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A rigid anionic Janus bis(NHC) – new opportunities in NHC chemistry†

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A phosphanido-type bridged bis(imidazolium) salt, readily prepared in two steps *via* reductive deselenization of a tricyclic 1,4-diphosphinine diselone, affords access to a novel anionic P-functional tricyclic bis(NHC) *via* deprotonation. The former also offers a P-functionalization/deprotonation sequence to access the first mixed P-substituted tricyclic bis(NHCs), as well as coordination of the phosphorus centers to rhodium(I) fragments.

Introduction

Owing to the wide range of structural and property modifications of N-heterocyclic carbenes (NHCs), they have become potent ligands in organometallic chemistry and catalysis.[1,2] It has been reported that the incorporation of an anionic functionality confers higher stability to resulting NHC complexes compared to related neutral donor substituents.[3] Backbone-functionalized NHCs having anionic heteroatom substituents especially facilitate π-electron interactions with the heterocyclic ring, which can lead to electronic tuning of the donor properties of the carbene.[4] Only a small number of NHCs of type **I** possessing an anionic low-coordinate moiety such as enolate,[5] borate,[6] amido[7] and phosphanido,[8] have been re-ported (Fig. 1). Some of these enabled an additional and/or competing metal binding site, resulting in ligand polytopicity or ambidenticity in bimetallic coordination.[9,10] The anionic bis-(NHC) **II** has been reported, obtained *via* reduction of a bis-(imidazol-2-thione-4-yl)phosphane using a large excess of potassium metal;[11] but **II** could neither be isolated nor structurally confirmed.

A new ambidentate Janus-type ligand combining a carbene and an anionic imidate centers within the same heterocyclic framework was reported by Lavigne *et al.*, appears to be suitable for the directed construction of a variety of homo-and/or heteropolymetallic complexes.[3c] In 2017, a dianionic bis(maloNHC)[3d] was reported as a bridging ligand to construct zwitterionic complexes by Tapu *et al.* Furthermore, it served as building block for the preparation of novel organometallic frameworks, not handy with neutral Janus-type bis(NHC)s. Due to their unique electronic properties, these zwitterionic NHC-metal species exhibit potentially valuable advantages such as enhanced catalytic activity and solubility relative to the classical cationic metal complexes of the neutral NHCs.

Recently, we established a new series of tricyclic rigid Janus bis(NHCs) **III**, tuned by PR_n moieties in different phosphorus oxidation states, and reported on their use in coinage metal(I) complex chemistry.[12] Thereafter, continuing efforts have been made to establish anionic low-coordinate P-linked bis(NHCs) in order to achieve tuneable electronic communication and redox activity.

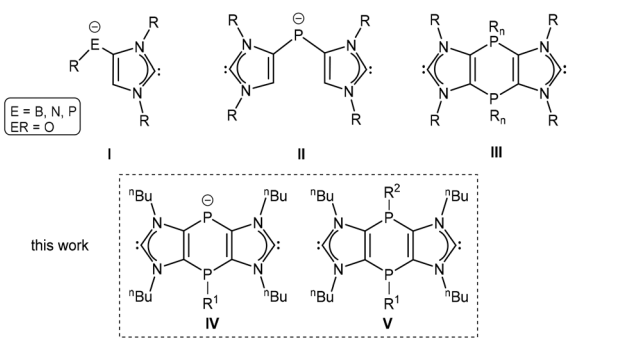

Fig. 1 Anionic mono and bis(NHCs) **I**, **II** and rigid Janus bis(NHCs) **III**–**V** (R,R^1,R^2 = organic substituents).

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Herein, we report on the synthesis of a stable anionic Janus-type tricyclic bis(NHC) **IV** having a P-localized charge, and its use in main group and transition metal chemistry to access, *e.g.*, bis(NHCs) **V**, having a mixed P-substitution pattern.

Results and discussion

Synthesis of anionic bis(NHC) 4 *via* reductive deselenization

Following our recent synthetic protocol,[13] the new tricyclic 1,4 diphosphinine diselone **1** (Scheme 1) was synthesized *via* mild reduction of the *P*–Cl substituted 1,4-dihydro-1,4-diphosphi-nine[12] precursor and, finally, isolated as a deep violet solid. According to TD-DFT calculations, the colour of this electron-delocalized compound could be attributed to a HOMO–LUMO transition (details in the ESI†). Diselone **1** has been treated with 2 equivalents of trifluoromethyl methylsulfonate (MeOTf) in dichloromethane to afford the doubly *Se*-methylated salt **2** which was isolated as a yellow solid and fully characterized, including single crystal X-ray diffraction analysis (Fig. 2).

The centrosymmetric molecular structure of **2** has a C2–Se1 bond distance of 1.896(4) Å that is slightly elongated compared to 1.8240(16) Å for C=Se in the precursor **1** (ESI†), but remains significantly shorter than the 1.952(4) Å Se–C8 bond to the methyl group.

Doubly Se-methylated salt **2** was subjected to reductive deselenization with $NaBH_4$ in the presence of [2.2.2]-cryptand in methanol to afford (somewhat surprisingly) bis(imidazolium) salt **3** (Scheme 1) with an anionic phosphorus centre. Salt **3**, obtained in pure form *via* extraction with dichloromethane followed by washing with diethylether, showed two resonance signals in a 1 : 1 ratio in the ^{31}P NMR spectrum at 20.1 ppm (POMe) and −67.3 ppm (anionic P), but no $^{3}J_{(P,P)}$ coupling (Table 1). Further confirmation for **3** was obtained from NMR and MS experiments as well as elemental analysis. DFT calculations, performed on *N*-Me model compounds,[14] reveal that the aro-matic character of the middle ring in **3′** is lower (NICS(0) = −4.9) than in **1′**[14] ((NICS(0) = −8.1) or **2′** (NICS(0) = −10.0); nevertheless some – apparently hyperconjugative – cyclic conjugation is still operative. In contrast, the outer rings retain high aromatic character (NICS(0) = −11.1).

To access the first example of an anionic P-functional bis (NHC), deprotonation of the bis(imidazolium) salt **3** was performed in THF using two equivalents of KHMDS (Scheme 2).

