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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-diphosphinane 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 amido⁷ and phosphanido,⁸ have been re-reported (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.

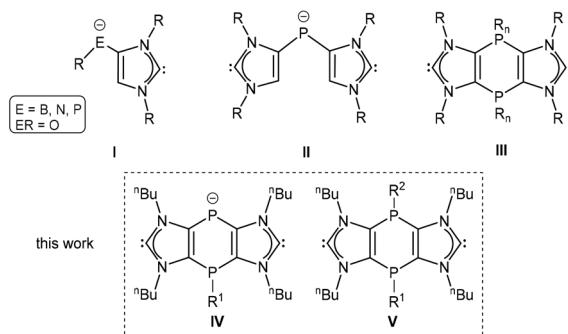


Fig. 1 Anionic mono and bis(NHCs) I, II and rigid Janus bis(NHCs) III–V ($R, R^1, R^2 = \text{organic substituents}$).

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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-diphosphine-nine¹² 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 NaBH₄ 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 ³¹P NMR spectrum at 20.1 ppm (POMe) and –67.3 ppm (anionic P), but no ³J_{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 aromatic 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).

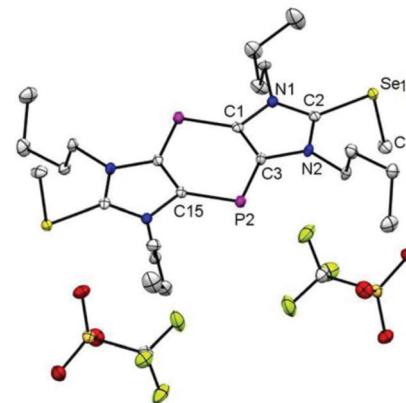


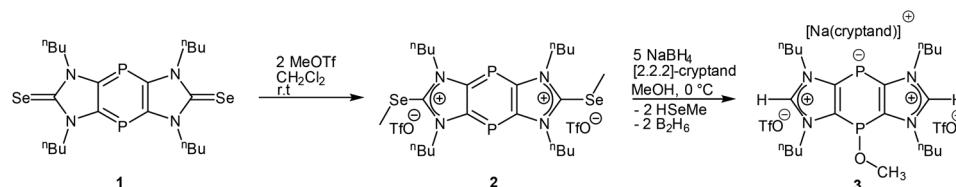
Fig. 2 Molecular structure of compound **2** (ellipsoids at the 50% probability-substituted level); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C2–Se1 1.896(4), Se1–C8 1.952 (4), C2–N2 1.339(5), N2–C3 1.397(5), C3–P2 1.736(4), C1–C3 1.412(6); N1–C2–N2 108.8(3), C3–P2–C15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

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

	$\delta(^{31}\text{P})/\text{ppm} (\text{CD}_2\text{Cl}_2)$	$\delta(^{13}\text{C})/\text{ppm} (\text{CD}_2\text{Cl}_2)^b$
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}	$\delta = -71.58$ (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}	$\delta = -74.0$ (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)

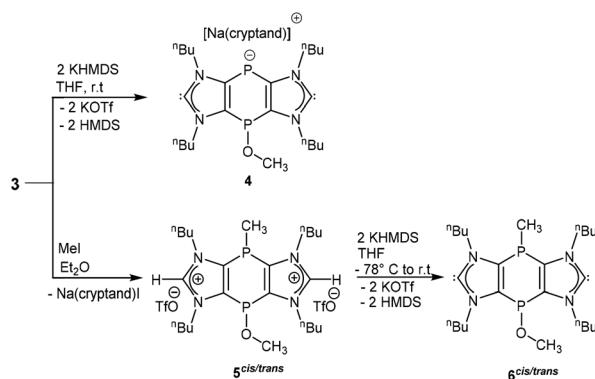
^a In case of **4** and **6**^{cis/trans} (1 : 0.4) THF-d8. ^b C² carbon.

