene pentametals

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Dedicated to Bob Bergman, my mentor during the past, and hopefully the next, 38 years

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ABSTRACT

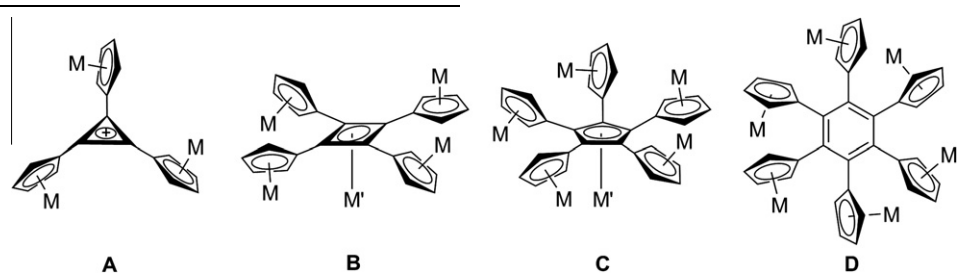
Radial (tetracyclopentadienyl)cyclobutadiene pentametals have been synthesized by the Pd-catalyzed coupling of cyclopentadienyltin or of (CpM)zinc reagents with (tetraiodocyclobutadiene)iron(tricabonyl). X-ray structural and NMR data reveal that, while these arrays are crowded, the substituents enjoy considerable rotational freedom.

The method constitutes a significant complement to currently existing strategies for the construction of persubstituted cyclobutadiene complexes.



## 1. Introduction

Radial oligocyclopentadienyl metals constitute a class of novel organometallic compounds in which metallacyclopentadienyl substituents perdecorate the periphery of a central annulenic core, e.g., **A**–**D** [1]. They are not only appealing aesthetically, but also represent organometallic arrays of importance with respect to their potentially unique physical, chemical, and materials properties. Before we became interested in these systems, there were only two examples known, one of type **A**, the triferrocenylcyclopropenyl cation [2], and one of category **B**, CpCo(tetraferrocenylcyclobutadiene) [3]. We have recently added several derivatives of form **C** [4] and one of type **D**, hexaferrocenylbenzene [5], to this list. This paper describes synthetic advances toward a flexible construction of molecules of topology **B**. Such (tetracyclopentadienyl)cyclobutadienes are of interest as metallated precursors to the elusive tetrakis(cyclopentadienylidene) radialene [6], as "star"-shaped dendritic substructures for electronic and optical materials [7]—in particular molecular squares for the assembly of quantum-dot cellular automata (QCA) devices [8], as stencils for catalytic frames [9] or molecular machines [10], and as potential synthetic building blocks for a host of other oligometallic constructs [11].




## 2. Results and discussion

The most general current strategy toward the preparation of cyclobutadiene complexes is metal-catalyzed alkyne cyclodimerization, often (but not always) proceeding through

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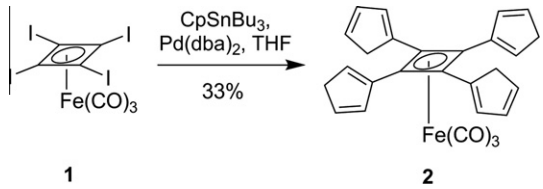



**Scheme 1.**

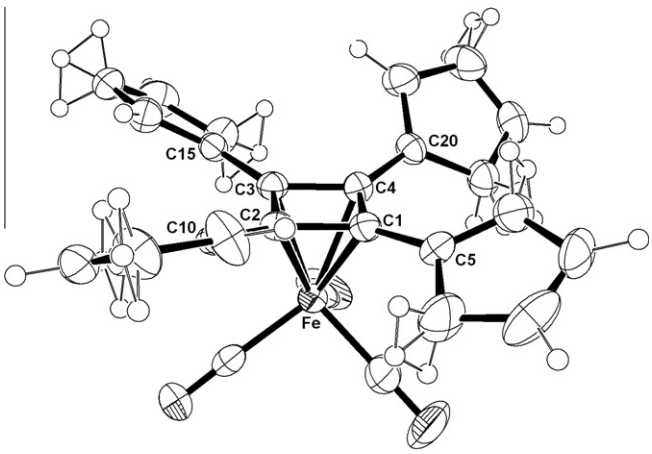
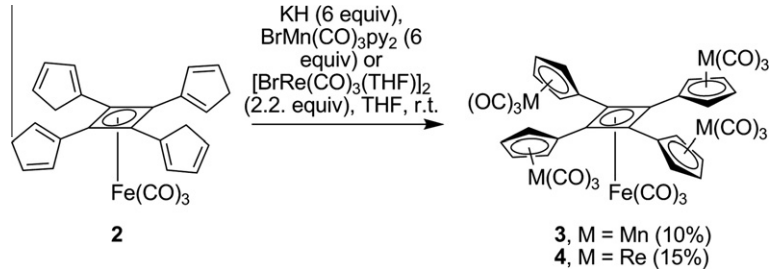


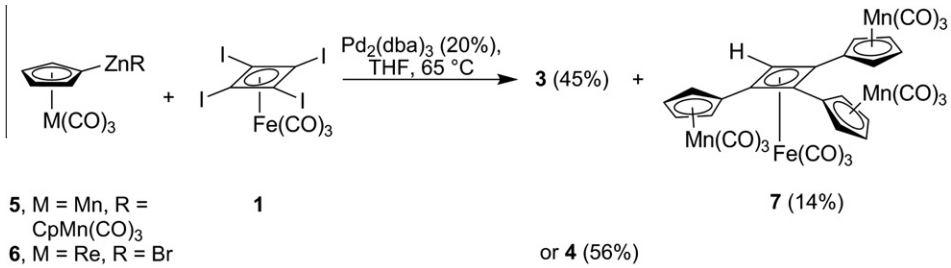

**Fig. 1.** Complex **2** in the solid; displacement ellipsoids at 50% probability. Selected bond lengths (Å) and angles [°]: $Cbd_{centroid}$–Fe 1.810, C1–C2 1.448(4), C2–C3 1.476(4), C3–C4 1.470(4), C1–C4 1.464(4), C1–C5 1.464(4), C2–C10 1.470(4), C3–C15 1.460(4), C4–C20 1.463(4); $Cbd_{centroid}$–C1–C5 173.5, $Cbd_{centroid}$–C2–C10 170.2, $Cbd_{centroid}$–C3–C15 171.1, $Cbd_{centroid}$–C4–C20 169.1, dihedral angles between planes of cyclobutadiene and cyclopentadienyls (point of attachment) C5 27.2, C10 30.4, C15 29.7, C20 42.9.

