Radial (tetracyclopentadienyl)cyclobutadiene pentametals

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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.

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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 triferoencylclopropenyl 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) radiale [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].
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 (CpSnBu3) [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 1H NMR spectrum shows complicated multiplets in the alkene and allylic hydrogen region, integrating in the ratio 3:2. The 13C 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)3pyr2 (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 complex.
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 zinicate species BrZnCpM(CO)3 (M = Mn, Re) as coordination complexes with N,N,N0,N0-tetramethylethylenediamine [21], used in twofold excess in their reactions with 1. With tetrakis(triphenylphosphine)palladium as the catalyst in THF-d8 clean transformations to 3 and 4, respectively, were recorded, the only side products constituting the known products of oxidative homocoupling of the zinicate, FvMn2(CO)6 [22] and FvRe2(CO)6 [23], respectively (Fv = fulvalene = g5:g5-bicyclopentadienyl).

In a vein similar to that of Scheme 3, (tetraferrocenylcyclobutadiene)iron(tricarbonyl) (9) was built by reaction of diferrocenyl-zinc 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 Cbdcentroid–Cbdquat–Cpquat 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...
planes of the two rings being 15.5° (3) and 14.3° (4), respectively. The distances between the C\text{p} centroid–Mn (avg. 1.778 Å), C\text{p} centroid–Re (avg. 1.964 Å) or C\text{b} 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 C\text{p}Co(tetraferrocenylcyclobutadiene) [8b] is far more symmetrical with respect to the persubstituted cyclobutadiene scaffold. Excluding the C\text{p}Co fragment, the remainder of the molecule has C\text{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)\text{3} relative 9 is isostructural with the C\text{p}Co 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)₅. The ferrocenyls branch away from the core, as reflected in the Cdbquat-Cbdquart-Cpquat 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 ¹H NMR experiments with 9 and 11. Thus, the latter shows only slight line broadening of the pendant CpRe(CO)₅ signals on cooling to −90 °C (THF-d₅), 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 (CH₂Cl₂, NBut₄PF₆, versus [CP₂FePO][CP₂FeO⁺]) involving the four ferrocenyl units. These data are similar to those of its Cp₄ analog [8b]. −0.085, 0.075, 0.225, and 0.283 V (CH₂CN–CH₂Cl₂, NBut₄PF₆, versus [CP₂FePO][CP₂FeO⁺]).

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 N₂ immediately prior to use; CH₂Cl₂, benzene, N,N,N,N,N'-pentamethylene diamine (TMEDA), and triethylamine were distilled from CaH₂ under N₂ and stored in a Schlenk flask. Zinc bromide (115 mg, 0.20 mmol) and Bu₃SnCp (2.47 ml, 8.0 mmol) under nitrogen at 0°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 (CH₂Cl₂, NBut₄PF₆, versus [CP₂FePO][CP₂FeO⁺]), involving the four ferrocenyl units. These data are similar to those of its Cp₄ analog [8b]. −0.085, 0.075, 0.225, and 0.283 V (CH₂CN–CH₂Cl₂, NBut₄PF₆, versus [CP₂FePO][CP₂FeO⁺]).

