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A novel, rigid diphosphine with an active NHC spacer; di- and trinuclear complexes of d^{10} coinage metals

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1. Synthesis and characterisation

1.1 General methods

All manipulations involving organometallics were performed under nitrogen or argon in a Braun glove-box or using standard Schlenk techniques. Solvents were dried using standard methods and distilled under nitrogen prior use or passed through columns of activated alumina and subsequently purged with nitrogen or argon. The starting materials 1-(di-phenylphosphino)imidazole,\(^1\) (\(t\)-Bu)\(_2\)PBr,\(^2\) [Au(tht)]OTf, [CuN(SiMe\(_3\))]\(_4\)\(^3\) and [AgN(SiMe\(_3\))]\(_2\)\(^5\) were prepared according to the literature.

1.2 1-(di-tert-butylphosphino)imidazole

To a solution of imidazole (1.43 g, 21.04 mmol) and triethylamine (2.21 g, 21.80 mmol) in Et\(_2\)O (15 ml) was added a solution of di-tert-butylchlorophosphine (3.62 g, 20.04 mmol) in Et\(_2\)O (10 ml). After stirring overnight at room temperature, the precipitate was filtered off and washed twice with Et\(_2\)O. The combined solutions were evaporated to dryness under reduced pressure. The residue was extracted twice with pentane and the filtrate was evaporated to dryness giving \(1\) as a colourless powder (4.03 g, 95%). The characterization data agree with those reported by Hofmann for the same compound.\(^6\)

1.3 1,3-bis(di-tert-butylphosphino)-imidazolium triflate (1a)

To a solution of 1-(di-tert-butylphosphino)imidazole (2.13 g, 10.03 mmol) and sodium triflate (2.01 g, 11.68 mmol) in THF (30 ml) was added dropwise at 0 °C pure di-tert-butylbromophosphine (2.59 g, 11.51 mmol). The reaction mixture was allowed to warm slowly to room temperature and was stirred for 24 h. The solvent was removed in vacuo, and the residue was extracted with CH\(_2\)Cl\(_2\) (3×30 ml). The extracts were evaporated to dryness under reduced pressure, and the residue was washed with pentane (2×40 ml) to give \(1a\) as a colourless powder (4.30 g, 85%). X-ray quality crystals were obtained by slow diffusion of pentane into a THF solution of \(1a\). Analysis: Found (Calc. for C\(_{20}\)H\(_{39}\)F\(_3\)N\(_2\)O\(_3\)P\(_2\)S•0.1CH\(_2\)Cl\(_2\)): C, 46.45 (46.87), H, 7.61 (7.67), N, 5.35 (5.44). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.43 (s, 1H, NCH), 8.18 (s, 2H, im-H), 1.27 (d, 36H, 3 \(J\)\(\text{HP} = 13.7\) Hz, C(CH\(_3\))\(_3\)). \(^13\)C\(^{1\text{H}}\) NMR (125 MHz, CDCl\(_3\)): \(\delta\) 146.9 (t, \(2J_{\text{CP}} = 31.6\) Hz, NCH), 129.1 (NCH=CHN), 121.0 (q, \(1J_{\text{CF}} = 319.8\) Hz, CF\(_3\)), 35.5 (d, \(1J_{\text{CP}} = 29.4\) Hz, C(CH\(_3\))\(_3\)), 28.6 (d, \(2J_{\text{CP}} = 16.0\) Hz, C(CH\(_3\))\(_3\)). \(^31\)P\(^{1\text{H}}\) NMR (161 MHz, CDCl\(_3\)): \(\delta\) 120.3 (s).

