1,2,4,5-Tetra([5]trovacenyl)benzene: an organometallic tetraradical displaying pronounced electro- and magnetocommunication†‡

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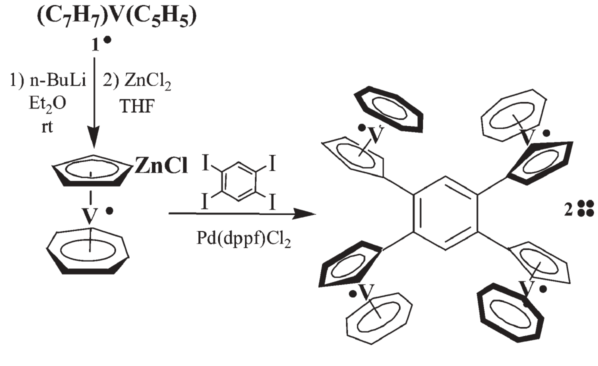
The organometallic tetraradical 1,2,4,5-[(η^7-C$_7$H$_7$)V(η^5-C$_5$H$_4$)]$_4$C$_6$H$_2$ has been prepared and structurally characterized. The isotropic EPR spectrum displays 29 $a(^{51}V)$ hyperfine lines, the intensity distribution slightly deviating from binomial. Exchange coupling therefore approaches the strong exchange limit, $J_{ortho} \neq J_{meta} \neq J_{para} \gtrsim 50\ a(^{51}V)$ with $a(^{51}V) = 0.0067\ cm^{-1}$. According to magnetic susceptometry, the interaction is antiferromagnetic. While redox splittings $\delta E_{1/2}$ are resolved for the four reduction steps this is not the case for oxidation.



Scheme 1

Linked metallocenes have been used extensively in studies concerned with intramolecular communication mediated by organic spacers.[2] Half-sandwich units have also been employed for this purpose.[3] While for heterovalent species questions related to the mixed *vs.* intermediate valence problem are at stake, homovalent species lend themselves to the determination of the potential differences of subsequent electron transfer steps (redox splitting $\delta E_{1/2}$) and for the case of paramagnetic metallocenes to assessments of electron–electron spin–spin interaction (exchange coupling *J*). In this endeavour, an eminently suitable paramagnetic sandwich complex is (η^7-**tro**pylium)**va**nadium(η^5-cyclop**en**tadi**e**nyl), trovacene $\mathbf{1}^\bullet$, because of its orbitally non-degenerate $^2A_1$ ground state (configuration $e_2{}^4a_1{}^1e_1{}^0$) with attendant low EPR linewidths, the presence of the magnetic nucleus ^{51}V (I = 7/2, 99.75%) in high abundance, access to two reversible redox couples $\mathbf{1}^{+/0/-}$ and comparative ease of derivatization.[4] In the past we have studied di[5]trovacenyls void of a spacer[4a,b] as well as separated by alkane, alkene[1] and by alkyne units.[4c] A conjugated spacer which potentially can accommodate up to six trovacenyl units is the benzene ring, as exemplified by 1,3,5-tris([5]trovacenyl)benzene.[4d] Here we report on the synthesis, structural characterization, cyclic voltammetry, and EPR spectroscopy of the unprecedented organometallic tetraradical 1,2,4,5-tetra([5]trovacenyl)benzene ($\mathbf{2}^{::}$).

The title compound $\mathbf{2}^{::}$ was prepared *via* Negishi coupling (Scheme 1).§ Separation from unreacted $\mathbf{1}^\bullet$ can be effected by vacuum-sublimation at 420° (5 × 10^{-5} bar), which attests to the high thermal stability of the trovacene unit. Recrystallization from THF yielded crystals suitable for X-ray diffraction; an ORTEP-plot for $\mathbf{2}^{::}$ is displayed in Fig. 1.¶

The structural parameters of the trovacenyl units in $\mathbf{2}^{::}$ deviate insignificantly from those of parent $\mathbf{1}^\bullet$.[5] The central benzene ring appears to be slightly stretched in the C14···C14′ direction, the bonds between substituted *ortho*-carbon atoms, C13–C13′ and C13(a)–C13′(a), being longer [1.411(7) Å] than the remaining ones [1.375(7) Å]. The ring is puckered to the extent that the C–C bond vectors are twisted by 4.4° with regard to a C$_6$ best plane. These deformations stem from severe compression strain of neighboring trovacene units, which manifests itself most clearly in the dihedral angles between the cyclopentadienyl- and benzene planes