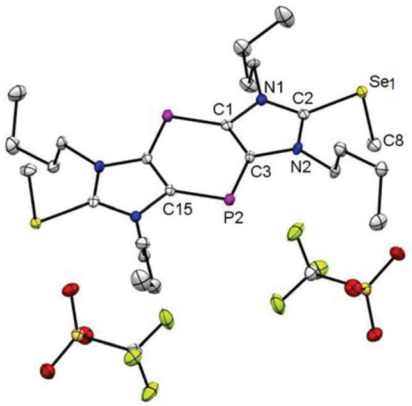


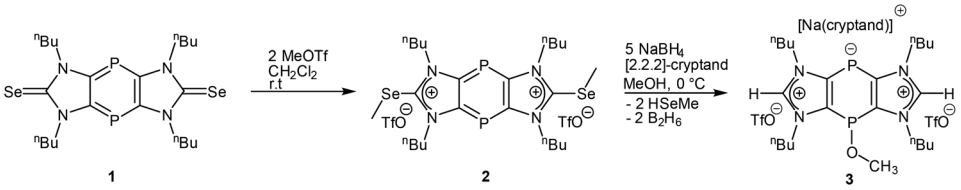
Fig. 2 Molecular structure of compound **2** (ellipsoids at the 50% probability-substituted level); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C2–Se1 1.896(4), Se1–C8 1.952 (4), C2–N2 1.339(5), N2–C3 1.397(5), C3–P2 1.736(4), C1–C3 1.412(6); N1–C2–N2 108.8(3), C3–P2–C15 96.3(2).

Table 1 $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR data for **3**, **4**, **5**$^{cis/trans}$ (1 : 0.3) and **6**$^{cis/trans}$ (1 : 0.3)

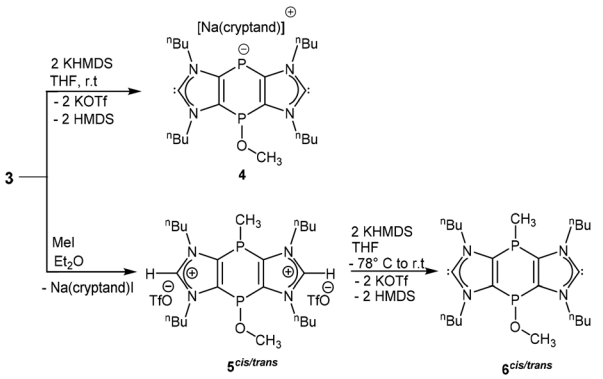
	$\delta(^{31}P)$/ppm (CD_2Cl_2)	$\delta(^{13}C)$/ppm (CD_2Cl_2)[b]
3	20.1 (s), −67.3 (s)	137.3 (d, $^{3}J_{P,C}$ = 4.5 Hz)
4[a]	25.2 (s), −74.8 (s)	208.8 (br)
5$^{cis/trans}$	δ = −71.58 (d, $^{3}J_{P,H}$ = 5.2 Hz), −66.23 (d, $^{3}J_{P,H}$ = 4.9 Hz), 39.57 (br), 43.7 (br)	142.4 (br), 143.37 (br)
6$^{cis/trans}$	δ = −74.0 (d, $^{2}J_{P,H}$ = 4.8 Hz), −68.6 (d, $^{2}J_{P,H}$ = 3.7 Hz), 37.2(d, $^{3}J_{P,H}$ = 4.6 Hz), 41.3 (d, $^{3}J_{P,H}$ = 3.8 Hz)	224.2, 223.8, (t, $^{3}J_{P,C}$ = 2.7 Hz)

[a] In case of **4** and **6**$^{cis/trans}$ (1 : 0.4) THF-d8. [b] C^2 carbon.

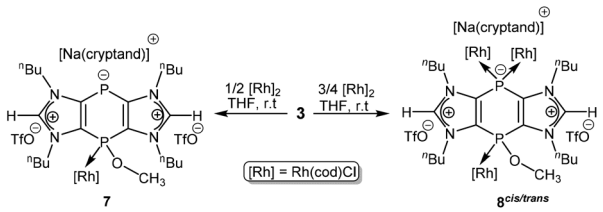
After extraction with THF/diethyl ether (1 : 1.5), compound **4** was isolated as a dark orange solid which has two resonances in its ^{31}P NMR spectrum at 25.2 ppm (P-OMe) and −74.8 ppm (anionic P). The ^{1}H-NMR spectrum confirms the absence of the C^2–H proton and the $^{13}C\{^{1}H\}$ NMR spectrum a broad resonance at 208.8 ppm assigned to the C^2 atom of dicarbene **4**. The proposed constitution of **4** is also supported by HR-MS (negative ESI; exp. 449.2605 *vs.* calc. 449.2607). In order to establish the stability of the carbene **4**, an isodesmic reaction (see ESI†) yields 113.3 kcal mol^{-1} stabilization for **4′**.[14] This is very similar to our earlier reported 111.1 kcal mol^{-1} value[12] for **III** (R : Me, R′ : *cis*-NEt_2), indicating that the carbene character



Scheme 1 Synthesis of doubly Se-methylated salt **2** and bis(imidazolium) salt **3** starting from tricyclic diselone **1**.



Scheme 2 Synthesis of anionic bis(NHC) **4**, $P^{III/III}$ bis(imidazolium) salts $\mathbf{5}^{cis/trans}$ (1 : 0.3) and mixed substituted bis(NHCs) $\mathbf{6}^{cis/trans}$ (1 : 0.3).