1.4 1-(di-tert-butylphosphino)-3-(diphenylphosphino)-imidazolium triflate (1b)

To a solution of 1-(di-phenylphosphino)imidazole (2.02 g, 8.01 mmol) and sodium triflate (1.70 g, 9.88 mmol) in THF (25 ml) was added dropwise at 0 °C pure di-tert-butylbromophosphine (2.10 g, 9.33 mmol). The reaction...
mixture was allowed to warm slowly to room temperature and stirred for 24 h. After removal of the solvent under reduced pressure, the residue was extracted with CH$_2$Cl$_2$ (3×25 ml). The extracts were evaporated to dryness and the solid residue was washed with Et$_2$O (2×30 ml) to give 2a as a colourless powder (1.70 g, 39%). This imidazolium is very sensitive to air. Due to its sensitivity, a correct elemental analysis could not be obtained. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.41 (s, 1H, NCH), 7.82 (s, 1H, imH), 7.43–7.24 (m, 11H, imH and ArH), 1.08 (d, 18H, 3J$^{HP} = 13.7$ Hz, C(C$_3$H$_7$)$_3$). $^{13}$C{$_1$H} NMR (75.5 MHz, CDCl$_3$): $\delta$ 145.4 (d, 2J$^{CP} = 33.8$ Hz, NCH), 132.9 (d, 3J$^{CP} = 23.3$ Hz), 132.6, 131.3 (d, 3J$^{CP} = 15.4$ Hz), 130.1 (d, 3J$^{CP} = 7.6$ Hz), 129.0, 127, CF$_3$ carbon cannot be detected, 35.5 (d, 1J$^{CP} = 30.0$ Hz, C(C$_3$H$_7$)$_3$), 28.6 (d, 2J$^{CP} = 16.6$ Hz, C(C$_3$H$_7$)$_3$). $^{31}$P{$_1$H} NMR (161 MHz, CDCl$_3$): $\delta$ 122.2 (s), 69.7 (s).

1.5 1,3-bis(di-tert-butylphosphino)-imidazole-2-yldene (2a)

To a suspension of 1a (2.00 g, 3.95 mmol) in ether (15 ml) at 0 °C was added dropwise a solution of sodium hexamethyldisilazide (0.76 g, 4.15 mmol) in ether (8 ml). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. Evaporation of the solvent under reduced pressure, extraction of the residue into pentane (3×20 ml), evaporation of the extracts to dryness and washing of the solid residue with pentane (5 ml) at -40 °C gave 1b as a colourless powder (0.70 g, 50%). X-ray quality crystals were obtained by slow cooling (-20 °C) of dilute pentane solutions for two days. $^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 6.93 (dd, 2H, 3J$^{HP} = 4.0$ Hz, 3J$^{HH} = 1.6$ Hz, imH), 1.32 (d, 36H, 3J$^{HP} = 12.5$ Hz, C(C$_3$H$_7$)$_3$), 1.03 (d, 18H, 3J$^{HP} = 12.0$ Hz, C(C$_3$H$_7$)$_3$). $^{13}$C{$_1$H} NMR (125 MHz, C$_6$D$_6$): $\delta$ 232.7 (NCH), 126.5 (dd, 2J$^{CP} = 34.2$ Hz, 3J$^{CP} = 7.0$ Hz, NCH=CHN), 35.4 (d, 1J$^{CP} = 24.6$ Hz, C(C$_3$H$_7$)$_3$), 29.6 (d, 2J$^{CP} = 16.1$ Hz, C(C$_3$H$_7$)$_3$). $^{31}$P{$_1$H} NMR (161 MHz, C$_6$D$_6$): $\delta$ 98.7 (s). Due to the sensitivity of 2a, a correct elemental analysis could not be obtained.

1.6 1,2-bis(di-tert-butylphosphino)-1H-imidazole (3a)