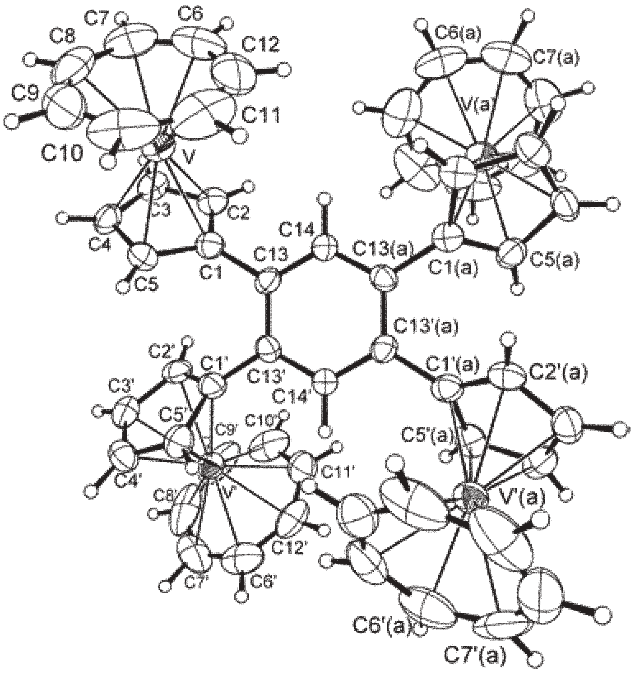


Fig. 1 ORTEP representation (50% probability ellipsoids) of the structure of $\mathbf{2}^{::}$.

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‡ Dedicated to Professor Peter Paetzold on the occasion of his 70th birthday.

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amounting to 44.9° [C1–C5, C1(a)–C5(a)] and 46.4° [C1′–C5′, C1′(a)–C5′(a)], respectively. Due to the peculiar torsional pattern of $\mathbf{2}^{::}$, the intermetallic distances V···V adopt the gradation *meta* (6.60 Å) $<$ *ortho* (7.14 Å) $<$ *para* (9.01 Å).

Fluid solution EPR performed on $\mathbf{2}^{::}$ gives rise to a spectrum consisting of 29 hyperfine components separated by 1.78 mT, which constitutes one quarter of the hyperfine coupling constant $a(^{51}\mathrm{V}) = 7.18$ mT of the mononuclear complex [5]trovacenylbenzene, where the unpaired electron is confined to a single vanadium atom (Fig. 2A). Although the similar magnitudes of linewidths and splitting result in an S-shaped trace it is nonetheless discernible that the intensity distribution deviates from binomial. Therefore, exchange interaction in $\mathbf{2}^{::}$ is settled at the border between "strong" [$J \geqslant 1000\ a(^{51}\mathrm{V})$] and "intermediate" [$J \approx a(^{51}\mathrm{V})$]. A comparison with model simulations[1,6] for spacered di[5]trovacenyls suggests that $J(\mathbf{2}^{::}) \gtrsim 50\ a(^{51}\mathrm{V})$ *i.e.* $J(\mathbf{2}^{::}) \gtrsim 0.33\ \mathrm{cm}^{-1}$ applies, based on the value $a(^{51}\mathrm{V}, \mathbf{1}^{\bullet}) = 7.18$ mT (0.0067 cm^{-1}) for mononuclear phenyl-[5]trovacene.[4a] An accurate analysis of the EPR spectrum of the tetraradical $\mathbf{2}^{::}$ would necessitate the use of two degenerate sets of three exchange coupling constants J_{ortho} (13,13′;13a,13′a), J_{meta} (13,13a;13′,13′a) and J_{para} (13,13′a;13′,13a). Although related parameters are known from 1,2-di([5]trovacenyl)benzene ($|J_{ortho}| = 0.04\ \mathrm{cm}^{-1}$)[7], 1,3-di([5]trovacenyl)benzene ($|J_{meta}| = 0.4\ \mathrm{cm}^{-1}$)[8] and 1,4-di([5]trovacenyl) benzene ($|J_{para}| = 0.2\ \mathrm{cm}^{-1}$)[7], simulation of an exchange-coupled EPR spectrum of the tetraradical $\mathbf{2}^{::}$ with three non-equivalent J values and hyperfine interaction with four ^{51}V nuclei would be a formidable task. Furthermore, it is questionable whether the values for the di([5]trovacenyl)benzene derivatives given above can be applied to complex $\mathbf{2}^{::}$ because the conformations in the three diradicals and the tetraradical may not be identical, rendering the transfer of these parameters from the dinuclear complexes to tetranuclear $\mathbf{2}^{::}$ problematic.