Scheme 3 Synthesis of mononuclear rhodium complex **7** and trinuclear rhodium complexes $\mathbf{8}^{cis/trans}$ (1 : 0.7).

in the anionic tri-cycle is virtually unchanged. Compared to **3′**, the aromaticity of the middle ring is slightly higher (NICS(0) = −5.5), while that of the outer rings is lower (NICS(0) = −9.0), as is usual for NHCs if compared to imidazolium salts.[15]

Formation of mixed substituted $P^{III/III}$ bridged bis(NHCs) $6^{cis/trans}$

We then targeted to use the P-anionic functionality to access bis(NHCs) with a mixed P-substitution pattern. Therefore, **3** was treated with MeI in diethyl ether at −80 °C which resulted in a clean formation of bis(imidazolium) salt $\mathbf{5}^{cis/trans}$ with an isomeric ratio of 1 : 0.3 (signals not assigned) (Scheme 2). The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture showed two sets of signals for two isomers at δ(P–CH_3) = −71.6 (d, $^{3}J_{P,H}$ = 5.0 Hz), −66.2 (d, $^{3}J_{P,H}$ = 5.0 Hz) and δ(P–OCH_3) = 39.6 (br), 43.7 (br) (ratio 1 : 0.4). The isolated mixture of $\mathbf{5}^{cis/trans}$ (1 : 0.3) was subsequently deprotonated using two equiv. of KHMDS in THF to afford the mixed-substituted bis(NHCs) $\mathbf{6}^{cis/trans}$ (ratio 1 : 0.3).

Clear evidence for the latter came from the ^{1}H NMR spectrum of this mixture, since the former C^2–H signal (δ = 9.47 (t, $^{3}J_{P,H}$ = 3.03 Hz), 9.56 (br)) of $\mathbf{5}^{cis/trans}$ were absent. This was further supported by the $^{13}C\{^{1}H\}$ NMR spectrum as the characteristic downfield signals for the C^2-nuclei were found (Table 1), revealing the formation of the bis(NHCs) $\mathbf{6}^{cis/trans}$ (ratio 1 : 0.3). $\mathbf{6}^{trans}$ and $\mathbf{6}^{cis}$ are computed to have high stability (the isodesmic reaction energies are 108.8 for $\mathbf{6'}^{trans}$ [14] and 108.6 kcal mol^{-1} for $\mathbf{6'}^{cis}$). The aromatic character of the middle ring is significantly lower (NICS(0) = −0.1), indicating that when both phosphorus centres are saturated the central ring loses its aromaticity, whilst that of the outer rings (NICS(0) = −9.7) remains high.

Initial coordination chemistry experiments were undertaken to explore the reactivity of tricyclic bis(imidazolium) salt **3**. Thus, reaction with a half equiv. of $[Rh(cod)Cl]_2$ affords exclusively the mono rhodium(I) complex **7** (Scheme 3). The coordination of **3** to the Rh(cod)Cl fragment is confirmed by the ^{31}P NMR spectrum as resonances of **7** appeared at high-field (−70.6 (s, anionic P) and 47.5 (d) ppm) having a rhodium–phosphorus coupling of $^{1}J_{Rh,P}$ = 192.4 Hz, assigned to the neutral phosphorus atom. This coordination mode is surprising since the HOMO of **3′** is located at the dicoordinate (anionic) phosphorus atom, and the involved tricoordinate phosphorus, largely representing HOMO−1, is lower in energy by as much as 1.9 eV (see ESI†). Nevertheless, our calculations on the isomeric complexes of **7′** showed that the favoured coordination site is indeed the tricoordinate phosphorus, **7′** being more stable than the possible isomers (*cis* and *trans*) by more than 5 kcal mol^{-1} (see ESI†). To examine how many Rh(I) fragments could be coordinated to **3**, it was then treated with 1.5 equiv. of the rhodium dimer which afforded selectively an isomeric mixture of trinuclear phosphanido complexes $\mathbf{8}^{cis/trans}$ (ratio 0.9 : 1) (Scheme 3). Upon coordination, two sets of signals are present in the ^{31}P NMR spectrum at 65.0 (d, $^{1}J_{Rh,P}$ = 195.6 Hz) (minor)/64.1 (dd, $^{1}J_{Rh,P}$ = 200.1 Hz, $^{3}J_{P,P}$ = 5.3 Hz) (major) and −120.3 (t br, $^{1}J_{Rh,P}$ = 126.9 Hz) (major)/−123.4 (t, $^{1}J_{Rh,P}$ = 126.9 Hz) (minor).

Cyclic voltametric studies supported by DFT calculations

The electrochemical properties of bis(NHCs) **4** and $\mathbf{6}^{cis/trans}$ (1 : 0.3) were investigated by cyclic voltammetry (CV) in THF (0.2 M [nBu$_4$N][PF_6]) at gold ceramic screen printed electrodes (Au CSPE) in an Ar-filled glove box. Voltammetric data were measured on solutions containing 1.0 mM analyte and representative CVs are presented in Fig. 3 (and in greater detail in the ESI†). The observed behaviour of $\mathbf{6}^{cis/trans}$ (Fig. 3b) is reminiscent of dicarbenes **III** (R_n = $P^{III}NEt_2$)[12] and we therefore start the analysis here.

There are a series of facile, chemically irreversible oxidations with anodic peak potentials E_p^{a1} = −0.29 V, E_p^{a2} = −0.07 V and E_p^{a3} = +0.65. The processes are nonetheless repeatable and stable to scanning first in anodic or cathodic directions, and continue right up to the anodic potential limit at around +1.0 V. This is consistent with oxidations involving the carbene σ(p)-centred HOMO and HOMO−1 as determined from B3LYP/6-31+G*//M06-2X/6-31+G* computations undertaken on the model structures $\mathbf{6'}^{cis/trans}$ [15] (Fig. 4). The more positive first oxidations E_p^{a1} = −0.29 V for $\mathbf{6}^{cis/trans}$ compared to **III** (R_n = $P^{III}NEt_2$), for which E_p^{a1} = −0.61 V (ref. 12) reflect the lower lying HOMO energies of −5.93/−5.92 eV of the former *versus* −5.78/−5.77 eV for the latter; as before, we are not able to identify separate CV processes for the two geometrical isomers that are known to co-exist in solution. The true electrochemical reductions for the two types of P^{III} dicarbenes both occur at

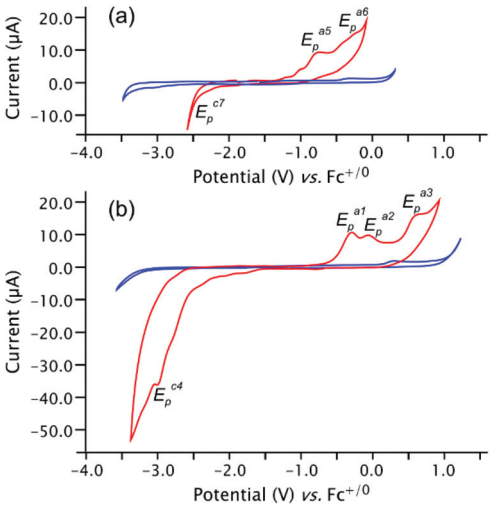


Fig. 3 CV diagrams (a) of **4**, and (b) of **6′*cis/trans*** (scan rate: 200 mV s^{-1}). In each case, the blue trace indicates the solvent/electrolyte background (0.2 M) [nBu$_4$N][PF$_6$] in (THF), and the red that from a 1.0 mM solution of analyte.