A Young’s NMR tube charged with 2a (ca. 12 mg) and toluene-d$_8$ (0.4 ml) was heated to 120 °C overnight. In the $^{31}$P{$_1$H} NMR the peak for 2a at 98 ppm disappeared. $^1$H NMR (400 MHz, toluene-d$_8$): $\delta$ 7.32 (s, 1H, im-H), 7.09-7.08 (2H, im-H and toluene), 1.37 (d, 18H, 3J$^{HP} = 11.7$ Hz, C(CH$_3$)$_3$), 1.03 (d, 18H, 3J$^{HP} = 12.0$ Hz, C(CH$_3$)$_3$). $^{13}$C{$_1$H} NMR (125 MHz, toluene-d$_8$): $\delta$ 156.1 (dd, 1J$_{CP} = 24.8$ Hz, 2J$_{CP} = 19.9$ Hz, NCH), 131.3 (NCH=CHN), 124.3 (d, 3J$_{CP} = 7.0$ Hz, NCH=CHN), 35.7 (d, 1J$_{CP} = 32.5$ Hz, C(CH$_3$)$_3$), 34.6 (d, 1J$_{CP} = 20.7$ Hz, C(CH$_3$)$_3$), 31.2 (d, 2J$_{CP} = 14.7$ Hz, C(CH$_3$)$_3$), 29.8 (d, 2J$_{CP} = 17.2$ Hz, C(CH$_3$)$_3$). $^{31}$P{$_1$H} NMR (161 MHz, toluene-d$_8$): $\delta$ 78.2 (d, 3J$^{PP} = 90.0$ Hz, (t-Bu)$_2$P), 7.9, 7.9 (d, 3J$^{PP} = 90.0$ Hz, (t-Bu)$_2$P-C).

1.7 1-(di-tert-butylphosphino)-2-(diphenylphosphino)-1H-imidazole (3b)

To a suspension of 1b (0.52 g, 0.95 mmol) in Et$_2$O (8 ml) at 0 °C was added dropwise a solution of sodium hexamethyldisilazide (0.18 g, 1.00 mmol) in Et$_2$O.
(5 ml). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. Evaporation of the volatiles under reduced pressure, extraction of the residue with pentane (3×20 ml), evaporation of the extracts to dryness and washing of the remaining solid with pentane (5 ml) at -40 °C gave 3b as a colourless powder (0.10 g, 27%). Analysis: Found (Calc. for C_{23}H_{30}N_{2}P_{2}) (%): C, 69.42 (69.68), H, 7.52 (7.63), N, 6.90 (7.07). 1H NMR (400 MHz, CD_{2}Cl_{2}): δ 7.45 (dd, 1H, 3^3_J_{HP} = 2.1 Hz, 3^3_J_{HH} = 1.3 Hz, im-H), 7.43-7.38 (4H, Ar-H), 7.32-7.29 (6H, Ar-H), 7.26 (t, 1H, 3^3_J_{HH} = 1.2 Hz, im-H), 1.11 (d, 18H, 3^3_J_{HP} = 12.6 Hz, C(CH_{3})_{3}). 13C{1H} NMR (125 MHz, CD_{2}Cl_{2}): δ 155.7 (d, 1^1_J_{CP} = 22.8 Hz, N-CN), 137.0 (dd, 1^1_J_{CP} = 21.0 Hz, Ar-CP), 132.2, 129.0, 128.5 (d, 1^1_J_{CP} = 7.3 Hz), 125.4 (d, J = 7.4 Hz), 35.6 (dd, 1^1_J_{CP} = 28.7 Hz, J = 2.1 Hz, C(CH_{3})_{3}), 29.1 (d, 3^1_J_{CP} = 16.2 Hz, C(CH_{3})_{3}). 31P{1H} NMR (161 MHz, CD_{2}Cl_{2}): δ 80.0 (d, 3^3_J_{PP} = 115.4 Hz, P(t-Bu)_{2}), -28.2 (d, 3^3_J_{PP} = 115.4 Hz, PPh_{2}).

1.8 [Cu_{3}{μ}_{3-κ^{3}P,C,P}][CF_{3}SO_{3}]_{3} (Cu-1)

