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Regiospecific high yield reductive coupling of diynes to give a luminescent rhodium complex†

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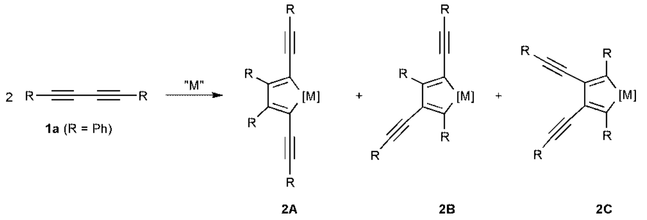
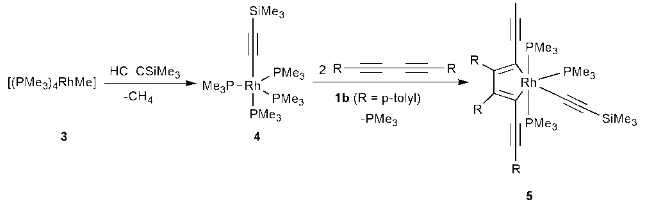
Reaction of 2 equivalents of 1,4-bis(*p*-tolylethynyl)buta-1,3-diyne with [(PMe$_3$)$_4$Rh(–C≡CSiMe$_3$)] gives the unusual, highly luminescent *mer,cis*-[tris(trimethylphosphine)trimethylsilylethynyl-2,5-bis(*p*-tolylethynyl)-3,4-bis(*p*-tolyl)rhodacyclopenta-2,4-diene] 5 in quantitative yield which has been fully characterised by ^{1}H and ^{31}P{^{1}H} NMR, IR, UV–VIS and luminescence spectroscopies, elemental analysis and single crystal X-ray diffraction.

Rigid rod conjugated systems, such as 1,4-bis(phenylethynyl)benzenes,[1–12] 9,10-bis(phenylethynyl)anthracenes[13,14] and 2,5-bis(phenylethynyl)thiophenes,[2] display interesting structural, electronic, non-linear optical and luminescent properties. The same can be expected from structurally similar 2,5-bis(phenylethynyl)metallacyclopentadienyl derivatives **2A** (Scheme 1), which can be prepared by a reductive coupling of two diarylbuta-1,3-diyne molecules **1** on a transition metal centre.[15–22] However, in the few reported syntheses of such compounds, various products are formed, including two other isomers of **2** (**B** and **C**), and the yields of the desired isomer **2A** are small: 1.5–4% in the reaction of diphenylbuta-1,3-diyne **1a** with [Ru$_3$(CO)$_{10}$(NCMe)$_2$] in the presence of Me$_3$NO {[M] = Ru(NMe$_3$)(CO)$_3$} and 2% in the reaction of **1a** with [CpCo(PPh$_3$)$_2$] at 60 °C {[M] = CoCp(PPh$_3$)}, although the reaction of the latter with hexa-2,4-diyne yields 32% of **2A**. The only other analogous monometallic compounds of which we are aware[23] are those containing titanium and zirconium for which isomer **2A** is not observed.[21,22] In the course of our work on rhodium alkynyl complexes,[24–29] we developed a high-yield one-pot synthesis of a luminescent complex **5** *via* the reaction sequence in Scheme 2.



Scheme 1



Scheme 2

Reaction of [(PMe$_3$)$_4$RhMe] **3**[30] (20 mg, 4.74 × 10^{-5} mol) with HC≡CSiMe$_3$ (6.7 μl, 4.74 × 10^{-5} mol) in THF (1 ml), gave the alkynyl complex **4** in quantitative yield with loss of methane.[25,26,29] To this, a solution of two equivalents (21.8 mg) of 1,4-bis(*p*-tolyl)buta-1,3-diyne **1b** in THF (2 ml) was added. The reaction was monitored *in situ* by ^{31}P{^{1}H} NMR spectroscopy, which showed a partial conversion into a new (PMe$_3$)$_3$-Rh^{III} complex **5**. After stirring for 2 min, all solvent was removed *in vacuo* and the residue was redissolved in THF (3 ml), thus facilitating the reaction by removing the liberated, volatile PMe$_3$. This cycle was repeated five times, until the NMR spectra showed the conversion to be complete. Bright yellow product **5** was isolated in 95% yield (40 mg) after recrystallisation from THF–hexane.‡

An X-ray diffraction study of **5**§ revealed a distorted octahedral coordination of the Rh atom (Fig. 1) with a meridonal disposition of the three phosphine ligands. The rhodacyclopentadiene ring is nearly planar: the Rh atom deviates by 0.13 Å from the C(15)C(16)C(17)C(18) plane.