After extraction with THF/diethyl ether (1 : 1.5), compound **4** was isolated as a dark orange solid which has two resonances in its ³¹P NMR spectrum at 25.2 ppm (P-OMe) and –74.8 ppm (anionic P). The ¹H-NMR spectrum confirms the absence of the C²-H proton and the ¹³C{¹H} NMR spectrum a broad resonance at 208.8 ppm assigned to the C² 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} value¹² for **III** (R : Me, R' : *cis*-NET₂), 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/IV} bis(imidazolium) salts **5**^{cis/trans} (1 : 0.3) and mixed substituted bis(NHCs) **6**^{cis/trans} (1 : 0.3).

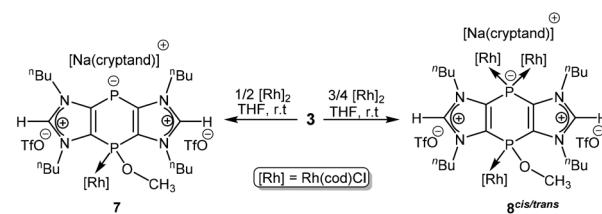
in the anionic tri-cycle is virtually unchanged. Compared to 3', the aromaticity of the middle ring is slightly higher (NICS(0) = -5.5), while that of the outer rings is lower (NICS(0) = -9.0), as is usual for NHCs if compared to imidazolium salts.¹⁵

Formation of mixed substituted P^{III/IV} 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 **5**^{cis/trans} with an isomeric ratio of 1 : 0.3 (signals not assigned) (Scheme 2). The ³¹P{¹H} NMR spectrum of the reaction mixture showed two sets of signals for two isomers at $\delta(\text{P}-\text{CH}_3) = -71.6$ (d, $^3J_{\text{P},\text{H}} = 5.0$ Hz), -66.2 (d, $^3J_{\text{P},\text{H}} = 5.0$ Hz) and $\delta(\text{P}-\text{OCH}_3) = 39.6$ (br), 43.7 (br) (ratio 1 : 0.4). The isolated mixture of **5**^{cis/trans} (1 : 0.3) was subsequently deprotonated using two equiv. of KHMDS in THF to afford the mixed-substituted bis(NHCs) **6**^{cis/trans} (ratio 1 : 0.3).

Clear evidence for the latter came from the ¹H NMR spectrum of this mixture, since the former C^2 -H signal ($\delta = 9.47$ (t, $^3J_{\text{P},\text{H}} = 3.03$ Hz), 9.56 (br)) of **5**^{cis/trans} were absent. This was further supported by the ¹³C{¹H} NMR spectrum as the characteristic downfield signals for the C^2 -nuclei were found (Table 1), revealing the formation of the bis(NHCs) **6**^{cis/trans} (ratio 1 : 0.3). **6**^{trans} and **6**^{cis} are computed to have high stability (the isodesmic reaction energies are 108.8 for **6**^{trans}¹⁴ and 108.6 kcal mol⁻¹ for **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 ³¹P 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 $^1J_{\text{Rh},\text{P}} = 192.4$ Hz, assigned



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

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 **8**^{cis/trans} (ratio 0.9 : 1) (Scheme 3). Upon coordination, two sets of signals are present in the ³¹P NMR spectrum at 65.0 (d, $^1J_{\text{Rh},\text{P}} = 195.6$ Hz) (minor)/64.1 (dd, $^1J_{\text{Rh},\text{P}} = 200.1$ Hz, $^3J_{\text{P},\text{P}} = 5.3$ Hz) (major) and -120.3 (t br, $^1J_{\text{Rh},\text{P}} = 126.9$ Hz) (major)/-123.4 (t, $^1J_{\text{Rh},\text{P}} = 126.9$ Hz) (minor).

Cyclic voltammetric studies supported by DFT calculations

The electrochemical properties of bis(NHCs) **4** and **6**^{cis/trans} (1 : 0.3) were investigated by cyclic voltammetry (CV) in THF (0.2 M [nBu₄N][PF₆]) 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 **6**^{cis/trans} (Fig. 3b) is reminiscent of dicarbenes **III** ($R_n = \text{P}^{\text{III}}\text{NEt}_2$)¹² and we therefore start the analysis here.