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 F². 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(db₃)_2 (115 mg, 0.20 mmol) and Bu₃SnCp (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 Bu₃SnCp (0.62 ml, 0.2 mmol), followed by stirring for 24 h. The solution was removed and the resulting brown product vigorously shaken in ether (20 mL) and 10% aqueous KOH (100 mL). The solution was dried with MgSO₄ and chromatographed over neutral alumina (hexane, activity II), eluting with hexane/CH₂Cl₂ (30:1) to render 2 as a yellow solid (140 mg, 33.4%); mp 105–110°C (decomp; from hexane). ¹H NMR (400 MHz, CD₂Cl₂): δ = 6.0–6.8 (m, 12H), 2.9–3.2 (m, 4H), 2.67 (m, 4H) ppm; ¹³C NMR (100 MHz, CD₂Cl₂): δ = 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, 133.7, 133.68, 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, 44.3, 44.2, 44.2, 44.2, 42.2, 42.2, 42.15, 42.10, 42.03 ppm; UV/Vis (hexane): λ_max (log ε) = 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 [M⁺], 420 (32) [M–CO]⁺, 392 (50) [M–2CO]⁺, 364 (90) [M–3CO]⁺, 152 (100). HRMS (El) calc. for Cp₂H₃SnFeO₃: 448.0762, found: 448.0752.
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)₃py₂ (478 mg, 1.268 mmol), and KH (54 mg, 1.35 mmol) under nitrogen, dry THF (20 mL) added, and the mixture was allowed to warm to 23°C. In a separate two-necked flask under N₂ at r.t., a solution of tert-BuLi (0.66 mL, 1.6 M in hexanes, 1.1 mmol). After stirring for 5 min, the zinc reagent was transferred into CpRe(CO)₃ (0.27 g, 0.81 mmol) in THF (10 mL) and washed with CH₂Cl₂–EtOAc–hexane (10:1:0.35), to furnish first 3 (135 mg, 45%), then 7 (34 mg, 14%); yellow crystals: mp 128–130°C (from hexane). ¹H NMR (300 MHz, acetone-d₆): δ = 5.36 (t, J = 2.2 Hz, 8H, Cp), 2129, 96.7, 84.8, 84.2, 77.5 ppm; UV/Vis (CH₂Cl₂): λmax (log ε) = 253 s (427, 340 s) nm; IR (KBr): 2055, 2028, 1989, 1937 cm⁻¹; MS (EI, 70 eV): m/z (relative intensity) 1526 (5) [M+CO]+, 1442 (100). HRMS: [FAB]: calc. for C₃₉H₁₄FeMnO₁₅Re₄: 797.7898, found: 797.7889. Anal. Calc. for C₃₉H₁₄FeMnO₁₅Re₄: 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)Br₂ (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 (31 mg, 15%); mp 120–125°C (decomp.) ¹H NMR (400 MHz, acetone-d₆), assignments by 2D NMR): δ = 5.97 (t, J = 2.2 Hz, 8H, Cp₃Re), 5.76 (t, J = 2.2 Hz, 8H, C₃Re); ¹³C NMR (100 MHz, acetone-d₆): δ = 213.3 (CO₃Re), 194.4 (CORe), 97.5 (Cp₃Re), 88.5 (Cp₃Re), 77.3 (Cbd); UV/Vis (CH₃CN): λmax (log ε) = 244 sh (4.01) nm; IR (CdCl₃): 2056, 2028, 1989, 1937 cm⁻¹; MS (El, 70 eV) m/z (relative intensity) 1526 (5) [M]+, 1498 (10) [M – CO]+, 1442 (100) [M – 3CO]+. HRMS: (FAB): calc. for [M – 3CO]+ C₃₉H₁₄FeRe₂O₂: 1439.8166, found: 1439.8159. Anal. Calc. for C₃₉H₁₄FeRe₂O₂: C, 30.71; H, 0.16. 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 ZnBr₂ (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), Pd₂(dbal)₂ (75 mg, 0.10 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 CH₂Cl₂ (3 × 20 mL), and washed with brine (30 mL). The solvent was evaporated and the resulting yellow solid separated by silica gel chromatography using CH₂Cl₂–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 (0.86 mL, 1.6 M in hexanes, 1.1 mmol). After stirring for 30 min, ZnBr₂ (0.225 g, 1.6 mmol) was added quickly and the mixture

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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)2CpRe(CO)3: 1H NMR (300 MHz, THF-d8): δ = 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); 13C NMR (300 MHz, THF-d8): δ = 92.6, 85.6, 73.0, 56.2, 48.0, 46.8, CCO not detected; IR (NaCl): 2024, 1924 cm−1. Anal. Calc. for C41H21CoO12Re4: C, 32.63; H, 1.40. Found: C, 32.58; H, 1.64%.

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.jica.2010.10.004.

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A 50 mL three-necked round bottom flask was charged with 1 (0.21 g, 0.30 mmol), Pd2(dba)3 (0.60 g, 0.07 mmol), dry degassed THF (25 mL), and a magnetic stir bar. The flask was equipped with a reflux condenser, a rubber septum, and a glass stopper. A solution of A 50 mL three-necked round bottom flask was charged with 1 (0.21 g, 0.30 mmol), Pd2(dba)3 (0.60 g, 0.07 mmol), dry degassed THF (25 mL), and a magnetic stir bar. The flask was equipped with a reflux condenser, a rubber septum, and a glass stopper. A solution of