metallacyclopentadiene intermediates [12]. We sought to provide a complementary route in which cyclopentadienyl substituents would be introduced into an already existing perhalogenated cyclobutadiene core through an extension of the successful methodology that led to derivatives of **C** [4,13] and **D** [5]. The only known such starting material was (tetraiodocyclobutadiene)iron(tricarbonyl) (**1**) [14], and it was consequently chosen as the substrate for our investigations. This substance had already been used successfully by Bunz in fourfold Sonogashira couplings [15]. Gratifyingly, (cyclopentadienyl)tributyltin ($CpSnBu_3$) [16] underwent similar palladium-catalyzed Stille coupling [17] to generate the tetra(cyclopentadienyl) system **2** in 33% yield as a yellow solid that is very soluble in all common organic solvents (Scheme 1). Its structural assignment rests on the spectral data, with the complication that the molecule exists as a mixture of cyclopentadiene tautomers (only one of which is depicted), each substituent ring adopting either the 1,3- or the 1,4-cyclopentadiene configuration. Thus, the $^1$H NMR spectrum shows complicated multiplets in the alkene and allylic hydrogen region, integrating in the ratio 3:2. The $^{13}$C NMR spectrum consists of four signal groups for the carbonyl (3 peaks), alkene (29), cyclobutadiene (5), and saturated carbons (11). There are six possible isomers of **2**, which, in a fully resolved spectrum, should give rise to 6, 48, 12, and 12 absorptions in the respective positions. Further structural confirmation derived from an X-ray structural analysis, in which the cyclopentadienyls were modeled as 1:1 mixtures of the 1,3- and 1,4-diene isomers (Fig. 1). The geometric details of the attachment of the five-membered rings are very similar to those in the related (pentacyclopentadienyl)cymanthrene [13,18], except that the degree of non-coplanarity is somewhat attenuated, probably the result of lesser steric encumbrance of the radiating bonds around the smaller core. Indeed, invoking such was crucial for the next step of our strategy, namely the permetallation of **2**, a step that had failed completely with the five-membered ring analog [4]. Encouragement for its successful execution with **2** came from a report of the (albeit low yielding) tetrakis(tricarbonyl)chromation of CpCo(tetraphenylcyclobutadiene) [19].

Mixing **2** with KH and $BrMn(CO)_3pyr_2$ (pyr = pyridine) or $[BrRe(CO)_3(THF)]_2$ yielded, after adding THF as solvent [20], 10 and 15% of the tetrametallated complexes **3** and **4**, respectively (Scheme 2). The outcome of these transformations showed that, in principle, **2** can function as a building block for the title




**Scheme 2.**




**Scheme 3.**

compounds. However, in view of the disappointing yields, the direct Negishi coupling protocol that was successful in the synthesis of compounds of the type **C** and **D** [4,5] was scrutinized, now featuring **5** and **6** and their respective reactions with **1**. This switch improved yields considerably, the two targets being formed in 45 and 56% yield, respectively (Scheme 3). A minor side product in the preparation of **3** by this method was the tris(cyclopentadienylated) complex **7**. The yields were not optimized, but NMR monitoring indicated that such should be possible. These experiments were facilitated by the isolation (and full characterization; see Experimental Section) of the zincated species $BrZnCpM(CO)_3$ (M = Mn, Re) as coordination complexes with N,N,N′,N′-tetramethylethylenediamine [21], used in twofold excess in their reactions with **1**. With tetrakis(triphenylphosphine)palladium as the catalyst in THF-$d_8$ clean transformations to **3** and **4**, respectively, were recorded, the only side products constituting the known products of oxidative homocoupling of the zincate, $FvMn_2(CO)_6$ [22] and $FvRe_2(CO)_6$ [23], respectively (Fv = fulvalene = $\eta^5$:$\eta^5$-bicyclopentadienyl).

In a vein similar to that of Scheme 3, (tetraferrocenylcyclobutadiene)iron(tricarbonyl) (**9**) was built by reaction of diferrocenylzinc **8** with **1**, affording the target in 60% yield (Scheme 4). Reagent **8** was prepared in situ following the method of Iyoda [24], in which ferrocene is deprotonated with *tert*-butyllithium at −78 °C, followed by addition of zinc bromide and warming the solution to room temperature.

For comparative purposes (vide infra), the CpCo analog of **4**, complex **11**, was made by cyclodimerization of alkyne **10** [25,26] according to Scheme 5 and in analogy to the preparation of CpCo(tetraferrocenylcyclobutadiene) [3].

The radial complexes are generally air stable, with the exception of the Mn systems **3** and **7**. They are also fairly soluble in common organic solvents, with the exception of the Re derivative **4**, which is insoluble in hexane, toluene, and ether, only sparingly soluble in benzene, THF, and chlorinated solvents, but dissolves in acetone. The NMR spectral data are consistent with the presence of four sterically relatively unrestricted, symmetrical molecules.

The X-ray structural renditions of **3**, **4**, **7**, **9**, and **11** are depicted in Figs. 2–6.

Focusing initially on the isostructural **3** and **4** (Figs. 2 and 3), the two systems show a remarkably similar relative orientation of the pendant groups, considering their overall lack of symmetry in the crystal. The observed sequence is down-down-side-up, in which "down" is loosely defined as M located *syn* to the iron(tricarbonyl) unit, "up" as placed *anti*, and "side" as exhibiting the Cp–M bond nearly perpendicular to the cyclobutadiene ring. This arrangement suggests that the centrally attached $Fe(CO)_3$ moiety exerts little steric influence. The potential effects of the latter may be further attenuated by the pyramidalization of the cyclobutadiene carbons, which directs the CpM groups away from iron, a well known feature of (cyclobutadiene)$Fe(CO)_3$ complexes [27] and one that is noticeable also in the other structures reported in this paper. This deformation is quantifiable by the average deviation of the vector $Cbd_{centroid}$–$Cbd_{quat}$–$Cp_{quat}$ from 180°; for **3** this value is 11.2°, for **4** it is 11.6°. Not surprisingly, steric interactions prevent coplanarization of the radial substituents. Only one of them adopts a conformation in the solid state that would allow for significant π-overlap with the core, the angles between the