There are a series of facile, chemically irreversible oxidations with anodic peak potentials $E_p^{\text{a}1} = -0.29$ V, $E_p^{\text{a}2} = -0.07$ V and $E_p^{\text{a}3} = +0.65$. 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 $\sigma(\text{p})$ -centred HOMO and HOMO-1 as determined from B3LYP/6-31+G*/M06-2X/6-31+G* computations undertaken on the model structures **6**^{cis/trans}¹⁵ (Fig. 4). The more positive first oxidations $E_p^{\text{a}1} = -0.29$ V for **6**^{cis/trans} compared to **III** ($R_n = \text{P}^{\text{III}}\text{NEt}_2$), for which $E_p^{\text{a}1} = -0.61$ 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

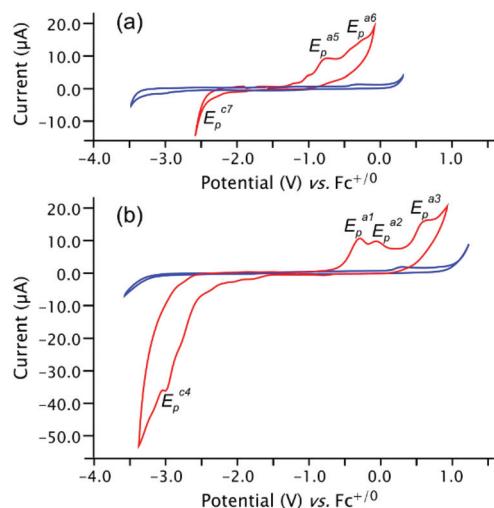
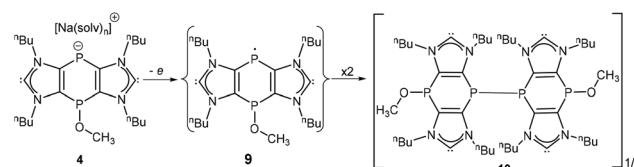


Fig. 3 CV diagrams (a) of **4**, and (b) of **6**^{cis/trans} (scan rate: 200 mV s⁻¹). In each case, the blue trace indicates the solvent/electrolyte background (0.2 M) [nBu₄N][PF₆] in (THF), and the red that from a 1.0 mM solution of analyte.



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

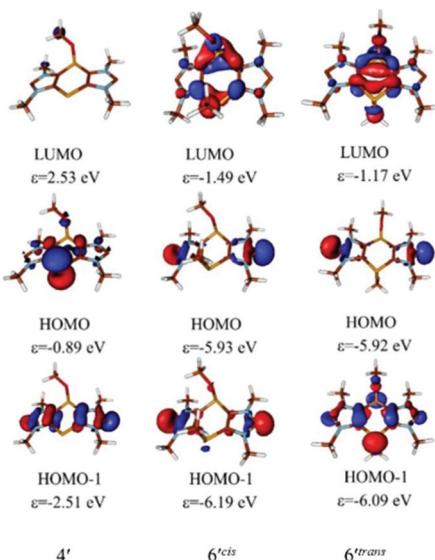


Fig. 4 FMO topologies and energies for the model ($R = \text{CH}_3$) calculated structures of **4'**, **6'**^{cis} and **6'**^{trans} at the B3LYP/6-31+G*//M06-2X/6-31+G* level of theory (PCM solvent model).

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 $1e$ oxidation of such a localized MO, followed by further processes after a considerable gap.