To a solution of (CuO_{3}SCF_{3})_{2}•Toluene (0.11 g, 0.21 mmol) in THF (8 ml) was added a solution of 2a (0.10 g, 0.28 mmol) in THF (5 ml) at -10 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 3 h leading to the formation of a precipitate. After removal of the mother liquor by filtration, the solid was washed with ether (2×10 ml) and dried under vacuum to give Cu-1 as a white powder (0.17 g, 90%). X-ray quality crystals were obtained by slow diffusion of ether into dichloromethane solution of Cu-1. Analysis: Found (Calc. for C_{41}H_{76}Cu_{3}F_{9}N_{4}O_{9}P_{4}S_{3}) (%): C, 35.96 (36.46), H, 5.76 (5.67), N, 3.83 (4.15). 1H NMR (400 MHz, CD_{2}Cl_{2}): δ 8.09 (s, 4H, im-H), 1.51 (t, 72H, 3^3_J_{HP} = 8.4 Hz, C(CH_{3})_{3}). 13C{1H} NMR (125 MHz, CD_{2}Cl_{2}): δ 194.2 (t, 2^1_J_{CP} = 22.4 Hz, N-CN), 128.1 (NCH = CHN), 120.9 (q, 1^1_J_{CP} = 320.4 Hz, CF_{3}), 38.5 (C(CH_{3})_{3}), 29.6 (C(CH_{3})_{3}). 31P{1H} NMR (161 MHz, CD_{2}Cl_{2}): δ 102.1 (s).

1.9 [Ag_{3}{μ}_{3-κ^{3}P,C,P}][CF_{3}SO_{3}]_{3} (Ag-1)

To a solution of AgO_{3}SCF_{3} (0.13 g, 0.50 mmol) in THF (8 ml) was added a solution of 2a (0.10 g, 0.28 mmol) in THF (5 ml) at -10 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 3 h. A precipitate formed and after removing of the supernatant, the solid was washed with ether (2×10 ml) and dried under vacuum to give Ag-1 as a white powder (0.22 g, 89%). X-ray quality crystals were obtained by slow diffusion of ether into dichloromethane solution of Ag-1. Analysis: Found (Calc. for C_{41}H_{76}Ag_{3}F_{9}N_{4}O_{9}P_{4}S_{3}•CH_{2}Cl_{2}) (%): C, 31.92 (32.16), H, 5.07 (5.01), N,
3.59 (3.57). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 7.97 (s, 4H, im-H), 1.45 (t, 72H, $^3J$$_{HP}$ = 8.2 Hz, C(CH$_3$)$_3$).

$^{13}$C($^1$H) NMR (125 MHz, CD$_3$CN): $\delta$ 200.3 (overlapping m, 1 $^1J$$_{CP}$ = 213.1 Hz, $^1J$$_{CP}$ = 184.2 Hz, NCN), 128.6 (NCH=CHN), 122.4 (q, $^1J$$_{CF}$ = 321.4 Hz, CF$_3$), 38.7 (C(CH$_3$)$_3$), 29.3 (C(CH$_3$)$_3$).

$^{31}$P($^1$H) NMR(161 MHz, CD$_3$CN): two doublets at $\delta$ 119.4 ($^1J$$_{P-109Ag}$ = 541.0 Hz, $^1J$$_{P-107Ag}$ = 467.3 Hz).

1.10 [Au$_3$($\mu$-3$^1$P,C,P)$_2$](CF$_3$SO$_3$)$_3$ (Au-1)

To a solution of [Au(tht)$_2$]O$_3$SCF$_3$ (0.091 g, 0.17 mmol) in THF (4 ml) was added a solution of 2a (0.042 g, 0.12 mmol) in THF (6 ml) at -10 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 3 h leading to the formation of a precipitate. After removal of the mother liquor by filtration, the solid was washed with dichloromethane (3 ml) and dried under vacuum to give Au-1 as a white powder (0.056 g, 56%). X-ray quality crystals were obtained by slow diffusion of ether into acetonitrile solution of Au-1.

Analysis: Found (Calc. for C$_{41}$H$_{76}$Au$_3$F$_9$N$_4$O$_9$P$_4$S$_3$•0.5CH$_3$CN) (%): C, 28.85 (28.47), H, 4.60 (4.41), N, 3.09 (3.56). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.17 (s, 4H, im-H), 1.57 (t, 72H, $^3J$$_{HP}$ = 9.5 Hz, C(CH$_3$)$_3$).