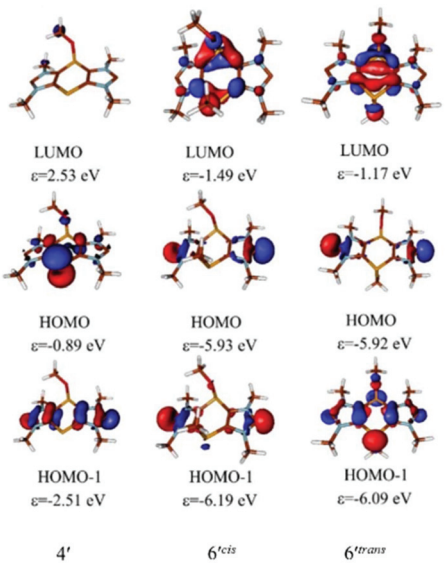
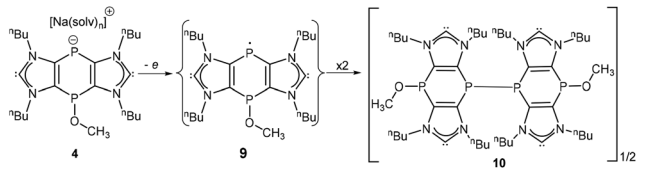


Fig. 4 FMO topologies and energies for the model (R = CH_3) calculated structures of **4′**, **6′*cis*** and **6′*trans*** at the B3LYP/6-31+G*//M06-2X/6-31+G*level of theory (PCM solvent model).

very low potentials (less than −3.5 V) and probably cannot be measured accurately; the shoulder on the main reduction wave in the CVs (*e.g.* E_p^{c1}) are likely from breakdown products of the IRR oxidations (see ESI† for further explanations).

In contrast to this established behaviour of the diphosphinine dicarbenes, the CVs measured on **4** are less well defined although the onset of oxidation is definitely lower in potential than in **6*cis/trans*** with E_p^{a5} = −0.74 V (Fig. 3a). The computed HOMO of model system **4′** is very different (Fig. 4) and is essentially localized at the anionic P atom, and, as expected for an anion, is also at a much higher computed energy (−0.89 eV). Experimentally, the onset of oxidation does not have the expected well-separated peak for a first 1*e* oxidation of such a localized MO, followed by further processes after a considerable gap.



Scheme 4 One electron reduction of **4** to neutral **9** with rapid dimerization to **10**.

A plausible explanation for the observed behaviour is that 1*e* oxidation gives P-centred radical bis(NHC) **9** which rapidly dimerizes to give tetrakis NHC **10** (Scheme 4). Related tricyclic dithione P-radicals have been shown to be very short-lived furnishing structurally verified dimers with a P–P bond.[16] On this view, the remaining processes such as E_p^{a6} = −0.30 V and E_p^{c1} = −2.5 V recorded in the CVs of 4 (Fig. 3a) are best under-stood as redox processes of such a tetrakis NHC.

Experimental section

Experimental details and devices

All experiments were done under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, *n*-pentane and diethyl ether were dried over sodium wire/benzophenone and further purified by subsequent distillation. The precursor for **1**, the 1,4-dichloro-1,4-dihydro-1,4-diphosphinine, was synthesized using standard protocols.[12] All NMR spectra were recorded on a Bruker AX-300 spectrometer (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P) and pollux-500 (500.1 MHz for ^{1}H, 125.75 MHz for ^{13}C, and 500.0 MHz for ^{31}P) spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standard, respectively. Elemental analyses were carried out on a Vario EL gas chromatograph. Melting points were determined in one-side melted off capillaries using a Büchi Type S or a Carl Roth Type MPM-2 apparatus, they are uncorrected Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. IR spectra of all compounds were recorded on a Thermo IR spectrometer with an attenuated total reflection (ATR) attachment. The X-ray analyses were performed on a Bruker APEX-II CCD or a Bruker X8-KappaApexII type diffractometer at 100(2) K. The structures were solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97 [17] program packages. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2032731 (**1**), 2032732 (**2**).†

Synthesis of compounds

1. To a clear solution of 1,4-bis(diethylamino)-1,4-dihydro-1,4-diphosphinine[12] (2.5 g, 3.5 mmol) in dichloromethane, PCl_3 (0.61 mL, 6.9 mmol) was added and stirred for 4 hours at −40 °C. The reaction mixture was then warmed to room temperature and tris(*n*-butyl)phosphane (0.34 mL, 1.4 mmol) was added in a dropwise manner. After 10 minutes stirring, a colour change of the solution from orange to violet was observed. After concentrating the reaction mixture under reduced pressure, the residue was filtered *via* a silica® bed with diethyl ether and toluene mixture (1 : 1). It was then dried under reduced pressure (6×10^{-3} mbar and washed with *n*-pentane (3 × 10 mL) to get rid of the aminophosphane Et_2NPCl_2. Finally, the solution was con-centrated *in vacuo* (6×10^{-3} mbar) to get **1** as pure compound. Yield: 1.2 g (2.1 mmol) 61%; violet solid. M.p. 223 °C. ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 0.8 (t, 12H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.2–1.4 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.8–1.9 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 4.4–4.4 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): δ = 13.55 (s, $NCH_2CH_2CH_2\underline{Me}$), 19.9 (s, $NCH_2CH_2\underline{CH_2}Me$), 28.9 (t, $^3J_{P,C}$ = 1.6 Hz, $NCH_2\underline{CH_2}CH_2Me$), 48.1 (t, $^3J_{P,C}$ = 4.6 Hz, $NCH_2\underline{CH_2}CH_2Me$), 152.2 (t, $^1J_{P,C}$ = 23.1 Hz, P–$\underline{C}$ of the middle ring), 168.32 (br, $\underline{C}^2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 25 °C): δ = 78.2 (s). ^{77}Se NMR (57.28 MHz, $CDCl_3$): 179.4 (s). IR [cm^{-1}]: $\tilde{\nu}$ = 2998.1 (v), 2752.8 (m), 2654.0 (m), 1487.0 (s), 1289.1 (s), 1201.5 (s), 1098.2 (m), 964.0 (s). MS (EI, 70 eV): *m*/*z* (%) = 578.0 (100) $[M]^{\bullet+}$, 498.1 (20) $[M - Se]^{\bullet+}$. UV-vis (CH_2Cl_2): λ_{max} [nm] (abs.): 296 (1.375), 383 (0.156), 554(0.139). EA [%]: theor./exp. C 45.84/45.64, H 6.30/6.46; N 9.72/9.63.