A plausible explanation for the observed behaviour is that $1e$ 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 understood 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 ¹H, 75.5 MHz for ¹³C, and 121.5 MHz for ³¹P) and pollux-500 (500.1 MHz for ¹H, 125.75 MHz for ¹³C, and 500.0 MHz for ³¹P) spectrometer. The ¹H and ¹³C NMR spectra were referenced to the residual proton resonances and the ¹³C NMR signals of the deuterated solvents and ³¹P to 85% H₃PO₄ 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 SHELXL97¹⁷ 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-diphosphinine¹² (2.5 g, 3.5 mmol) in dichloromethane, PCl₃ (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 Et₂NPCl₂. Finally, the solution was concentrated *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. ¹H NMR (300.1 MHz, C₆D₆, 25 °C): δ = 0.8 (t, 12H, ³J_{H,H} = 7.3 Hz, NCH₂CH₂CH₂Me), 1.2–1.4 (m, 8H, NCH₂CH₂CH₂Me), 1.8–1.9 (m, 8H, NCH₂CH₂CH₂Me), 4.4–4.4 (m, 8H, NCH₂CH₂CH₂Me). ¹³C{¹H} NMR (75.5 MHz, C₆D₆, 25 °C): δ = 13.55 (s, NCH₂CH₂CH₂Me), 19.9 (s, NCH₂CH₂CH₂Me), 28.9 (t, ³J_{P,C} = 1.6 Hz, NCH₂CH₂CH₂Me), 48.1 (t, ³J_{P,C} = 4.6 Hz, NCH₂CH₂CH₂Me), 152.2 (t, ¹J_{P,C} = 23.1 Hz, P-C of the middle ring), 168.32 (br, C²). ³¹P{¹H} NMR (121.5 MHz, C₆D₆, 25 °C): δ = 78.2 (s). ⁷⁷Se NMR (57.28 MHz, CDCl₃): 179.4 (s). IR [cm⁻¹]: ν = 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]⁺, 498.1 (20) [M - Se]⁺. UV-vis (CH₂Cl₂): 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. Two 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. ¹H NMR (300.1 MHz, CDCl₃, 25 °C): 1.04 (t, 12H, ³J_{H,H} = 7.4 Hz, NCH₂CH₂CH₂Me), 1.52–1.62 (m, 8H, NCH₂CH₂CH₂Me), 2.05–2.15 (m, 8H, NCH₂CH₂CH₂Me), 2.8 (s, 6H, SeMe) 4.89–4.94 (m, 8H, NCH₂CH₂CH₂Me). ¹³C{¹H} NMR (75.5 MHz, CDCl₃, 25 °C): δ = 11.72 (s, SeMe), 13.44 (s, NCH₂CH₂CH₂Me), 20.16 (s, NCH₂CH₂CH₂Me), 30.73 (s, NCH₂CH₂CH₂Me), 52.18 (s, NCH₂CH₂CH₂Me), 148.84 (t, ³J_{P,C} = 4.6 Hz, Se-C²), 154.94 (t, ¹J_{P,C} = 26.1 Hz, P-C of the middle ring). ³¹P NMR (121.5 MHz, CDCl₃, 25 °C): δ = 119.95 (s). ⁷⁷Se NMR (57.28 MHz, CDCl₃): 138.89 (s). IR [cm⁻¹]: ν = 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: [C₂₅H₄₂F₃N₄O₃P₂SSe₂]⁺ 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 ¹H NMR (300.1 MHz, CD₂Cl₂, 25 °C): δ = 1.0 (t, 12H, ³J_{H,H} = 7.3 Hz, NCH₂CH₂CH₂Me), 1.3–1.5 (m, 8H, NCH₂CH₂CH₂Me), 1.9–2.1 (m, 8H, NCH₂CH₂CH₂Me), 2.4 (d, 3H, ³J_{P,H} = 7.3 Hz, O-Me) 2.6 (t, 12H, cryptand), 3.6 (t, 12H, cryptand), 3.7 (s, 12H, cryptand), 4.1–4.6 (m, 8H, NCH₂CH₂CH₂Me), 8.9 (t, 2H, ⁴J_{P,H} = 1.7 Hz, C²-H). ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂, 25 °C): δ = 13.2 (s, NCH₂CH₂CH₂Me), 19.6 (s, NCH₂CH₂CH₂Me), 30.2 (s, NCH₂CH₂CH₂Me), 47.8 (s, NCH₂CH₂CH₂Me), 67.5 (s, cryptand), 68.5 (s, cryptand), 120.9 (d, ²J_{P,C} = 7.3 Hz, O-CH₃), 121.7 (q, ¹J_{P,F} = 321.0 Hz, CF₃), 137.2 (d, ³J_{P,C} = 4.5 Hz, H-C²), 155.5 (ddd, ^{1/2}J_{P,C} = 47.0 Hz, C^{4/5}). ³¹P NMR (121.5 MHz, CD₂Cl₂, 25 °C): δ = 20.12 (P-OMe), -67.34 (anion P). IR [cm⁻¹]: ν = 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(C₁₈N₂H₃₆O)₆]⁺. HRMS: [C₂₃H₄₁N₄OP₂]⁺ theor./exp. 451.2750 (451.2754). UV-vis (CH₂Cl₂): 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. ¹H NMR (500.1 MHz, THF, 25 °C): δ = 0.9 (t, 12H, ³J_{H,H} = 6.5 Hz, NCH₂CH₂CH₂Me), 1.2–1.3 (m, 8H, NCH₂CH₂CH₂Me), 1.8–1.9 (m, 8H, NCH₂CH₂CH₂Me), 2.1 (d, 3H, ⁴J_{P,H} = 6.3 Hz, O-Me) 2.5 (t, 12H, cryptand), 3.5 (t, 12H, cryptand), 3.6 (s, 12H, cryptand), 3.8–4.5 (m, 8H, NCH₂CH₂CH₂Me). ¹³C{¹H} NMR (75.5 MHz, THF-d₈, 25 °C): δ = 13.5 (s, NCH₂CH₂CH₂Me), 20.1 (s, NCH₂CH₂CH₂Me), 32.3 (s, NCH₂CH₂CH₂Me), 47.5 (s, NCH₂CH₂CH₂Me), 67.6 (s, cryptand), 70.4 (s, cryptand), 120.2 (d, ²J_{P,C} = 7.5 Hz, O-CH₃), 154.2 (d, ^{1/2}J_{P,C} = 43.9 Hz, C^{4/5}), 215.5 (d, ¹J_{P,C} = 2.7, C²). ³¹P NMR (500.0 MHz, THF-d₈, 25 °C): δ = 25.15 (P-OMe), -74.78 (anion P). IR [cm⁻¹]: ν = 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: [C₂₃H₃₉N₄OP₂]⁻ theor./exp. 449.2605 (449.2608). UV-vis (THF): λ [nm] (abs.): 407 (0.517).