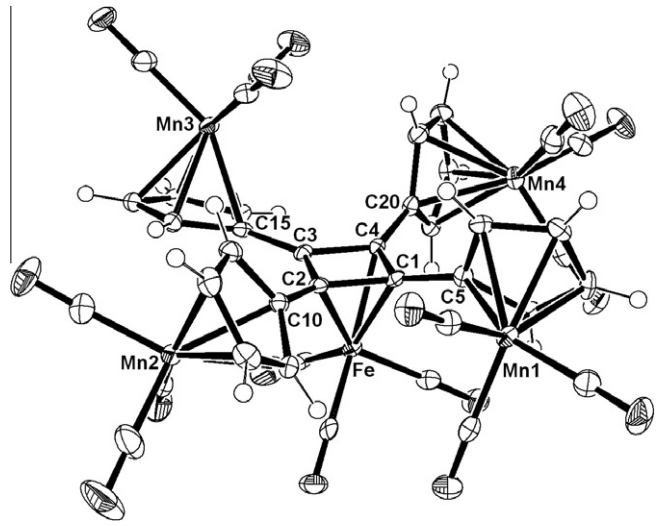
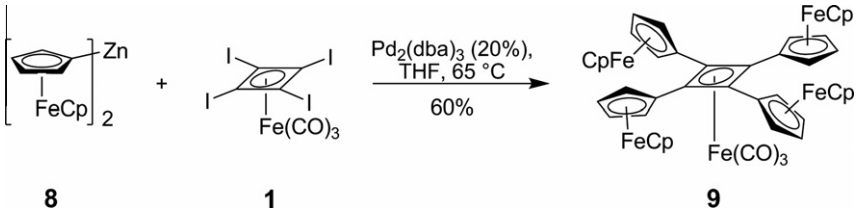
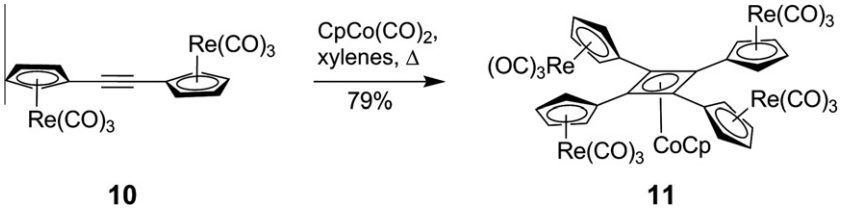



**Fig. 2.** Complex **3** in the solid; displacement ellipsoids at 50% probability. Selected bond lengths (Å) and angles [°]: $Cp_{centroid}$–Mn1 1.777, $Cp_{centroid}$–Mn2 1.776, $Cp_{centroid}$–Mn3 1.781, $Cp_{centroid}$–Mn4 1.781, $Cbd_{centroid}$–Fe 1.784, C1–C2 1.469(5), C2–C3 1.444(4), C3–C4 1.467(5), C1–C4 1.487(5), C1–C5 1.471(5), C2–C10 1.476(5), C3–C15 1.465(4), C4–C20 1.466(4); $Cbd_{centroid}$–C1–C5 164.0, $Cbd_{centroid}$–C2–C10 169.2, $Cbd_{centroid}$–C3–C15 175.7, $Cbd_{centroid}$–C4–C20 166.2, dihedral angles between planes of cyclobutadiene and cyclopentadienyls (point of attachment) C5 69.7, C10 55.2, C15 15.5, C20 86.4.




**Scheme 4.**




**Scheme 5.**

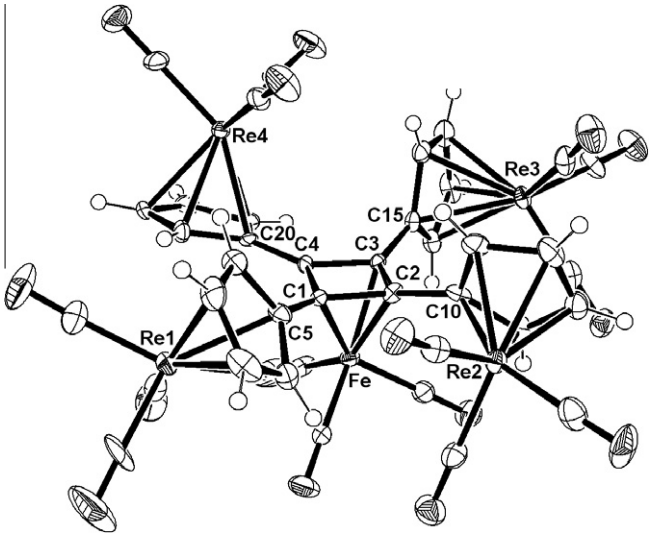



**Fig. 3.** Complex **4** in the solid; displacement ellipsoids at 50% probability. Selected bond lengths (Å) and angles [°]: $Cp_{centroid}$–Re1 1.959, $Cp_{centroid}$–Re2 1.967, $Cp_{centroid}$–Re3 1.966, $Cp_{centroid}$–Re4 1.965, $Cbd_{centroid}$–Fe 1.776, C1–C2 1.465(10), C2–C3 1.467(10), C3–C4 1.477(10), C1–C4 1.466(10), C1–C5 1.460(11), C2–C10 1.479(11), C3–C15 1.471(11), C4–C20 1.451(10); $Cbd_{centroid}$–C1–C5 168.4, $Cbd_{centroid}$–C2–C10 164.8, $Cbd_{centroid}$–C3–C15 164.8, $Cbd_{centroid}$–C4–C20 175.7, dihedral angles between planes of cyclobutadiene and cyclopentadienyls (point of attachment) C5 55.7, C10 69.7, C15 86.3, C20 14.3.