2. 2 equivalents of trifluoromethyl methylsulfonate (0.4 mL, 3.4 mmol) was added to a solution of **1** (1.0 g, 1.7 mmol) in dichloromethane, at room temperature. The reaction mixture was stirred for 2 hours resulting in a color change from violet to light yellow. After concentrating the reaction mixture under reduced pressure (6×10^{-3} mbar), the residue was washed with *n*-pentane (2 × 5 mL) to get **2** as pure light yellow solid. Yield 1.4 g (1.5 mmol) 91%; light yellow solid. M.p. 96 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): 1.04 (t, 12H, $^3J_{H,H}$ = 7.4 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.52–1.62 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 2.05–2.15 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 2.8 (s, 6H, $Se\underline{Me}$) 4.89–4.94 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 11.72 (s, $Se\underline{Me}$), 13.44 (s, $NCH_2CH_2CH_2\underline{Me}$), 20.16 (s, $NCH_2CH_2\underline{CH_2}Me$), 30.73 (s, $NCH_2\underline{CH_2}CH_2Me$), 52.18 (s, $NCH_2\underline{CH_2}CH_2Me$), 148.84 (t, $^3J_{P,C}$ = 4.6 Hz, Se–$\underline{C}^2$), 154.94 (t, $^1J_{P,C}$ = 26.1 Hz, P–$\underline{C}$ of the middle ring). ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 119.95 (s). ^{77}Se NMR (57.28 MHz, $CDCl_3$): 138.89 (s). IR [cm^{-1}]: $\tilde{\nu}$ = 3009.1 (v), 2992.8 (m), 2954.0 (m), 1623.0 (w), 1529.1 (w), 1461.5 (m), 1236.2 (m), 1201.3 (w), 1075.4 (m), 1032.2 (v), 974.0 (s). Pos. ESI-MS: $[C_{25}H_{42}F_3N_4O_3P_2SSe_2]^+$ calcd (found) 757.0728 (757.0750). neg. ESI-MS: TfO^- theor./exp. 148.9(149.5). EA [%]: theor./exp. C 34.52/34.33, H 4.68/4.71; N 6.19/6.0, S 7.08/6.99.

3. To a solution of **2** (1.5 g, 1.6 mmol) in methanol, 5 equivalents of sodium tetrahydridoborate (0.3 g, 8.2 mmol) and one equivalent of [2.2.2]-cryptand was added as solid at 0 °C. The reaction mixture turned to orange-red with strong odour due to a liberation of methylselane (HMeSe). The solution was then concentrated *in vacuo* (6×10^{-3} mbar) after 30 minutes stirring. Extraction was done with dichloromethane followed by washing with diethyl ether (2 × 5 mL) to get **3** as pure orange red solid. Yield: 1.2 g (1.04 mmol) 65%; red orange solid, M.p. 142 °C ^{1}H NMR (300.1 MHz, CD_2Cl_2, 25 °C): δ = 1.0 (t, 12H, $^3J_{H,H}$ = 7.3 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.3–1.5 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.9–2.1 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 2.4 (d, 3H, $^3J_{P,H}$ = 7.3 Hz, *O*–$\underline{Me}$) 2.6 (t, 12H, cryptand), 3.6 (t, 12H, cryptand), 3.7 (s, 12H, cryptand), 4.1–4.6 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$), 8.9 (t, 2H, $^4J_{P,H}$ = 1.7 Hz, C^2–$\underline{H}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 25 °C): δ = 13.2 (s, $NCH_2CH_2CH_2\underline{Me}$), 19.6 (s, $NCH_2CH_2\underline{CH_2}Me$), 30.2 (s, $NCH_2\underline{CH_2}CH_2Me$), 47.8 (s, $N\underline{CH_2}CH_2CH_2Me$), 67.5 (s, cryptand), 68.5 (s, cryptand), 120.9 (d, $^2J_{P,C}$ = 7.3 Hz, *O*–$\underline{CH_3}$), 121.7 (q, $^1J_{F,F}$ = 321.0 Hz, $\underline{C}F_3$), 137.2 (d, $^3J_{P,C}$ = 4.5 Hz, H–$\underline{C}^2$), 155.5 (ddd, $^{1/2}J_{P,C}$ = 47.0 Hz, $\underline{C}^{4/5}$). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ = 20.12 (P–OMe), −67.34 (anion P). IR [cm^{-1}]: $\tilde{\nu}$ = 2984 (v), 2921.8 (m), 2894.0 (m), 1542.0 (w), 498.1 (w), 1423.5 (m), 1246.2 (m), 1206.3 (w), 1012.4 (m), 968.4 (s). Pos. ESI-MS: *m*/*z* (%) = 451.3 (100) $[M]^+$, 399.1 (97) $[Na(C_{18}N_2H_{36}O_6)]^{\bullet+}$. HRMS: $[C_{23}H_{41}N_4OP_2]^+$ theor./exp. 451.2750 (451.2754). UV/vis (CH_2Cl_2): λ [nm] (abs.): 346 (0.791). EA [%]: theor./exp. C 44.94/45.12, H 6.75/6.64; N 7.31/6.74, S 5.58/5.68.