$^{13}$C($^1$H) NMR (125 MHz, CD$_3$CN): $\delta$ 194.3 (t, 2 $^1J$$_{CP}$ = 14.6 Hz, NCN), 129.8 (NCH=CHN), 122.2 (q, $^1J$$_{CF}$ = 321.7 Hz, CF$_3$), 41.5 (C(CH$_3$)$_3$), 29.5 (C(CH$_3$)$_3$).

$^{31}$P($^1$H) NMR (161 MHz, CD$_3$CN): $\delta$ 141.0 (s).

1.11 [Cu$_2$($\mu$-2$^1$C,P)$_2$](CF$_3$SO$_3$)$_2$ (Cu-2)

To a suspension of [CuN(SiMe$_3$)$_2$] (0.11 g, 0.50 mmol) in THF (7 ml) was added a solution of 1a (0.25 g, 0.50 mmol) in THF (8 ml) at -10 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 1 h resulting in the formation of a precipitate. After evaporation of the solvent under reduced pressure, the residue was washed with ether (10 ml) and dried under vacuum to give Cu-2 as a white powder (0.25 g, 88%). X-ray quality crystals were obtained by slow diffusion of pentane into a THF solution of Cu-2. Analysis: Found (Calc. for C$_{40}$H$_{76}$Cu$_2$F$_6$N$_4$O$_6$P$_4$S$_2$) (%): C, 42.32 (42.21), H, 6.93 (6.73), N, 4.90 (4.92). $^1$H NMR (400 MHz, THF-d$_8$): $\delta$ 7.86 (s, 4H, im-H), 1.40 (b, 72H, C(CH$_3$)$_3$).

$^{13}$C($^1$H) NMR (125 MHz, THF-d$_8$): $\delta$ 201.5 (NCN), 126.6 (NCH=CHN), 122.1 (q, $^1J$$_{CF}$ = 323.2 Hz, CF$_3$), 36.1 (b, C(CH$_3$)$_3$), 29.6 (b, C(CH$_3$)$_3$).

$^{31}$P($^1$H) NMR (161 MHz, THF-d$_8$): $\delta$ 94.5 (b).

1.12 [Ag$_2$($\mu$-2$^1$C,P)$_2$](CF$_3$SO$_3$)$_2$ (Ag-2)

Method a: A solution of AgO$_3$SCF$_3$ (0.128 g, 0.50 mmol) and NaN(SiMe$_3$)$_2$ (0.092 g, 0.50 mmol) in toluene (8 ml) was stirred for 15 min at room temp. in the dark. A solution of 1a (0.253 g, 0.50 mmol) in THF (8 ml) was added and stirred for another 20 min. After removal of the mother liquor by
filtration, dissolution of the solid in CH₂Cl₂, filtration and evaporation of the filtrate to give a mixture of Ag-1 and Ag-2 as a white powder. $^1$H NMR (400 MHz, CD₂Cl₂): $\delta$ 7.82 (s, 4H, im-H), 1.36 (d, 72H, $^3J_{HP} = 14.5$ Hz, C(CH₃)₃). $^{13}$C{$^1$H} NMR (125 MHz, CD₂Cl₂): $\delta$ 203.5 (overlapping m, NCN), 127.0 (NCH=CHN), 120.9 (q, $^{13}$JC = 322.1 Hz, CF₃), 36.4 (b, C(CH₃)₃), 28.8 (b, C(CH₃)₃). $^{31}$P{$^1$H} NMR (161 MHz, CD₂Cl₂): two broad multiplets at $\delta$ 116.7.

**Method b**: To a suspension of Ag₂O (0.136 g, 0.27 mmol) with molecular sieves 4 Å (ca. 0.4 g) in CH₂Cl₂ (10 ml) was added a solution of 1a (0.062 g, 0.27 mmol) in CH₂Cl₂ (10 ml). The reaction mixture was stirred for 3 days at room temperature. After filtering off the solid, the filtrate was evaporated to dryness under reduced pressure to give Ag-2 as a white powder.