Besides the uncertainty of J_{ortho} ($\mathbf{2}^{::}$), J_{meta} ($\mathbf{2}^{::}$) and J_{para} ($\mathbf{2}^{::}$), limitation of computer power prohibits the diagonalization of a 65536 × 65536 matrix. This large number of basis functions arises from the general form $|S_{1..4}, M_{S\ 1..4}, I_{1..4}, M_{I\ 1..4}>$ for a tetraradical ($S_{1..4} = \frac{1}{2}$, $M_{S\ 1..4} = +\frac{1}{2}, -\frac{1}{2}$) with four interacting nuclei ($I_{1..4} = {}^{7}/_{2}$, $M_{I\ 1..4} = +{}^{7}/_{2}\ldots, -{}^{7}/_{2}$), which generates $2^4 \cdot 8^4$ different spin functions. In the case of $\mathbf{2}^{::}$ this *tour de force* of spectral simulation is not warranted as the principal conclusions can be derived from a simple line counting routine. Apart from pointing to the mere fact of magnetocommunication, the hyperfine pattern observed for $\mathbf{2}^{::}$ suggests that for non-equal exchange coupling constants J which all largely exceed the magnitude of the hyperfine parameter $a(^{51}\mathrm{V})$, differences in the J values fail to shape the hyperfine pattern and an isotropic EPR spectrum is observed which is indistinguishable from that of a fully delocalized (class III[9]) monoradical ion.

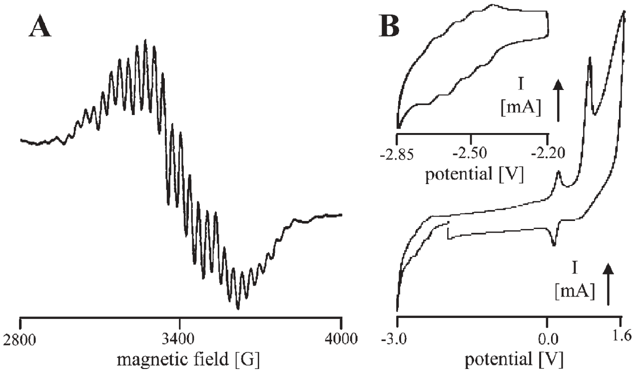

Fig. 2 **A** EPR spectrum of $\mathbf{2}^{::}$ in fluid solution (toluene, 357 K, f = 9.2070 GHz). **B** Electrochemical traces for $\mathbf{2}^{::}$ (cyclic voltammetry, glassy carbon working electrode, SCE reference electrode, 0.1 V s^{-1}, dimethoxyethane, $(n\text{-Bu})_4\mathrm{NClO}_4$, −40 °C).

An alternative to EPR is the determination of the exchange coupling parameter J by means of magnetic susceptometry. For oligotrovacenyls the two methods are complementary in that, given the magnitude of $a(^{51}\mathrm{V})$, EPR is applicable to $J \lesssim 1\ \mathrm{cm}^{-1}$ whereas bulk susceptibility studies require $J \gtrsim 1\ \mathrm{cm}^{-1}$. Therefore, in the case of $\mathbf{2}^{::}$ a plot of χ^{-1} *versus* T down to $T \approx 10$ K displays Curie–Weiss behavior. It is only below 10 K that χ^{-1} rises slightly, thereby indicating weak antiferromagnetic interaction and, accordingly, a negative sign of the J values for $\mathbf{2}^{::}$. Whereas, admittedly, the assignment of molecular antiferromagnetism based on susceptibility data collected at extremely low temperatures is somewhat ambiguous because small intermolecular interaction cannot be excluded with certainty, the fairly large value $J_{meta} = -1.66\ \mathrm{cm}^{-1}$ determined for 1,3-di([5]trovacenyl)benzene[8] may confidently be traced to intramolecular antiferromagnetic coupling. We assume that this also applies to the *meta* connectivity present in $\mathbf{2}^{::}$. Irrespective of the sign question, susceptometry points to an upper limit of the magnitudes of J_{ortho}, J_{meta} and J_{para} in $\mathbf{2}^{::}$.

In the absence of J values gathered by simulation of the EPR spectrum and the susceptibility curve, all that can be said is that the results from the two methods define the bracket in which the J values for $\mathbf{2}^{::}$ are settled in that EPR indicates the lower and susceptometry the upper limit. Even this statement must be furnished with the caveat that conformational differences in solution (EPR) and in the solid (susceptometry) should give rise to J variance.