4. A solution of potassium hexamethyldisilazide (KHMDS) (0.7 g, 3.5 mmol) in 5 mL of THF was added dropwise to a solution of **3** (2 g, 1.7 mmol) in 10 mL of THF at room temperature. After 1 h, all volatiles were removed *in vacuo* (6×10^{-3} mbar). The residue was washed (twice) with diethyl ether followed by extraction with mixture of THF and diethyl ether (1 : 1.5) to remove the potassium triflate. After concentrating the extracted solution, the product **4** was obtained as dark orange solid. Yield: 1.1 g (1.3 mmol) 76%; Dark orange. M. p. 207 °C. ^{1}H NMR (500.1 MHz, THF, 25 °C): δ = 0.9 (t, 12H, $^3J_{H,H}$ = 6.5 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.2–1.3 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.8–1.9 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 2.1 (d, 3H, $^4J_{P,H}$ = 6.3 Hz, *O*–$\underline{Me}$) 2.5 (t, 12H, cryptand), 3.5 (t, 12H, cryptand), 3.6 (s, 12H, cryptand), 3.8–4.5 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, 25 °C): δ = 13.5 (s, $NCH_2CH_2CH_2\underline{Me}$), 20.1 (s, $NCH_2CH_2\underline{CH_2}Me$), 32.3 (s, $NCH_2\underline{CH_2}CH_2Me$), 47.5 (s, $N\underline{CH_2}CH_2CH_2Me$), 67.6 (s, cryptand), 70.4 (s, cryptand), 120.2 (d, $^2J_{P,C}$ = 7.5 Hz, *O*–$\underline{CH_3}$), 154.2 (d, $^{1/2}J_{P,C}$ = 43.9 Hz, $\underline{C}^{4/5}$), 215.5 (d, $J_{P,C}$ = 2.7, $\underline{C}^2$). ^{31}P NMR (500.0 MHz, THF-d_8, 25 °C): δ = 25.15 (P–OMe), −74.78 (anion P). IR [cm^{-1}]: $\tilde{\nu}$ = 3191.2 (w), 3045.0 (m), 2975.7 (m), 1623.4 (m), 1436.3 (m), 1375.3 (m), 1245.7 (s), 1184.8 (s), 1016.5 (s), 968.5 (s). Neg. ESI-MS: *m*/*z* (%) = 449.261 (15) $[M]^+$, HRMS: $[C_{23}H_{39}N_4OP_2]^-$ theor./exp. 449.2605 (449.2608). UV/vis (THF): λ [nm] (abs.): 407 (0.517).

5$^{cis/trans}$. To a suspension of **3** (2.5 g, 2.1 mmol) in 50 mL of diethyl ether, methyl iodide (1.35 mL, 2.1 mmol) was added dropwise at −80 °C. The reaction mixture was stirred for 18 hours and warmed to room temperature. All volatiles were removed *in vacuo* (6×10^{-3} mbar). Residue was extracted with

dichloromethane followed by washing (twice) with diethyl ether. The solvent was removed under vacuum (6×10^{-3} mbar) which resulted in a pure colorless liquid. Yield: 1.2 g (1.6 mmol) 75%; colorless liquid. Ratio of two isomers 1 : 0.3. M.p. – (liquid at r.t.). ^{1}H NMR (300.1 MHz, CD_2Cl_2, 25 °C): δ = 1.04, 1.06 (t, 12H, $^3J_{H,H}$ = 7.4 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.41–1.54 (m, 8H, $PCH_2CH_2\underline{CH_2}Me$), 1.67 (d, $^2J_{P,H}$ = 5.2 Hz, *P–Me*), 1.87 (d, $^2J_{P,H}$ = 6.8 Hz, *O–Me*);1.92–2.11 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$, 4.28–4.57 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$), 9.47 (t, 2H, $^3J_{P,H}$ = 3.03 Hz, C^2–*H*), 9.56 (brs, C^2–*H*) 2nd isomer. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 25 °C): δ = 13.08, 13.10 (s, $NCH_2CH_2CH_2\underline{Me}$ of two isomers), 19.52 (br, *P–Me*), 19.68 (s, $NCH_2CH_2\underline{CH_2}Me$), 29.68 (br, $NCH_2\underline{CH_2}CH_2Me$), 31.78 (d, $^3J_{P,C}$ = 2.6 Hz, $NCH_2\underline{CH_2}CH_2Me$), 32.23 (d, $^3J_{P,C}$ = 2.4 Hz, $NCH_2\underline{CH_2}CH_2Me$) (2nd isomer), 49.13 (ddd, $^3J_{P,C}$ = 9.1 Hz, $N\underline{CH_2}CH_2CH_2Me$), 49.96 (ddd, $^3J_{P,C}$ = 8.2 Hz, $N\underline{CH_2}CH_2CH_2Me$) (2nd isomer), 122.84 (q, $^1J_{P,F}$ = 319.5 Hz, $\underline{C}F_3$), 131.54 (d, $^2J_{P,C}$ = 9.5 Hz, *O–CH*$_3$), 135.38 (ddd, $^{1/2}J_{P,C}$ = 3.7 Hz, *P–C* of the middle ring), 135.72 (t, $^{1/2}J_{P,C}$ = 3.0 Hz, *P–C* of the middle ring) (2nd isomer), 142.38 (br, H–C^2), 143.37 (br, H–C^2) 2nd isomer. ^{31}P NMR (500.0 MHz, CD_2Cl_2, 25 °C): δ = −71.58 (d, $^3J_{P,H}$ = 5.2 Hz, *P–Me*), −66.23 (d, $^3J_{P,H}$ = 4.9 Hz, *P–Me*); 39.57 (br, *P–OMe*) & 43.7 (br, *P–OMe*). IR [cm^{-1}]: $\tilde{\nu}$ = 3204.7 (m), 3145 (m), 2975.5 (w), 2768.8 (m), 1534.3 (w), 1445.3 (s), 1317.7 (m), 1206.8 (m), 1046.9 (m), 1009.5 (s), 921.5 (s). Pos. ESI-MS: *m*/*z* (%) = 615.251 (54) $[M - TfO]^+$; HRMS: $[C_{25}H_{44}F_3N_4O_4P_2S]^+$ theor./exp. 615.2505 (615.2511). EA [%]: theor./exp. C 40.84/40.53, H 5.80/5.93, N 7.33/7.36.