## 2. X-ray crystallography

Summary of the crystal data, data collection and refinement for structures of 1a, 2a, Cu-1•2CH₂Cl₂, Ag-1•2CH₂Cl₂, Au-1•2MeCN and Cu-2 are given in Table S1. The crystals were mounted on a glass fiber with grease, from Fomblin vacuum oil. Data sets were collected on a Bruker APEX II DUO diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software) from reflections taken from three sets of 12 frames, each at 10 s exposure. The structures were solved by direct methods using the program SHELXS-97. The refinement and all further calculations were carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$.

The following special comments apply to the models of the structures:

For 1a, the methyls groups C9, C10, C11 are disordered on two positions. A squeeze procedure was applied and the residual electron density was assigned to half a molecule of THF.

The asymmetric unit of Cu-1•2CH₂Cl₂ contains half a molecule of the copper complex, three half molecules of triflate and two half molecules of dichloromethane. The atoms C1, C11, C21, C22, C23, C24, C25, O2, O3, O6, F2, F3, F6, S1, S2, S3, Cu1, Cl1, Cl2, Cl3 and Cl4 are in special position (population 50%). The methyls : C8, C9 and C10 are disordered on two positions.

In the structure of Ag-1•2CH₂Cl₂, the asymmetric unit contains half a molecule of this complex, three half molecules of triflates and two half molecules of dichloromethane. The atoms : C1, C11, C21, C22, C23, C24, C25, O2, O4, O6, F2, F4, F6, S1, S2, S3, Ag1, Cl1, Cl2, Cl3 and Cl4 are in special position (population 50%). The methyls : C18, C19 and C20 are disordered on two positions.

The asymmetric unit of Au-1•2MeCN contains two half molecules of the cation, 3 molecules of triflate and 2 molecules of MeCN. One triflate anion is disordered over two positions.
## 2.1 Summary of crystal data

**Table S1.** Crystal data for compounds 1a, 2a, Cu-1•2CH2Cl2, Ag-1•2CH2Cl2, Au-1•2MeCN and Cu-2.

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<td>90</td>
<td>90</td>
<td>90.5620(10)</td>
<td>94.3950(10)</td>
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<td><strong>γ/°</strong></td>
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<td>90</td>
<td>90</td>
<td>90</td>
<td>116.8880(10)</td>
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<tr>
<td><strong>Unit cell volume/Å³</strong></td>
<td>2951.1(8)</td>
<td>4502.5(4)</td>
<td>6417.7(9)</td>
<td>6605.3(4)</td>
<td>3221.0(3)</td>
<td>2736.4(3)</td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
<td>173(2)</td>
<td>173(2)</td>
<td>17(3)</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
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<tr>
<td><strong>Space group</strong></td>
<td>P21/c</td>
<td>C2/c</td>
<td>Pnma</td>
<td>Pnma</td>
<td>P-1</td>
<td>P21/c</td>
</tr>
<tr>
<td><strong>Formula units / cell, Z</strong></td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>4</td>
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<td><strong>Absorption coefficient, μ/mm⁻¹</strong></td>
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<td>0.196</td>
<td>1.425</td>
<td>1.308</td>
<td>7.09</td>
<td>1.034</td>
</tr>
<tr>
<td><strong>No. of reflections measured</strong></td>
<td>20827</td>
<td>48197</td>
<td>25849</td>
<td>34171</td>
<td>59662</td>
<td>22020</td>
</tr>
<tr>
<td><strong>No. of independent reflections</strong></td>
<td>7188</td>
<td>6585</td>
<td>8034</td>
<td>10868</td>
<td>20683</td>
<td>7272</td>
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<tr>
<td><strong>Rint</strong></td>
<td>0.0703</td>
<td>0.0294</td>
<td>0.102</td>
<td>0.0382</td>
<td>0.0313</td>
<td>0.0486</td>
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<tr>
<td><strong>Final R1 values (I &gt; 2 σ(I))</strong></td>
<td>0.0806</td>
<td>0.0436</td>
<td>0.0741</td>
<td>0.0454</td>
<td>0.0372</td>
<td>0.0742</td>
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<tr>
<td><strong>Final wR2 values (I &gt; 2 σ(I))</strong></td>
<td>0.1835</td>
<td>0.1054</td>
<td>0.1619</td>
<td>0.0904</td>
<td>0.0713</td>
<td>0.2009</td>
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<tr>
<td><strong>Final R1 values (all data)</strong></td>
<td>0.1344</td>
<td>0.0581</td>
<td>0.1819</td>
<td>0.0973</td>
<td>0.0593</td>
<td>0.119</td>
</tr>
<tr>
<td><strong>Final wR2 values (all data)</strong></td>
<td>0.2026</td>
<td>0.116</td>
<td>0.216</td>
<td>0.1137</td>
<td>0.0782</td>
<td>0.2284</td>
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<tr>
<td><strong>Goodness of fit on F²</strong></td>
<td>1.018</td>
<td>1.107</td>
<td>1.022</td>
<td>1.048</td>
<td>1.064</td>
<td>1.038</td>
</tr>
</tbody>
</table>
2.2 The crystal structure of 1a