In addition to magnetocommunication, $\mathbf{2}^{::}$ also exhibits electrocommunication as apparent from the cyclovoltammetric trace shown in Fig. 2B. Oxidation of $\mathbf{2}^{::}$ at 0.31 V gives rise to a wave which fulfils the criteria of reversible one-electron transfer but, as shown by the addition of a one-electron standard, represents the transfer of four electrons. This is the Savéant–Bard–Anson case of multiple electron transfer to vanishingly interacting identical redox centers. Contrarily, reductions at −2.34, −2.45, −2.59, −2.72 V feature resolution of the redox splittings $\delta E_{1/2}$ for the cascade $\mathbf{2}^{::}$ ($0 \rightarrow - \rightarrow 2- \rightarrow 3- \rightarrow 4-$). Larger redox splittings for reductions compared to oxidations of metal centered oligonuclear complexes can be traced to central-metal orbital expansion upon acquisition of negative charge and attendant increase of metal–ligand interaction. This observation signals that electrocommunication in spacered oligotrovacenyls is not exclusively of Coulombic origin but partly ligand-assisted. Since the latter mechanism is also responsible for superexchange, which governs the magnetic properties of $\mathbf{2}^{::}$, electro- and magnetocommunication are related. In fact, it has been pointed out repeatedly that the formal treatments of electron spin coupling, electron transfer, and even energy transfer, share a common basis.[10] Therefore, experimental evidence for correlations between exchange coupling J, redox splitting $\delta E_{1/2}$ and electron transfer rate constants k_{ET} is desirable. The synthesis and study of organometallic oligoradicals is intended to contribute to this goal. Current work in our laboratory is directed towards the synthesis of hexa([5]trovacenyl)benzene which, according to molecular modelling, should be feasible.

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Notes and references

§ Synthesis of $\mathbf{2}^{::}$: a mixture of trovacene $\mathbf{1}^{\bullet}$ (300 mg, 1.4 mmol) in diethylether (50 ml), and n-butyl lithium (0.9 ml, 1.6 mol l^{-1} in hexane) was stirred at room temperature for 10 h. A solution of anhydrous $ZnCl_2$ in tetrahydrofuran (1.6 ml, 0.9 mol l^{-1}) was added and the resulting mixture stirred at room temperature for 0.5 h to effect transmetallation. To a solution of 1,2,4,5-tetraiodobenzene (204 mg, 0.35 mmol) in 20 ml of tetrahydrofuran, the catalyst $Pd(dppf)Cl_2$ (20 mg, 4 mol% referred to $\mathbf{1}^{\bullet}$) was added; the mixture was stirred for 30 min and then injected into the solution of $(C_7H_7)V(C_5H_4ZnCl)$. The reaction mixture was refluxed for 120 min. The precipitate obtained after cooling to room temperature was washed with toluene and subjected to fractional sublimation (5×10^{-5} bar). At 240 °C unreacted $\mathbf{1}^{\bullet}$ sublimes as violet crystals, at 420 °C the product $\mathbf{2}^{::}$ forms a green microcrystalline zone 2 cm above the solid residue. Yield: 100 mg (7.5%). MS (EI): *m/z* (relative intensity) 898 (M^+, 100%), 807 ($M^+ - C_7H_7$, 12%), 449 (M^{2+}, 11%), 207 ($\mathbf{1}^+$, 15%). IR (KBr, cm^{-1}), 3040 w, 1800–1650 w, 1638 s, 1616 s, 774 vs, 430 s (410 shoulder). Anal. Calcd for $C_{54}H_{46}V_4$ (898.72): C, 72.17; H, 5.16%. Found: C, 71.46; H, 4.47%. For CV, EPR and magnetic susceptometry see text. Single crystals suitable for X-ray crystallography were obtained from the mother liquor of the initial precipitation. From this solution the solvent was removed *in vacuo* and the residue was taken up in 7 ml of toluene. Column chromatography (30×2.5 cm, Al_2O_3, 0% H_2O) yielded $\mathbf{1}^{\bullet}$ as the first fraction (elution with benzene). The second fraction, the product $\mathbf{2}^{::}$, was eluted with toluene–THF (10:1). The contents of this fraction were recrystallized from 5 ml of THF to yield $\mathbf{2}^{::}$ at 0 °C as green platelets.

¶ *Crystal data for* $\mathbf{2}^{::}$: $C_{54}H_{46}V_4 \cdot 2C_6H_5CH_3$, $M = 1082.94$, monoclinic, $a = 23.920(2)$, $b = 20.333(2)$, $c = 10.944(1)$ Å, $\beta = 99.100(10)°$, $V = 5255.8(8)$ Å^3, $T = 193(2)$ K, space group $C2/c$, $Z = 4$, μ(Mo-Kα) = 0.732 mm^{-1}, 15674 reflections measured, 5026 unique ($R_{int} = 0.1606$). Final $R_1 = 0.055$, $wR_2 = 0.1308$ (all data). CCDC 257225. See http://www.rsc.org/suppdata/cc/b4/b418831b/ for crystallographic data in CIF or other electronic format.

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