6$^{cis/trans}$. A solution of potassium hexamethyldisilazide (KHMDS) (1.04 g, 5.2 mmol) in 5 mL of THF was added dropwise to a solution of **5**$^{cis/trans}$ (2.0 g, 2.6 mmol) in 10 mL of THF at room temperature. After 1 h, all volatiles were removed *in vacuo* (6×10^{-3} mbar). Residue was extracted with diethyl ether to remove potassium triflate using filtering cannulation. After concentrating the extracted solution, the product **6**$^{cis/trans}$ was obtained as yellow liquid. Yield: 0.92 g (1.9 mmol) 76%; (ratio of two isomers 1 : 0.30). M.p. – (liquid at r.t.) ^{1}H NMR (500.1 MHz, THF-d8, 25 °C): δ = 0.8, 1.1 (t, 12H, $^3J_{H,H}$ = 7.1 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.2 (d, $^2J_{P,H}$ = 5.3 Hz, *P–Me*), 1.2–1.4 (m, 8H, $PCH_2CH_2\underline{CH_2}Me$), 1.9–2.1 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 2.7 (d, $^2J_{P,H}$ = 7.2 Hz, *O–Me*), 3.9–4.2 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$), 4.3–4.5 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$; 2nd isomer). $^{13}C\{^1H\}$ NMR (125.75 MHz, THF-d8, 25 °C): δ = 12.9, 12.8 (s, $NCH_2CH_2CH_2\underline{Me}$ of two isomers), 19.9 (s, *P–Me*), 23.7 (s, $NCH_2CH_2\underline{CH_2}Me$), 25.7 (s, $NCH_2\underline{CH_2}CH_2Me$), 32.8 (d, $^3J_{P,C}$ = 2.1 Hz, $NCH_2\underline{CH_2}CH_2Me$), 32.9 (d, $^3J_{P,C}$ = 2.2 Hz, $NCH_2\underline{CH_2}CH_2Me$; 2nd isomer), 48.5 (ddd, $^3J_{P,C}$ = 9.6 Hz, $N\underline{CH_2}CH_2CH_2Me$), 49.6 (ddd, $^3J_{P,C}$ = 8.3 Hz, $N\underline{CH_2}CH_2CH_2Me$; 2nd isomer), 118.5 (d, $^2J_{P,C}$ = 9.2 Hz, *O–CH*$_3$), 131.4 (br, *P–C* of the middle ring), 132.2 (d, $^{1/2}J_{P,C}$ = 2.5 Hz, *P–C* of the middle ring; 2nd isomer), 223.4 ((t, $^3J_{P,C}$ = 2.7 Hz, $\underline{C}^2$), 224.2 (t, $^3J_{P,C}$ = 2.7 Hz, $\underline{C}^2$; 2nd isomer). ^{31}P NMR (500 MHz, THF-d8, 25 °C): δ = −74.0 (d, $^3J_{P,H}$ = 4.8 Hz, *P–Me*), −68.6 (d, $^3J_{P,H}$ = 3.7 Hz, *P–Me*); 41.3 (d, $^3J_{P,H}$ = 3.8 Hz) & 37.2 (d, $^3J_{P,H}$ = 4.6 Hz). IR [cm^{-1}]: $\tilde{\nu}$ = 2992.2 (m), 2962.5 (m), 2842.2 (w), 1501.2 (w), 1472.4 (m), 1415.8 (s), 1367.3 (s), 1146.0 (s), 1052.1 (m), 986.5 (m). Pos. ESI-MS: *m*/*z* (%) = 465.290 (31) $[M + H]^{\bullet+}$ $[C_{24}H_{43}ON_4P_2]^{1+}$ theor./exp. 465.2907 (465.2909). UV/vis (CH_2Cl_2): λ [nm] (abs.): 347 (0.124).

7. To a solution of **3** (2.0 g, 1.7 mmol) in dichloromethane, $[Rh(cod)Cl]_2$ (0.43 g, 0.87 mmol) was added as solid at ambient temperature. Reaction mixture was stirred for 6 hours, at which point volatiles were removed *in vacuo* (6×10^{-3} mbar). Residue was washed (twice) with diethyl ether and subsequent drying *in vacuo* (6×10^{-3} mbar) resulted in an orange solid. Yield: 2.1 g (1.5 mmol) 88%; Orange solid; M. p. 82 °C. ^{1}H NMR (300.1 MHz, CD_2Cl_2, 25 °C): δ = 0.99 (t, 12H, $^3J_{H,H}$ = 7.2 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.26–1.57 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 1.92 (m, 4H, cod), 1.99–2.21 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 2.36 (m, 4H, cod), 2.56 (d, 8H, $^3J_{P,H}$ = 10.2 Hz, *O–CH*$_3$), 3.68 (m, 2H, cod), 4.06–4.21 (m, 8H, $N\underline{CH_2}CH_2CH_2Me$), 5.37 (m, 2H, cod), 8.99 (brs, C^2–*H*). $^{13}C\{^1H\}$ NMR (125.75 MHz, CD_2Cl_2, 25 °C): δ = 13.46 (s, $NCH_2CH_2CH_2\underline{Me}$), 19.95 (s, $NCH_2CH_2\underline{CH_2}Me$), 28.52 (s, cod), 30.14 (br, $NCH_2\underline{CH_2}CH_2Me$), 33.27 (s, cod), 49.48 ((d, $^3J_{P,C}$ = 7.2 Hz, $N\underline{CH_2}CH_2CH_2Me$), 69.6 (br, cod), 73.21 (d, $^1J_{Rh,C}$ = 11.2 Hz, cod), 122.13 (q, $^1J_{P,F}$ = 322.8 Hz, $\underline{C}F_3$), 108.68 (d, $^2J_{P,C}$ = 11.1 Hz, *O–CH*$_3$), 155.96 (br, *P–C* of the middle ring), 156.35 (d, $^{1/2}J_{P,C}$ = 44.2 Hz, *P–C* of the middle ring), 137.96 (br, H–$\underline{C}^2$). ^{31}P NMR (500.0 MHz, CD_2Cl_2, 25 °C): δ = −70.56 (s), 47.45 (d, $^1J_{Rh,P}$ = 188.2 Hz). IR [cm^{-1}]: $\tilde{\nu}$ = 2975.2 (m), 2931.4 (m), 2840.1 (w), 1511.4 (s), 1480.4 (m), 1398.1 (m), 1247.8 (s), 1175.5 (m), 1129.8 (m), 1007.1 (s), 910.2 (s). Neg. ESI-MS: *m*/*z* (%) = 995.151 (29) $[M]^{\bullet+}$. HRMS: $[C_{33}H_{53}ClF_3N_4O_7P_2RhS_2F_6]^+$ theor./exp. 995.1473 (995.1494). UV/vis (CH_2Cl_2): λ [nm] (abs.): 299 (0.924). EA [%]: theor./exp. C 43.89/43.89, H 6.43/6.73, N 6.02/76.03, S 4.59/4.34.