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.). ^1H NMR (300.1 MHz, CD_2Cl_2 , 25 °C): δ = 1.04, 1.06 (t, 12H, ${}^3J_{\text{H,H}} = 7.4$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 1.41–1.54 (m, 8H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 1.67 (d, ${}^2J_{\text{P,H}} = 5.2$ Hz, $\underline{\text{P-Me}}$), 1.87 (d, ${}^2J_{\text{P,H}} = 6.8$ Hz, $\underline{\text{O-Me}}$); 1.92–2.11 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$, 4.28–4.57 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 9.47 (t, 2H, ${}^3J_{\text{P,H}} = 3.0$ Hz, $\text{C}^2\text{-H}$), 9.56 (brs, $\text{C}^2\text{-H}$) 2nd isomer. $^{13}\text{C}\{{}^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2 , 25 °C): δ = 13.08, 13.10 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$ of two isomers), 19.52 (br, $\underline{\text{P-Me}}$), 19.68 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 29.68 (br, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 31.78 (d, ${}^3J_{\text{P,C}} = 2.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 32.23 (d, ${}^3J_{\text{P,C}} = 2.4$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$) (2nd isomer), 49.13 (ddd, ${}^3J_{\text{P,C}} = 9.1$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 49.96 (ddd, ${}^3J_{\text{P,C}} = 8.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$) (2nd isomer), 122.84 (q, ${}^1J_{\text{P,F}} = 319.5$ Hz, $\underline{\text{CF}_3}$), 131.54 (d, ${}^2J_{\text{P,C}} = 9.5$ Hz, $\underline{\text{O-CH}_3}$), 135.38 (ddd, ${}^1/{}^2J_{\text{P,C}} = 3.7$ Hz, $\underline{\text{P-C}}$ of the middle ring), 135.72 (t, ${}^1/{}^2J_{\text{P,C}} = 3.0$ Hz, $\underline{\text{P-C}}$ 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, ${}^3J_{\text{P,H}} = 5.2$ Hz, $\underline{\text{P-Me}}$), -66.23 (d, ${}^3J_{\text{P,H}} = 4.9$ Hz, $\underline{\text{P-Me}}$); 39.57 (br, $\underline{\text{P-OMe}}$) & 43.7 (br, $\underline{\text{P-OMe}}$). 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) [$\text{M} - \text{TfO}^+$; HRMS: $[\text{C}_{25}\text{H}_{44}\text{F}_3\text{N}_4\text{O}_4\text{P}_2\text{S}]^+$ 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.) ^1H NMR (500.1 MHz, THF-d8, 25 °C): δ = 0.8, 1.1 (t, 12H, ${}^3J_{\text{H,H}} = 7.1$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 1.2 (d, ${}^2J_{\text{P,H}} = 5.3$ Hz, $\underline{\text{P-Me}}$), 1.2–1.4 (m, 8H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 1.9–2.1 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 2.7 (d, ${}^2J_{\text{P,H}} = 7.2$ Hz, $\underline{\text{O-Me}}$), 3.9–4.2 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 4.3–4.5 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$; 2nd isomer). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (125.75 MHz, THF-d8, 25 °C): δ = 12.9, 12.8 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$ of two isomers), 19.9 (s, $\underline{\text{P-Me}}$), 23.7 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 25.7 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 32.8 (d, ${}^3J_{\text{P,C}} = 2.1$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 32.9 (d, ${}^3J_{\text{P,C}} = 2.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$; 2nd isomer), 48.5 (ddd, ${}^3J_{\text{P,C}} = 9.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 49.6 (ddd, ${}^3J_{\text{P,C}} = 8.3$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$; 2nd isomer), 118.5 (d, ${}^2J_{\text{P,C}} = 9.2$ Hz, $\underline{\text{O-CH}_3}$), 131.4 (br, $\underline{\text{P-C}}$ of the middle ring), 132.2 (d, ${}^1/{}^2J_{\text{P,C}} = 2.5$ Hz, $\underline{\text{P-C}}$ of the middle ring; 2nd isomer), 223.4 (t, ${}^3J_{\text{P,C}} = 2.7$ Hz, $\underline{\text{C}^2}$), 224.2 (t, ${}^3J_{\text{P,C}} = 2.7$ Hz, $\underline{\text{C}^2}$; 2nd isomer). ^{31}P NMR (500 MHz, THF-d8, 25 °C): δ = -74.0 (d, ${}^3J_{\text{P,H}} = 4.8$ Hz, $\underline{\text{P-Me}}$), -68.6 (d, ${}^3J_{\text{P,H}} = 3.7$ Hz, $\underline{\text{P-Me}}$); 41.3 (d, ${}^3J_{\text{P,H}} = 3.8$ Hz) & 37.2 (d, ${}^3J_{\text{P,H}} = 4.6$ 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) [$\text{M} + \text{H}]^+$ $[\text{C}_{24}\text{H}_{43}\text{ON}_4\text{P}_2]^+$ 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, $[\text{Rh}(\text{cod})\text{Cl}]_2$ (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. ^1H NMR (300.1 MHz, CD_2Cl_2 , 25 °C): δ = 0.99 (t, 12H, ${}^3J_{\text{H,H}} = 7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 1.26–1.57 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 1.92 (m, 4H, cod), 1.99–2.21 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 2.36 (m, 4H, cod), 2.56 (d, 8H, ${}^3J_{\text{P,H}} = 10.2$ Hz, $\underline{\text{O-CH}_3}$), 3.68 (m, 2H, cod), 4.06–4.21 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 5.37 (m, 2H, cod), 8.99 (brs, $\text{C}^2\text{-H}$). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (125.75 MHz, CD_2Cl_2 , 25 °C): δ = 13.46 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 19.95 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 28.52 (s, cod), 30.14 (br, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 33.27 (s, cod), 49.48 ((d, ${}^3J_{\text{P,C}} = 7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 69.6 (br, cod), 73.21 (d, ${}^1J_{\text{Rh,C}} = 11.2$ Hz, cod), 122.13 (q, ${}^1J_{\text{P,F}} = 322.8$ Hz, $\underline{\text{CF}_3}$), 108.68 (d, ${}^2J_{\text{P,C}} = 11.1$ Hz, $\underline{\text{O-CH}_3}$), 155.96 (br, $\underline{\text{P-C}}$ of the middle ring), 156.35 (d, ${}^1/{}^2J_{\text{P,C}} = 44.2$ Hz, $\underline{\text{P-C}}$ of the middle ring), 137.96 (br, H-C^2). ^{31}P NMR (500.0 MHz, CD_2Cl_2 , 25 °C): δ = -70.56 (s), 47.45 (d, ${}^1J_{\text{Rh,P}} = 188.2$ 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) [$\text{M}]^+$. HRMS: $[\text{C}_{33}\text{H}_{53}\text{ClF}_3\text{N}_4\text{O}_7\text{P}_2\text{RhS}_2\text{F}_6]^+$ 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 $[\text{Rh}(\text{cod})\text{Cl}]_2$ (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. ^1H NMR (500.1 MHz, CD_2Cl_2 , 25 °C): δ = 1.1–1.2 (t, 12H, ${}^3J_{\text{H,H}} = 7.0$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 1.5–1.7 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 2.2–2.4 (m, 24H, cod), 2.5–2.6 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 2.9, 3.0 (d, 3H, ${}^3J_{\text{P,H}} = 12.4$ Hz, $\underline{\text{O-CH}_3}$), 3.9 (m, 6H, cod), 4.2 (br, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Me}$), 5.2 (m, 6H, cod), 9.5 (brs, $\text{C}^2\text{-H}$), 9.7 (brs, $\text{C}^2\text{-H}$). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (125.75 MHz, CD_2Cl_2 , 25 °C): δ = 13.5, 13.8 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$) two isomers, 19.9, 20.1 (s, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$) two isomers, 28.4 (s, cod), 31.3 (br, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 32.7 (s, cod), 49.9 (d, ${}^3J_{\text{P,C}} = 6.3$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 49.9 (br, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Me}$), 72.0 (d, ${}^1J_{\text{Rh,C}} = 13.0$ Hz, cod), 72.6 (d, ${}^1J_{\text{Rh,C}} = 13.0$ Hz, cod), 73.21 (d, ${}^1J_{\text{Rh,C}} = 13.1$ Hz, cod), 74.2 (d, ${}^1J_{\text{Rh,C}} = 13.2$ Hz, cod), 74.6 (d, ${}^1J_{\text{Rh,C}} = 13.0$ Hz, cod), 75.4 (d, ${}^1J_{\text{Rh,C}} = 13.1$ Hz, cod), 113.4 (d, ${}^2J_{\text{P,C}} = 9.5$ Hz, $\underline{\text{O-CH}_3}$), 121.1 (q, ${}^1J_{\text{P,F}} = 332.7$ Hz, $\underline{\text{CF}_3}$), 131.9 (br, $\underline{\text{P-C}}$ of the middle ring), 133.3 (d, ${}^1/{}^2J_{\text{P,C}} = 45.2$ Hz, $\underline{\text{P-C}}$ of the middle ring), 141.9 (br, H-C^2), 142.4 (br, H-C^2) 2nd isomer. ^{31}P NMR (500.0 MHz, CD_2Cl_2 , 25 °C): δ = 65.0 (d, ${}^1J_{\text{Rh,P}} = 195.6$

Hz) (minor)/64.1 (dd, $^1J_{\text{Rh},\text{P}} = 200.1$ Hz, $^3J_{\text{P},\text{P}} = 5.3$ Hz) (major) and -120.3 (t br, $^1J_{\text{Rh},\text{P}} = 126.9$ Hz) (major)/ -123.4 (t, $^1J_{\text{Rh},\text{P}} = 126.9$ 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] $^{+}$. HRMS: [C₄₇H₇₆Cl₂N₄OP₂Rh₃] $^{+}$ theor./exp. 1153.2031 (1153.2043). UV/vis (CH₂Cl₂): 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 preference 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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