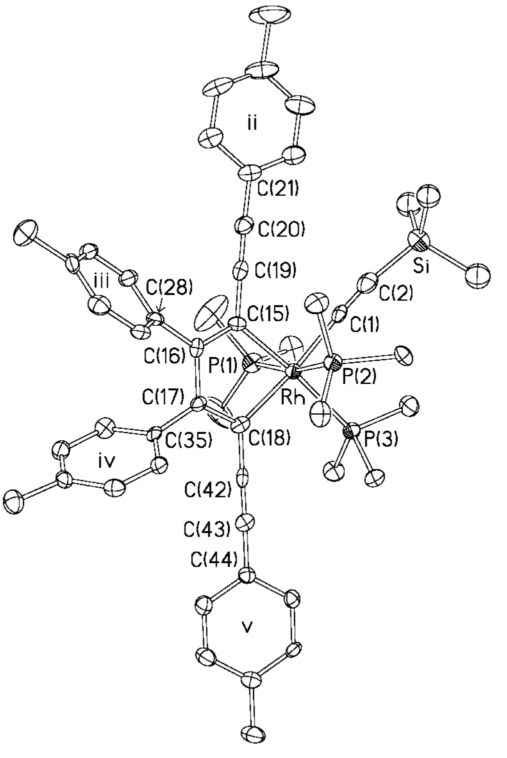


Fig. 1 Molecular structure of **5** showing 50% thermal ellipsoids. The rotational disorder of P(1)Me$_3$ and SiMe$_3$ groups is not shown (H atoms are omitted). Selected bond lengths (Å) and angles (°): Rh–P(1) 2.322(2), Rh–P(2) 2.325(1), Rh–P(3) 2.372(1), Rh–C(1) 2.068(6), Rh–C(15) 2.087(5), Rh–C(18) 2.110(5), C(2)–Si 1.848(7), C(20)–C(21) 1.426(7), C(43)–C(44) 1.432(7); P(1)–Rh–P(2) 168.39(5), C(1)–Rh–C(18) 173.5(2), C(15)–Rh–P(3) 173.9(2), C(1)–Rh–P(2) 85.3(1), P(1)–Rh–P(3) 96.67(5), C(15)–Rh–C(18) 78.8(2).

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† Electronic supplementary information (ESI) available: absorption, emission and luminescence spectra for **5**. See http://www.rsc.org/suppdata/cc/b1/b108625a/

Benzene rings *iii* and *iv,* immediately attached to the metallacycle, are inclined to the latter plane by 50 and 66° (due to steric overcrowding), while rings *ii* and *v* are inclined by only 10 and 22°, permitting π-electron conjugation along the 'rod'. Thus, in the metallacycle, the formally double bonds C(15)=C(16) [1.382(6) Å] and C(17)=C(18) [1.389(6) Å] are longer than in cyclopentadiene[31] (1.344 Å) and its derivatives[32] (average 1.341 Å). The C(16)–C(17) bond [1.465(6) Å] is relatively short compared with non-conjugated, *i.e.* non-planar, butadiene moieties[32] (1.478 Å). The C(15)–C(19) and C(18)–C(42) bonds [av. 1.415(7) Å] are short for a C(sp)–C(sp^2) bond[32] (1.431 Å). The alkyne bonds C(19)≡C(20) and C(42)≡C(43) [av. 1.214(7) Å] are longer than the standard value[32] (1.181 Å) as well as the non-conjugated C(1)≡C(2) bond [1.167(7) Å]. Although each of these differences is on the margin of statistical significance, they are all consistent with the model of conjugation. The alkynyl ligand lies close to the rhodacyclopentadiene plane, *trans* to the Rh–C(18) bond, which is longer [2.110(5) Å] than the Rh–C(15) bond [2.087(5) Å] due to the *trans*-influence. The SiMe$_3$ group and the P(1)Me$_3$ ligand are rotationally disordered, each between two orientations in 1 : 1 and 3 : 1 ratios, respectively.