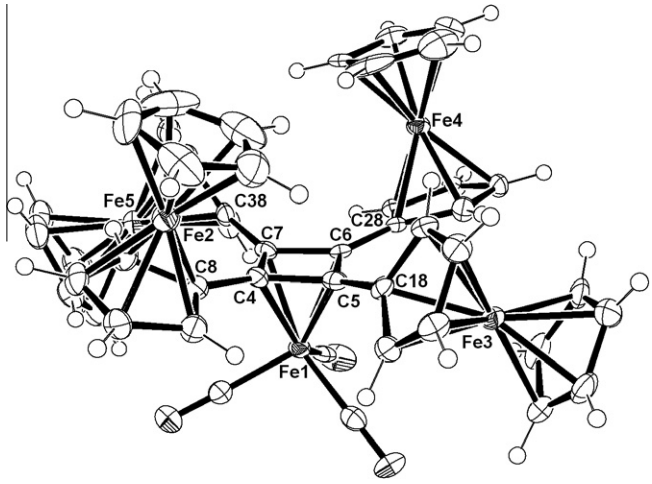



**Fig. 5.** Complex **9** in the solid (one of two molecules in the unit cell); displacement ellipsoids at 50% probability. Selected bond lengths (Å) and angles [°]:$Cp_{centroid}$–Fe2 1.653 ($C_5H_4R$) and 1.659 ($C_5H_5$), $Cp_{centroid}$–Fe3 1.654 ($C_5H_4R$) and 1.661 ($C_5H_5$), $Cp_{centroid}$–Fe4 1.650 ($C_5H_4R$) and 1.653 ($C_5H_5$), $Cp_{centroid}$–Fe5 1.650 ($C_5H_4R$) and 1.662 ($C_5H_5$), $Cbd_{centroid}$–Fe 1.791, C4–C5 1.462(6), C5–C6 1.451(6), C6–C7 1.468(6), C4–C7 1.462(6), C4–C8 1.466(6), C5–C18 1.461(6), C6–C28 1.467(6), C7–C38 1.471(6); $Cbd_{centroid}$–C4–C8 173.1, $Cbd_{centroid}$–C5–C18 166.7, $Cbd_{centroid}$–C6–C28 172.6, $Cbd_{centroid}$–C7–C38 165.7, dihedral angles between planes of cyclobutadiene and cyclopentadienyls (point of attachment) C8 19.4, C18 61.4, C28 17.9, C38 60.6.

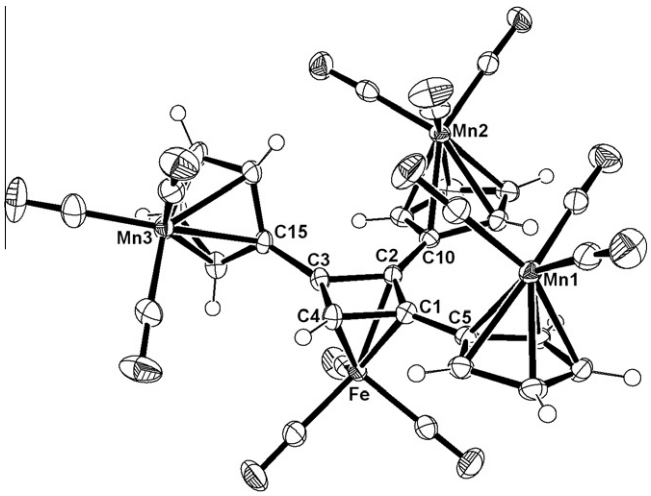



**Fig. 4.** Complex **7** in the solid; displacement ellipsoids at 50% probability. Selected bond lengths (Å) and angles [°]: $Cp_{centroid}$–Mn1 1.769, $Cp_{centroid}$–Mn2 1.774, $Cp_{centroid}$–Mn3 1.767, $Cbd_{centroid}$–Fe 1.784, C1–C2 1.465(3), C2–C3 1.473(3), C3–C4 1.441(3), C1–C4 1.438(3), C1–C5 1.460(3), C2–C10 1.460(3), C3–C15 1.473(3); $Cbd_{centroid}$–C1–C5 174.5, $Cbd_{centroid}$–C2–C10 171.8, $Cbd_{centroid}$–C3–C15 166.2, dihedral angles between planes of cyclobutadiene and cyclopentadienyls (point of attachment) C5 8.63, C10 15.6, C15 79.9.

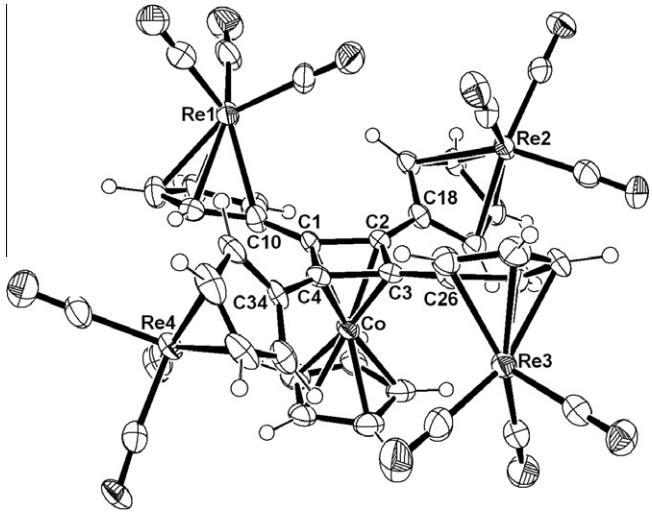



**Fig. 6.** Complex **11** in the solid (one of two molecules in the unit cell); displacement ellipsoids at 50% probability. Selected bond lengths (Å) and angles [°]: $Cp_{centroid}$–Re1 1.962, $Cp_{centroid}$–Re2 1.966, $Cp_{centroid}$–Re3 1.965, $Cp_{centroid}$–Re4 1.969, $Cbd_{centroid}$–Co 1.681, $Cp_{centroid}$–Co 1.664, C1–C2 1.478(13), C2–C3 1.470(14), C3–C4 1.489(14), C1–C4 1.459(14), C1–C10 1.451(14), C2–C18 1.459(14), C3–C26 1.457(14), C4–C34 1.464(14); $Cbd_{centroid}$–C1–C10 177.3, $Cbd_{centroid}$–C2–C18 178.9, $Cbd_{centroid}$–C3–C26 163.2, $Cbd_{centroid}$–C4–C34 169.8, dihedral angles between planes of cyclobutadiene and cyclopentadienyls (point of attachment) C10 19.4, C18 36.8, C26 41.3, C34 54.7.