8$^{cis/trans}$. To a solution of **3** (1.5 g, 1.3 mmol) in dichloromethane, 1.5 equivalent of $[Rh(cod)Cl]_2$ (0.97 g, 1.9 mmol) was added as solid at ambient temperature. Reaction mixture was stirred at ambient temperature for 12 hours. Solvent was then removed *in vacuo* (6×10^{-3} mbar) and the residue washed (twice) with diethyl ether. Subsequent drying *in vacuo* (6×10^{-3} mbar) resulted in a dark orange solid. Yield: 1.7 g (0.9 mmol) 69%; dark orange solid; (ratio of two isomers 1 : 0.7). M. p. 102 °C. ^{1}H NMR (500.1 MHz, CD_2Cl_2, 25 °C): δ = 1.1–1.2 (t, 12H, $^3J_{H,H}$ = 7.0 Hz, $NCH_2CH_2CH_2\underline{Me}$), 1.5–1.7 (m, 8H, $NCH_2CH_2\underline{CH_2}Me$), 2.2–2.4 (m, 24H, cod), 2.5–2.6 (m, 8H, $NCH_2\underline{CH_2}CH_2Me$), 2.9, 3.0 (d, 3H, $^3J_{P,H}$ = 12.4 Hz, *O–CH*$_3$), 3.9 (m, 6H, cod), 4.2 (br, 8H, $N\underline{CH_2}CH_2CH_2Me$), 5.2 (m, 6H, cod), 9.5 (brs, C^2–*H*), 9.7 (brs, C^2–*H*). $^{13}C\{^1H\}$ NMR (125.75 MHz, CD_2Cl_2, 25 °C): δ = 13.5, 13.8 (s, $NCH_2CH_2CH_2\underline{Me}$) two isomers, 19.9, 20.1 (s, $NCH_2CH_2\underline{CH_2}Me$) two isomers, 28.4 (s, cod), 31.3 (br, $NCH_2\underline{CH_2}CH_2Me$), 32.7 (s, cod), 49.9 (d, $^3J_{P,C}$ = 6.3 Hz, $N\underline{CH_2}CH_2CH_2Me$), 49.9 (br, $N\underline{CH_2}CH_2CH_2Me$), 72.0 (d, $^1J_{Rh,C}$ = 13.0 Hz, cod), 72.6 (d, $^1J_{Rh,C}$ = 13.0 Hz, cod), 73.21 (d, $^1J_{Rh,C}$ = 13.1 Hz, cod), 74.2 (d, $^1J_{Rh,C}$ = 13.2 Hz, cod), 74.6 (d, $^1J_{Rh,C}$ = 13.0 Hz, cod), 75.4 (d, $^1J_{Rh,C}$ = 13.1 Hz, cod), 113.4 (d, $^2J_{P,C}$ = 9.5 Hz, *O–CH*$_3$), 121.1 (q, $^1J_{P,F}$ = 332.7 Hz, $\underline{C}F_3$), 131.9 (br, *P–C* of the middle ring), 133.3 (d, $^{1/2}J_{P,C}$ = 45.2 Hz, *P–C* of the middle ring), 141.9 (br, H–$\underline{C}^2$), 142.4 (br, H–$\underline{C}^2$) 2nd isomer. ^{31}P NMR (500.0 MHz, CD_2Cl_2, 25 °C): δ = 65.0 (d, $^1J_{Rh,P}$ = 195.6

Hz) (minor)/64.1 (dd, $^{1}J_{Rh,P}$ = 200.1 Hz, $^{3}J_{P,P}$ = 5.3 Hz) (major) and −120.3 (t br, $^{1}J_{Rh,P}$ = 126.9 Hz) (major)/−123.4 (t, $^{1}J_{Rh,P}$ = 126.9 Hz) (minor). IR [cm^{-1}]: $\tilde{\nu}$ = 2984.1 (m), 2971.0 (m), 2861.8 (w), 1545.0 (s), 1491.7 (m), 1421.1 (m), 1327.8 (s), 1265.6 (m), 1129.8 (w), 1069.1 (s), 978.0 (s). Pos. ESI-MS: *m*/*z* (%) = 1153.205 (36) [M − Cl − 2TfO]$^{\bullet+}$. HRMS: $[C_{47}H_{76}Cl_2N_4OP_2Rh_3]^{\bullet+}$ theor./exp. 1153.2031 (1153.2043). UV/vis (CH_2Cl_2): λ [nm] (abs.): 386 (0.216). EA [%]: theor./exp. C 42.61/41.38, H 6.03/6.04, N 4.45/4.22, S 3.40/3.62.

Conclusion

The first example of an anionic P-bridged tricyclic bis(NHC) was obtained *via* an unexpected reductive deselenization combined with a subsequent deprotonation of the bis(imidazolium) salt. Reaction of the latter with MeI as electrophile resulted finally in the first example of a neutral P-functional bis(NHCs) with a mixed substitution pattern. Initial studies of the coordination properties of the tricyclic bis(imidazolium) salt revealed a pre-ference of the neutral P-ligands site over the anionic phosphorus centre. Detailed electrochemical studies of the anionic bis(NHC) showed multiple, closely spaced oxidation processes owing, most probably, to the formation of a short lived P-centred radical that yields a new intermediate, a tetrakis(NHC), having a P–P bond linkage.

Conflicts of interest

There are no conflicts of interest to declare.

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