Figure S1. Thermal ellipsoid representation (30% probability level) of the structures of 1a. One triflate anion and H atoms except those attached to the heterocyclic ring are omitted for clarity; only one disordered position of one tBu at P1 is shown. Selected bond lengths (Å) and angles [°]: C1-N1 1.320(4); C1-N2 1.331(4); C1-H1 0.9500; N1-P1 1.795(3); N2-P2 1.784(3); N1-C1-N2 110.9(3); N1-C1-H1 124.6; N2-C1-H1 124.6; C1-N1-P1 119.6(2); C1-N2-P2 119.8(2).

2.3 The crystal structure of 2a

Figure S2. Thermal ellipsoid representation (30% probability level) of the structures of 2a. H atoms except those attached to the heterocyclic ring are omitted for clarity. Selected bond lengths (Å) and angles [°]: C1-N1 1.3763(15); C1-N2 1.3779(14); N1-P1 1.7475(10); N2-P2 1.7531(11); N1-C1-N2 102.54(10); C1-N1-P1 128.91(8); C1-N2-P2 128.77(9).
2.4 The crystal structure of Ag-1•2CH2Cl2

Figure S3. Thermal ellipsoid representation (30% probability level) of the cation in the structure of Ag-1•2CH2Cl2. Hydrogen atoms, uncoordinated triflate anions, disordered atoms and two molecules of solvent of crystallisation (CH2Cl2) are omitted for clarity. Selected bond lengths (Å) and angles [°]: C1-N1 1.337(4); C1-Ag1 2.152(4); C11-N2 1.332(4); C11-Ag1 2.161(4); N1-P1 1.745(3); N2-P2 1.754(3); P1-Ag2 2.4076(9); P2-Ag2 2.4046(9); Ag1-Ag2 2.7599(3); O3-Ag2 2.896; O3-Ag1 2.929; N1-C1-N1' 107.6(4); N1-C1-Ag1 126.19(19); N2-C11-N2' 108.4(4); N2-C11-Ag1 125.8(2); C1-N1-P1 125.2(2); C11-N2-P2 125.4(2); N1-P1-Ag2 109.12(9); C1-Ag1-C11 178.4(2); C1-Ag1-Ag2 90.368(14); C11-Ag1-Ag2 89.754(14); Ag2-Ag1-Ag2' 171.41(2); P2-Ag2-P1 164.93(4); P2-Ag2-Ag1 89.12(3); P1-Ag2-Ag1 88.85(2); Ag2-O3-Ag1 56.56; O3-Ag1-O3' 49.20.