planes of the two rings being 15.5° (**3**) and 14.3° (**4**), respectively. The distances between the $Cp_{centroid}$–Mn (avg. 1.778 Å), $Cp_{centroid}$–Re (avg. 1.964 Å) or $Cb_{centroid}$–Fe (1.784 Å for **3** and 1.776 Å for **4**) are unremarkable. Removing one of the CpMn appendages from **3,** as in **7** (Fig. 4), appears to relieve congestion sufficiently around the cyclobutadiene ring to allow near-coplanarization of two (surprisingly) adjacent Cp units (angles between planes 8.63° and 15.6°, respectively), pushing the third to adopt a "side" arrangement (79.9°). Returning to **3** and **4**, by comparison, the solid state structure of CpCo(tetraferrocenylcyclobutadiene) [8b] is far more symmetrical with respect to the persubstituted cyclobutadiene scaffold. Excluding the CpCo fragment, the remainder of the molecule has $C_{2v}$ symmetry, the ferrocenyl "arms" aligned in the same chiral sense around the periphery and with perfect 'up-down-up-down' alternation. The "down" ferrocenes are relatively more skewed, while the "up" ferrocenes are much more coplanar with the central ring. Interestingly, on the other hand, the $Fe(CO)_3$ relative **9** is isostructural with the CpCo system (Fig. 5). The angles between the planes of the appended cyclopentadienyl and the central cyclobutadiene rings average 18.7° for the upward facing

ferrocenyls and 61.0° for those *syn* to the $Fe(CO)_3$. The ferrocenyls branch away from the core, as reflected in the $Cbd_{centroid}$–$Cbd_{quat}$–$Cp_{quat}$ deviations from linearity, averaging 10.5°. Finally, the CpRe substituents in **11** (Fig. 6), unlike those in **4** and the other complexes, do not adopt "side" configurations or alternate "up-down," but rather "down-down-up-up." In short, the seemingly random topologies of these molecules are clearly indicative of extensive flexibility of the pendant CpM units, the observed patterns presumably largely dictated by crystal packing forces.

Mobility, not surprisingly exceeding that observed for derivatives of **C** and **D** [4,5], is also indicated by VT $^1$H NMR experiments with **9** and **11**. Thus, the latter shows only slight line broadening of the pendant $CpRe(CO)_3$ signals on cooling to −90 °C (THF-$d_8$), while the former does so extensively at −80 °C, although decoalescence could not be achieved because of solubility problems at lower temperatures. Complex **9** appears to be very similar to CpCo(tetraferrocenylcyclobutadiene) [8b] in this respect, as might be expected considering the comparable X-ray structural features of the two complexes. The ease of rotational movement of the ferrocenyl groups may be detrimental to the proper functioning of a QCA device based on such arrays [28], a drawback that should be surmountable by surface immobilization [29]. Derivative **9** appears promising in this regard, because the carbonyl ligands should be readily replaceable by appropriate linkers. Preliminary cyclic voltammetry measurements reveal suitable electrochemical behaviour with four reversible oxidations at −0.020, 0.115. 0.232, and 0.312 V ($CH_3CN$, $NBu_4PF_6$, versus $[Cp_2Fe]^0/[Cp_2Fe]^+$), involving the four ferrocenyl units. These data are similar to those of its CpCo analog [8b], −0.085, 0.075, 0.225, and 0.283 V ($CH_3CN$–$CH_2Cl_2$, $NBu_4PF_6$, versus $[Cp_2Fe]^0/[Cp_2Fe]^+$).

## 3. Conclusions

This report shows that the Pd-catalyzed Stille or Negishi-type couplings used in the synthesis of radial oligocyclopentadienyls and their permetallated analogs with a central Cp or benzene core can also be employed for systems bearing a central, complexed cyclobutadiene moiety. The method constitutes a valuable addition to existing strategies for the construction of functionalized cyclobutadiene systems and provides access to novel pentametallic carbonyl arrays.

## 4. Experimental

### 4.1. General considerations

Unless otherwise indicated, all materials were obtained from commercial suppliers and used without purification. Solvents were dried by distillation over appropriate drying agents: THF, diethyl ether, and toluene were distilled from sodium/benzophenone under $N_2$ immediately prior to use; $CH_2Cl_2$, benzene, N,N,N′,N′-tetramethylethylenediamine (TMEDA), and triethylamine were distilled from $CaH_2$ under $N_2$ and stored in a Schlenk flask. Zinc bromide was dried under vacuum at 230 °C for 40 h, at 0.1 mm Hg. All glassware was dried overnight in a 200 °C heating oven, or flame dried immediately prior to use. Air-sensitive reagents and products were handled using standard Schlenk and glovebox techniques under $N_2$. Column chromatography was performed using activity I basic alumina (Fisher Scientific) or silica gel (mesh 230–400, ICN). Solvent mixtures were concentrated using a rotary evaporator operating at 30–40 torr. Microwave-assisted reactions were performed in a Personal Chemistry Smith Synthesizer producing radiation at 2450 MHz. The identity of products was established using $^1$H NMR, $^{13}$C NMR, IR, UV, and mass spectrometry. Purity was confirmed by melting point and elemental analysis; in certain cases, due to small quantities of material or the consistency (glassy solids) of prepared materials, purity was assessed by NMR. NMR spectra were recorded on Bruker 300, 400, and 500 MHz spectrometers and processed using XWINNMR or SpinWorks. NMR spectra are reported as the chemical shift in ppm downfield of the TMS peak, using the deuterated solvent as an internal standard ($CDCl_3$ −7.26, $C_6D_6$ −7.16, $CD_2Cl_2$ −5.32, acetone-$d_6$ −2.05, THF-$d_8$ −3.58 ppm). All $^{13}$C NMR spectra were recorded with simultaneous $^1$H decoupling (Waltz 16). Infrared spectra were measured on a Perkin–Elmer Model 2000 IR spectrometer using NaCl liquid cells or salt plates, all data are reported in wavenumbers. UV–Vis spectra were determined on a Hewlett–Packard Model 8453 UV–Vis spectrometer and reported in nm (log $\varepsilon$). Melting points were taken using a Thomas Hoover Unimelt apparatus in sealed capillaries. Electrochemical measurements were taken in a V.A.C. Nexus One glove box under $N_2$, using a BAS 100B cell stand employing a three electrode cell comprised of a glassy carbon working electrode, a platinum counter electrode, and a silver wire reference electrode. Mass spectra and combustion analyses were acquired by the Micro Mass Facility of the College of Chemistry, University of California at Berkeley. X-ray crystallographic data were obtained at the University of California CHEXRAY laboratory and at the Department of Natural Sciences, New Mexico Highlands University.