The ^{31}P{^{1}H} NMR spectrum[†] of **5** displays a doublet of doublets and a doublet of triplets consistent with a meridonal (PMe$_3$)$_3$Rh^{III} coordination, where the unique phosphine is *trans* to a Rh–C σ-bond ($^1J_{RhP}$ 82 Hz). The ^{1}H NMR spectrum indicated four non-equivalents *p*-tolyl groups, three meridonal PMe$_3$ ligands and a SiMe$_3$ group. Thus, the solution NMR data is entirely consistent with the solid-state structure.

The bright yellow compound **5** displays several intense absorptions in the UV–VIS spectrum with peaks at 480 (ε 36 000), 452 (ε = 43 000), 434 (ε = 31 000), 333 (ε = 36 000) and 312 nm (ε = 55 000 dm^3 mol^{-1} cm^{-1}). We noted that NMR samples of **5** in benzene or THF emitted green light when exposed to ordinary fluorescent room lighting. An examination of the luminescence spectra revealed that excitation at 452 nm gave rise to emission bands at 500 and 532 nm (green), whereas excitation at 333 nm showed these two bands as well as stronger emissions at 366 and 384 nm. The absorption spectrum and the emission spectrum resulting from 452 nm excitation are remarkably similar in wavelength and extinction coefficients to those observed previously for 9,10-bis(4-MeSC$_6$H$_4$C≡C)anthracene.[13] This is an exciting finding in light of the considerable current interest in luminescent organometallics,[2,33,34] which may have applications as the emissive material in OLEDs. Further photophysical studies on this and related compounds are underway in order to elucidate the nature of the states giving rise to the absorption and emission in **5**.

We have prepared a rare example of a 2,5-bis(arylethynyl)metallacyclopentadiene *via* the regiospecific reductive coupling of two butadiynes at a rhodium centre. The highly luminescent compound is formed in quantitative yield in minutes at room temperature. Solid samples of **5** appear relatively stable to the atmosphere, making this an attractive system for further study and possible applications. The compound offers exciting opportunities for functionalisation at the metal bound alkynyl ligand, the phosphines, and the starting diyne **1**, as well as the possibility of changing the metal centre from Rh to Co or Ir, all of which should allow tuning of the luminescent properties of the system.

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Notes and references

[‡] *NMR data*: δ_P (80.96 MHz, C$_6$D$_6$) −8.81 (2P, dd, $^1J_{RhP}$ 99, $^2J_{PP}$ 30 Hz), −23.22 (1P, dt, $^1J_{RhP}$ 82, $^2J_{PP}$ 30 Hz). δ_H (200.1 MHz, C$_6$D$_6$): 7.74 [2H, (AB)′, Ar], 7.43 [2H, (AB)′, Ar], 7.34 [2H, (AB)′, Ar], 7.23 [2H, (AB)′, Ar], 7.06 [2H, (AB)′, Ar], 7.03 [2H, (AB)′, Ar], 6.99 [2H, (AB)′, Ar], 6.92 [2H, (AB)′, Ar], 2.08 (6H, s, Me), 2.03 (3H, s, Me), 2.01 (3H, s, Me), 1.77 (9H, d, *J* 8 Hz, PMe$_3$ *trans* to C), 1.38 (18H, vt, *J* 3 Hz, PMe$_3$ *trans* to PMe$_3$), 0.42 (9H, s, TMS). Calc. for C$_{50}$H$_{64}$P$_3$RhSi: C, 68.65; H, 7.14. Found: C, 67.56; H, 7.26%. IR (solid-state): ν(C≡C) 2160, 2128, 2021 cm^{-1}.

[§] *Crystal data* for C$_{50}$H$_{64}$P$_3$RhSi **5**: yellow prismatic crystal (0.46 × 0.09 × 0.07 mm) grown by diffusion of hexane into a THF solution, $M = 888.92$, orthorhombic, space group *Pbca* (no 61), a = 10.500(2), b = 19.180(1), c = 47.927(6) Å, V = 9652(2) Å^3, Z = 8, $\mu = 0.51$ mm^{-1}, T = 120 K, SMART 1K CCD area detector, Mo-$K\alpha$ radiation, 41968 reflections (7981 independent, R_{int} = 0.095), SHELXTL software (Bruker AXS, Madison, WI, 1997), least squares refinement against F^2 of all data, final R = 0.067 [5801 reflections with $F^2 > 2\sigma(F^2)$], $wR(F^2)$ = 0.112. CCDC reference number 171634. See http://www.rsc.org/suppdata/cc/b1/b108625a/ for crystallographic data in CIF or other electronic format.

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