Supporting Information

Sodium and rhodium complexes of a spirocyclic Te_5 dianion supported by P_2N_2 rings

Andreas Nordheider,[a,b] Kasun S. Athukorala Arachchige,[a] Alexandra M. Z. Slawin[a], J. Derek Woollins[a] and Tristram Chivers[b]*

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I. Experimental Section

NMR spectra were recorded at 25 °C using a *JEOL DELTA EX 270*. 85 % H_3PO_4 was used as an external standard for $^{31}P\{^1H\}$ NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) relative to the solvent peaks.[1] Coupling constants (J) are given in Hertz (Hz). Mass spectrometry was performed on a Thermofisher LTQ Orbitrap XL at the EPSRC UK National MS Facility in Swansea. X-ray analysis was performed by a Rigaku Mo MM007 (dual port) high brilliance generator with Saturn 70 and Mercury CCD detectors, rotating anode/confocal optics and two XStream LT accessories at −180(1) °C, or a Nonius KappaCCD diffractometer at 173(2) K. All data were collected with Mo-Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarisation effects. The data for compounds **4** and **5** were collected and processed using CrystalClear (Rigaku).[2]

The crystal structures were solved using direct methods[3] or heavy-atom Patterson methods[4] and expanded using Fourier techniques.[5] The non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined using the riding model. All calculations were performed using CrystalStructure[6] crystallographic software package and SHELXL-97.[7]

All synthetic manipulations were performed under an atmosphere of dry argon using standard Schlenk-line techniques and/or a Saffron glovebox running with argon unless otherwise stated. All glass apparatus was stored in a drying oven (120 °C) and flame-dried *in vacuo* (10^{-3} mbar) before use. Dry solvents were collected from an *MBraun* solvent system under a nitrogen atmosphere and stored in Schlenk flasks over 4 Å molecular sieves or were dried and purified using common procedures.[8] All chemicals were purchased from *Sigma Aldrich* and used without further purification. $[\mathrm{Li(tmeda)}]_2$**1**,9[8] $[\mathrm{Na(tmeda)}]_2$**1**,[10] and $[\mathrm{Cp^*RhCl_2}]_2$ were synthesised according to the literature procedures.[11]

4: $[\mathrm{Na(tmeda)}]_2$**1** (500 mg, 0.57 mmol) was suspended in toluene and cooled to −78 °C. A solution of I_2 (72 mg, 0.28 mmol) in toluene (15 mL) was maintained at −78 °C and added dropwise over 15 min by cannula. The reaction mixture was stirred for 30 min before being allowed to warm to RT and then stirred for an additional 1 h. The precipitate was removed by filtration, dried and redissolved in *n*-hexane at −40 °C (very low solubility). After three days a few extremely air and thermally sensitive crystals suitable for X-ray crystallography were isolated. Mass spectrometry did not give any data that could be attributed to the product **4**. Elemental analysis was precluded due to rapid decomposition of the material. A new resonance in the ^{31}P NMR spectrum of the reaction mixture in toluene is tentatively attributed to **4**: ^{31}P NMR (109.37 MHz, C_6D_6 capillary): $\delta = -73.7$ (s, ^{1}J(P,Te) = 1198 Hz).

5: $[\mathrm{Li(tmeda)}]_2$**1** (300 mg, 0.35 mmol) was suspended in toluene and cooled to −78 °C. A solution of $[\mathrm{Cp^*RhCl_2}]_2$[11] (109 mg, 0.18 mmol) in toluene (15 mL) was maintained at −78 °C and added dropwise over 15 min by cannula. The reaction mixture was stirred for 30 min before being allowed to warm to RT and then stirred for an additional 1 h. The mixture was then filtered to remove the deposited elemental tellurium and the solvent was removed under reduced pressure. The solid residue was dissolved in *n*-hexane, filtered and the solvent was removed to afford a dark reddish black material (Yield 9 %). Recrystallisation from *n*-hexane afforded black crystals that were filtered, dried and identified as **5**. MS (ESI$^+$, *m/z*), 1580.05 [M^+] (calculated for $C_{42}H_{87}N_8P_4RhTe_5$: 1580.04 [M^+]).^{31}P NMR (109.37 MHz, [D$_8$]toluene): $\delta = -123.4$ (s, ^{1}J(P,Te) = 1136 Hz), −126.8 (d, ^{1}J(P,Te) = 1270 Hz; ^{2}J(P,Rh) = 4.5 Hz); attempts to record the ^{125}Te NMR spectrum were thwarted by a combination of the low solubility and decomposition of **5** in solution with formation of elemental tellurium.

II. X-ray crystallographic data

Table 1. Crystallographic data for compounds **4** and **5**.

Compound	4	5
Empirical formula	$C_{47.5}H_{108}N_{12}Na_2P_4Te_5$	$C_{42}H_{87}N_8P_4RhTe_5$
Formula weight	1655.33	1569.00
Temperature (K)	93	93
Crystal colour, habit	red chunk	red needle
Crystal dimensions (mm^3)	0.09 x 0.05 x 0.03	0.21 x 0.02 x 0.01
Crystal system	orthorhombic	monoclinic
a (Å)	32.355(3)	15.980(3)
b (Å)	34.276(3)	19.756(4)
c (Å)	25.584(2)	18.904(4)
α (°)	90.0000	90.0000
β (°)	90.0000	95.606(4)
γ (°)	90.0000	90.0000
Volume ($Å^3$)	28373(4)	5939(2)
Space group	Fdd2	P_12_1/c_1
Z value	16	4
D_{calc} (g/cm^3)	1.550	1.754
F_{000}	13104.00	3040.00
μ (Mo-K_α) (cm^{-1})	2.173	2.837
No. of reflections measured	44221	79608
R_{int}	0.1342	0.1111
Min. and max. Transmissions	0.645, 0.937	0.729, 0.972
Reflection/parameter ratio	11899 (637)	10824 (569)
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0508	0.0490
Residuals: wR_2 (all reflections)	0.0986	0.1352
Goodness of fit indicator	0.842	0.979
Max. peak in final diff. map ($e^-/Å^3$)	0.85	2.70
Min. peak in final diff. map ($e^-/Å^3$)	−0.73	−1.17

III. References

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