### 4.2. X-ray structure determinations

X-ray diffraction data were collected on a Siemens SMART and Bruker SMART APEX II (complex **11**) diffractometers, employing graphite monochromated Mo Kα radiation. Crystal data, data collection, and refinement parameters are summarized in Table 1. The structures were solved using direct methods [30], expanded using Fourier techniques [31], and refined by full-matrix least-squares procedures on $F^2$. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN™ crystallographic software package of Molecular Structure Corporation [32].

### 4.3. Synthesis of 1,2,3,4-(tetracyclopentadienylcyclobutadiene)iron(tricarbonyl) (**2**)

To **1** (695 mg, 1.0 mmol) in dry THF (20 mL) was added $Pd(dba)_2$ (115 mg, 0.20 mmol) and $Bu_3SnCp$ (2.47 ml, 8.0 mmol) under nitrogen at 0 °C. The solution was stirred in the dark, allowed to warm to r.t. over 15 h, and subsequently treated with additional $Bu_3SnCp$ (0.62 ml, 0.2 mmol), followed by stirring for 24 h. The solvent was removed and the resulting brown product vigorously shaken in ether (20 mL) and 10% aqueous KF (20 mL). Separation of the organic layer was aided by dilution with ether (100 mL) and water (100 mL). The solution was dried with $MgSO_4$ and chromatographed over neutral alumina (hexane, activity II), eluting with hexane/$CH_2Cl_2$ (30:1) to render **2** as a yellow solid (140 mg, 33.4%): mp 105–110 °C (decomp; from hexane). $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 6.0–6.8 (m, 12H), 2.9–3.2 (m, 4H), 2.67 (m, 4H) ppm; $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 215.3, 215.2, 215.1, 138.6, 138.42, 138.37, 138.32, 138.1, 137.8, 137.7, 135.4, 135.1, 134.9, 134.3, 133.9, 133.8, 133.73, 136.68, 133.63, 133.59, 133.53, 133.3, 133.17, 133.16, 133.0, 132.94, 132.88, 132.81, 132.6, 132.3, 131.8, 130.8, 84.2, 81.3, 81.2, 79.1, 78.2, 45.6, 44.95, 44.92, 44.3, 44.2, 43.8, 42.3, 42.2, 42.15, 42.10, 42.03 ppm; UV/Vis (hexane): $\lambda_{max}$ (log $\varepsilon$) = 262 (4.11), large end absorption tailing to 400 nm; IR (THF): 2028, 1962 cm$^{-1}$; MS (EI, 70 eV): *m/z* (rel intensity) 448 (26) $[M]^+$, 420 (32) $[M–CO]^+$, 392 (50) $[M–2CO]^+$, 364 (90) $[M–3CO]^+$, 152 (100). HRMS (EI) calc. for $C_{27}H_{20}FeO_3$: 448.0762, found: 448.0752.

**Table 1**
Crystallographic data for **2**, **3**, **4**, **7**, **9**, and **11**.

| | **2** | **3** | **4** | **7** | **9** | **11** |
|---|---|---|---|---|---|---|
| Lattice | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | triclinic |
| Formula | $C_{27}H_{20}FeO_3$ | $C_{39}H_{16}FeMn_4O_{15}$ | $C_{39}H_{16}FeO_{15}Re_4$ | $C_{31}H_{13}FeMn_3O_{12}$ | $C_{47}H_{36}Fe_5O_3$ | $C_{41}H_{21}CoO_{12}Re_4$ |
| Formula weight | 448.28 | 1000.13 | 1525.17 | 798.10 | 928.03 | 1509.31 |
| Space group | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 14.3630(10) | 11.80650(10) | 12.0886(11) | 12.8654(3) | 12.5654(7) | 8.272(2) |
| $b$ (Å) | 8.4566(6) | 23.1164(4) | 23.402(2) | 11.2161(2) | 16.7958(9) | 14.821(4) |
| $c$ (Å) | 18.5640(10) | 14.3862(3) | 14.3947(13) | 21.4857(5) | 18.366(1) | 31.284(7) |
| α (°) | 90 | 90 | 90 | 90 | 74.869(1) | 90.166(4) |
| β (°) | 104.832(2) | 110.7740(10) | 111.6710(10) | 105.719(1) | 83.460(1) | 92.747(4) |
| γ (°) | 90 | 90 | 90 | 90 | 85.092(1) | 90.998(4) |
| $V$ (Å$^3$) | 2179.7(2) | 3671.07(10) | 3784.4(6) | 2984.4(1) | 3711.0(3) | 3830.5(16) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.366 | 1.810 | 2.677 | 1.776 | 1.661 | 2.617 |
| $\mu$ (Mo Kα) (cm$^{-1}$) | 7.17 | 17.99 | 131.98 | 17.82 | 19.50 | 130.83 |
| $T$ (K) | 143(1) | 132(1) | 134(1) | 160(1) | 127(1) | 100(2) |
| Number of data | 3846 | 6202 | 6232 | 5334 | 11794 | 14951 |
| Number of parameters | 284 | 532 | 532 | 424 | 991 | 1045 |
| Goodness-of-fit GOF | 1.006 | 0.922 | 1.028 | 0.99 | 1.14 | 1.002 |
| $R$ | 0.0445 | 0.0358 | 0.0332 | 0.027 | 0.041 | 0.045 |
| $R_w$ | 0.0866 | 0.0769 | 0.0825 | 0.030 | 0.047 | 0.0975 |

### *4.4. Synthesis of 1,2,3,4-tetra[(cyclopentadienyl)manganese(tricarbonyl)](cyclobutadiene)iron(tricarbonyl) (**3**)*

From **2**: a Schlenk flask was loaded with **2** (100 mg, 0.223 mmol), $BrMn(CO)_3py_2$ (478 mg, 1.268 mmol), and KH (54 mg, 1.35 mmol) under nitrogen, dry THF (20 mL) added, and the yellow suspension stirred overnight in the dark. The mixture was concentrated to 5 mL, filtered through a short plug of neutral alumina (II), eluting with ether, and the solvent removed. The remainder was cooled to −78 °C and triturated with hexane (5 mL) to yield **3** as pale yellow crystals (22 mg, 10%): mp 188–200 °C (decomp). $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ = 5.36 (t, $J$ = 2.2 Hz, 8H), 5.18 (t, $J$ = 2.2 Hz, 8H) ppm; $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ = 224.8, 212.9, 96.7, 84.8, 84.2, 77.5 ppm; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 253 sh (4.27), 340 sh (3.95) nm; IR (KBr): 2055, 2023, 1993, 1934 cm$^{-1}$; MS (EI, 70 eV): $m/z$ (rel intensity) 1000 (5) [$M$]$^+$, 916 (62) [M−3CO]$^+$, 140 (100). HRMS (FAB): calc. for $C_{39}H_{16}FeMn_4O_{15}$: 999.7360, found: 999.7374. *Anal.* Calc. for $C_{39}H_{16}FeMn_4O_{15}$: C, 46.84; H, 1.61. Found: C, 46.67; H, 1.90%.

From **1** and **5**: Under $N_2$, *tert*-BuLi (2.46 mmol, 1.45 mL, 1.7 M in pentane) was added during 3 min to a solution of $CpMn(CO)_3$ (502 mg, 2.46 mmol) in THF (5 mL) at −78 °C. The mixture was stirred for 30 min at this temperature, then for another 30 min at −50 °C to give a brown solution. The latter was transferred at −78 °C into a solution of vacuum dried (230 °C, 40 h, 0.1 Torr) $ZnBr_2$ (277 mg, 1.23 mmol) in THF (5 mL) and stirred for 30 min at this temperature and then for 1 h at r.t. to form a dark red solution. In a separate two-necked flask under $N_2$ at r.t., a solution of **1** (0.21 g, 0.30 mmol) and $Pd_2(dba)_3$ (57 mg, 0.062 mmol) in THF (15 mL) was stirred for 5 min, rendering a black suspension. This mixture was placed in a preheated oil bath (65 °C), stirred for 3 min, and then treated with the above $R_2Zn$ reagent at an addition rate of 0.60 mL/min. Subsequently, the black solution was stirred at 65 °C for 5 h, cooled to r.t., treated with $H_2O$ (0.1 mL), agitated for 5 min, and filtered through a silica column (4 × 8 cm), eluting with $CH_2Cl_2$–EtOAc–hexane (1:1:1). The yellow product was chromatographed on silica, eluting with hexane–$CH_2Cl_2$–EtOAc (10:1:0.35), to furnish first **3** (135 mg, 45%), then **7** (34 mg, 14%): yellow crystals: mp 128–130 °C (from hexane). $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ = 5.37 (m, 2H), 5.36 (s, 1H), 5.32 (m, 2H), 5.23 (t, $J$ = 2.2 Hz, 2H), 5.09 (m, 4H), 5.01 (m, 2H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 224.9, 224.7, 213.4, 96.1, 93.6, 85.9, 84.5, 83.6, 83.1, 83.2, 82.7, 76.4, 75.6, 64.8; UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (log $\varepsilon$) = 338 (3.75) nm; IR (KBr): 2053, 2022, 1977, 1931 cm$^{-1}$. HRMS (FAB): calc. for $C_{31}H_{13}FeMn_3O_{12}$: 797.7898, found: 797.7889. *Anal.* Calc. for $C_{31}H_{13}FeMn_3O_{12}$: C, 46.65; H, 1.64. Found: C, 46.68; H, 1.63%.

### *4.5. Synthesis of 1,2,3,4-tetra[(cyclopentadienyl)rhenium(tricarbonyl)](cyclobutadiene)iron(tricarbonyl) (**4**)*

From **2**: As described for the preparation of **3**, **2** (100 mg, 0.223 mmol), $[Re(CO)_3(THF)Br]_2$ (381 mg, 0.451 mmol), and KH (54 mg, 1.35 mmol) were brought to reaction and the mixture worked up similarly, except that crystallization was effected in ether-hexane (1:1) at −78 °C to give **4** as pale yellow crystals (51 mg, 15%): mp 120–125 °C (decomp). $^1$H NMR (400 MHz, acetone-$d_6$, assignments by 2D NMR): $\delta$ = 5.97 (t, $J$ = 2.2 Hz, 8H, $Cp_{\alpha H}$), 5.76 (t, $J$ = 2.2 Hz, 8H, $Cp_{\beta H}$); $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ = 213.3 ($CO_{Fe}$), 194.4 ($CO_{Re}$), 97.5 ($Cp_{quat}$), 88.5 ($Cp_{\alpha C}$), 86.5 ($Cp_{\beta C}$), 77.3 (Cbd); UV/Vis ($CH_3CN$): $\lambda_{max}$ (log $\varepsilon$) = 244 sh (4.01) nm; IR ($CDCl_3$): 2056, 2028, 1989, 1937 cm$^{-1}$; MS (EI, 70 eV) $m/z$ (relative intensity) 1526 (5) [$M$]$^+$, 1498 (10) [M−CO]$^+$, 1442 (100) [M−3CO]$^+$. HRMS (FAB): calc. for [M−3CO]$^+$ $C_{36}H_{16}FeO_{12}Re_4$: 1439.8166, found: 1439.8159. *Anal.* Calc. for $C_{39}H_{16}FeO_{15}Re_4$: C, 30.71; H, 1.06. Found: C, 30.80; H, 1.34%.

From **1** and **6**: to $CpRe(CO)_3$ (0.27 g, 0.81 mmol) in THF (10 mL) at −78 °C was added *tert*-BuLi (0.55 mL, 1.6 M in hexanes, 0.88 mmol) over a period of 1 min, causing the solution to turn yellow. The mixture was stirred for 30 min, at which point $ZnBr_2$ (0.18 g, 0.8 mmol) was quickly added. Stirring was continued for 5 min, whereupon the yellow color dissipated, and the reaction mixture was allowed to warm to 23 °C. In a 25 mL round bottom flask, **1** (0.14 g, 0.20 mmol) was dissolved in THF (10 mL), $Pd_2(dba)_3$ (75 mg, 10 mol%) added, and the dark purple solution brought to boil. After 5 min, the zinc reagent was transferred into the flask through a steel cannula and boiling continued for 10 h. The resulting solution was decanted into saturated aqueous sodium bicarbonate, extracted with $CH_2Cl_2$ (3 × 20 mL), and washed with brine (30 mL). The solvent was evaporated and the resulting yellow solid separated by silica gel chromatography using $CH_2Cl_2$-hexanes (1:4) to afford **4** (0.170 mg, 56%).

### *4.6. Synthesis of $BrZn(TMEDA)_2CpM(CO)_3$ (M = Mn, Re)*

$CpM(CO)_3$ (1 mmol) in ether (15 mL) at −78 °C was treated with *tert*-BuLi (0.66 mL, 1.6 M in hexanes, 1.1 mmol). After stirring for 30 min, $ZnBr_2$ (0.225 g, 1 mmol) was added quickly and the mixture

stirred for another 5 min at −78 °C. After warming to 23 °C, the solution was treated with TMEDA (0.15 mL, 1 mmol). The mixture was cooled to 0 °C, and hexanes (20 mL) were added, causing a white precipitate to form. Stirring was halted and the solvent removed by syringe. Reprecipitation from dry ether-hexanes afforded $BrZn(TMEDA)_2CpMn(CO)_3$ (0.375 g, 81%) and $BrZn(TMEDA)_2$-$CpRe(CO)_3$ (0.445 g, 74%), respectively.

$BrZn(TMEDA)_2CpMn(CO)_3$: $^1H$ NMR (300 MHz, $C_6D_6$): $\delta = 4.53$ (br s, 2H), 4.45 (br s, 2H), 2.08 (s, 6H), 1.74 (s, 6H), 1.63 (AA′m, 2H), 1.36 (BB′m, 2H); $^{13}C$ NMR (300 MHz, $C_6D_6$): $\delta = 92.6$, 85.6, 73.0, 56.2, 48.0, 46.8, $C_{CO}$ not detected; IR (NaCl): 2024, 1924 $cm^{-1}$. *Anal.* Calc. for $C_{14}H_{20}BrMn\ N_2O_3Zn$: C, 36.19; H, 4.34; N, 6.03. Found: C, 36.11; H, 4.40; N, 5.77%.

$BrZn(TMEDA)_2CpRe(CO)_3$: $^1H$ NMR (300 MHz, THF-$d_8$): $\delta = 5.73$ (t, $J = 1.8$ Hz, 2H), 5.39 (t, $J = 2.4$ Hz, 2H), 2.92 (br s, 4H), 2.73 (br s, 12H); $^{13}C$ NMR (300 MHz, THF-$d_8$): $\delta = 198.0$, 94.7, 88.6, 86.2, 58.2, 48.55, 48.50; IR (NaCl): 2023, 1921 $cm^{-1}$. *Anal.* Calc. for $C_{14}H_{20}O_3ReZnBrN_2$: C, 28.22; H, 3.38; N, 4.70. Found: C, 28.02; H, 3.69; N, 4.90%.

### *4.7. Synthesis of (1,2,3,4-tetraferrocenylcyclobutadiene)-iron(tricarbonyl) (**9**)*

A 50 mL three-necked round bottom flask was charged with **1** (0.21 g, 0.30 mmol), $Pd_2(dba)_3$ (0.60 g, 0.07 mmol), dry degassed THF (25 mL), and a magnetic stir bar. The flask was fitted with a reflux condenser, a rubber septum, and a glass stopper. A solution of **8** (10 mL, 0.24 mM, 2.40 mmol) in THF was added slowly to the stirred reaction mixture over 2 min. The solution was brought to reflux for 16 h, using a heating mantle. After cooling to 23 °C, THF was removed in vacuo. The resulting solid was dissolved in ether (50 mL) and washed successively with the following (3 × 15 mL): aqueous saturated $NaHCO_3$, water, and brine. Flash chromatography on silica gel using a gradient of hexanes–EtOAc (10:1–1:10) yielded orange crystals of **9** (170 mg, 60%): mp 203–204 °C (from pentane–$CH_2Cl_2$). $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 4.93$ (t, $J = 1.8$ Hz, 8H, $Cp_{\alpha H}$), 4.15 (s, 20H, Cp), 4.39 (t, $J = 1.8$ Hz, 8H, $Cp_{\beta H}$); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta = 215.0$, 96.5 ($Cp_{quat}$), 78.6 (Cbd), 70.1 ($Cp_\alpha$), 69.8 (Cp), 68.2 ($Cp_\beta$); IR (NaCl): 3000, 2024, 1954, 1400, 1110, 1001, 819, 755 $cm^{-1}$; MS (FAB, NBA) *m/z* (relative intensity) 928 (35) $[M]^+$, 844 (100) $[M-3CO]^+$, 658 (20). *Anal.* Calc. for $C_{47}H_{36}O_3Fe_5$: C, 60.83; H, 3.91. Found: C, 60.56; H, 3.79%.

### *4.8. Synthesis of 1,2,3,4-tetra[(cyclopentadienyl)rhenium-(tricarbonyl)](cyclobutadiene)(cyclopentadienyl)cobalt (**11**)*

A 25 mL round bottom flask was charged with bis(cyclopentadienylrhenium tricarbonyl)acetylene (**10**, 100 mg, 0.14 mmol), dry degassed *m*-xylene (10 mL), and a magnetic stir bar. The flask was equipped with a reflux condenser capped by a rubber septum. After sparging the solution with $N_2$ for 5 min, $CpCo(CO)_2$ (15 mg, 0.08 mmol) was added by syringe. The resulting mixture was boiled for 8 h, turning from purple to brown. Flash chromatography on silica, eluting with toluene, gave light brown crystals of **11** (83 mg, 79%): mp 233–235 °C (from toluene). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 5.59$ (t, $J = 2.2$ Hz, 8H, $Cp_{\alpha H}$), 5.40 (t, $J = 2.2$ Hz, 8H, $Cp_{\beta H}$), 4.96 (s, 5H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 193.5$ (CO), 100.0 ($Cp_{quat}$), 86.7 ($Cp_\alpha$), 84.3 ($Cp_{\beta H}$), 83.1 (CpCo), 69.3 (Cbd); IR (NaCl): 2922, 2019, 1905, 1260, 1020, 800 $cm^{-1}$; MS (FAB, NBA) *m/z* (relative intensity) 1510 (100) $[M]^+$, 1169 (25), 535 (45), 461 (35). HRMS (FAB): calc. for $C_{41}H_{21}Co^{185}O_{12}Re_4{}^{187}$: 1509.8567, found: 1509.8533. *Anal.* Calc. for $C_{41}H_{21}CoO_{12}Re_4$: C, 32.63; H, 1.40. Found: C, 32.58; H, 1.64%.

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## Appendix A. Supplementary material

CCDC 784060, 784061, 784062, 784063, 784064, and 784065 contain the supplementary crystallographic data for complexes **2**, **3**, **4**, **7**, **9**, and **11**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.10.004.

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