References for the experimental part

3. Computational details

3.1 Methods and theory

Density functional theory (DFT) calculations were carried out using the Amsterdam Density Functional (ADF) program. The numerical integration was performed using the procedure developed by te Velde et al. The molecular orbitals were expanded in a large set of uncontracted Slater-type orbitals (STOs) of triple-ζ quality augmented with two sets of polarisation functions for all atoms (TZ2P basis set), i.e. 2p and 3d on H, 3d and 4f on C, N, and P. An auxiliary set of s, p, d, f and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field cycle. All the structures herein analysed were optimised without any symmetry restrictions in the gas phase at the BP86 level since BP86 has been shown to be one of the three best generalised gradient approximation (GGA) DFT functionals (along with PBE and PW91) for geometry optimisations with the ADF program package. The electronic exchange was described by Slater’s Xα potential with self-consistent nonlocal corrections of Becke, and the electron correlation was treated in the Vosko-Wilk-Nusair (VWN) parameterisation with self-consistent nonlocal corrections of Perdew (BP86). The gas-phase energy minima were verified to be equilibrium structures through vibrational analyses with detailed surface scans. The electron density distribution was analysed using the Hirshfeld scheme for computing atomic charges. The energy decomposition analysis of the N(C-PR₂) and Nimid–PR₂ bonds in the corresponding molecules was performed.

3.2 Structural and energy analysis

Table S2. Energy costs associated with the different syn, anti-conformations of imidazolium cation in 1a: relative energies (ΔE_{rel}, including zero-point energy corrections) and HOMO–LUMO gaps (ΔE_{H–L}) are given. Colour code: H, off-white; C, grey; N, blue; P, orange.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>ΔE_{rel}</th>
<th>ΔE_{H–L}</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn</td>
<td>0 kJ mol⁻¹</td>
<td>3.83 eV</td>
</tr>
<tr>
<td>anti-</td>
<td>+3 kJ mol⁻¹</td>
<td>3.73 eV</td>
</tr>
<tr>
<td>anti-</td>
<td>+9 kJ mol⁻¹</td>
<td>3.61 eV</td>
</tr>
</tbody>
</table>
Table S3. Energy costs associated with the formation of N(C-PR₂) and N_{imid}-PR₂ bonds in the optimised structures and their syn, anti-conformers: relative energies (\(\Delta E_{rel}\), including zero-point energy corrections) and HOMO–LUMO gaps (\(\Delta E_{H-L}\)) are given. Hydrogen atoms are not shown for clarity. Colour code: H, off-white; C, grey; N, blue; P, orange.

<table>
<thead>
<tr>
<th>syn, anti-conformers of N(C-PR₂) with R = t-Bu (top) and N(C-PR₂) with R = Ph (bottom)</th>
<th>syn, anti-conformers of N_{imid}-PR₂ with R = t-Bu (top) and N_{imid}-PR₂ with R = Ph (bottom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E_{rel} = +30 \text{kJmol}^{-1})</td>
<td>(\Delta E_{rel} = +99 \text{kJmol}^{-1})</td>
</tr>
<tr>
<td>(\Delta E_{H-L} = 3.99 \text{eV})</td>
<td>(\Delta E_{H-L} = 4.10 \text{eV})</td>
</tr>
<tr>
<td>(\Delta E_{rel} = 0 \text{kJmol}^{-1})</td>
<td>(\Delta E_{rel} = 0 \text{kJmol}^{-1})</td>
</tr>
<tr>
<td>(\Delta E_{H-L} = 3.75 \text{eV})</td>
<td>(\Delta E_{H-L} = 3.53 \text{eV})</td>
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<tr>
<td>(\Delta E_{rel} = +134 \text{kJmol}^{-1})</td>
<td>(\Delta E_{rel} = +115 \text{kJmol}^{-1})</td>
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<td>(\Delta E_{H-L} = 3.57 \text{eV})</td>
<td>(\Delta E_{H-L} = 4.02 \text{eV})</td>
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<td>(\Delta E_{rel} = +17 \text{kJmol}^{-1})</td>
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<td>(\Delta E_{H-L} = 3.53 \text{eV})</td>
<td>(\Delta E_{H-L} = 2.87 \text{eV})</td>
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<tr>
<td>(\Delta E_{rel} = +76 \text{kJmol}^{-1})</td>
<td>(\Delta E_{rel} = +115 \text{kJmol}^{-1})</td>
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<td>(\Delta E_{H-L} = 3.17 \text{eV})</td>
<td>(\Delta E_{H-L} = 2.80 \text{eV})</td>
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</table>
Hirshfeld charge analysis. The following evolution of the Hirshfeld atomic charges on phosphorous in the phosphenium R₂P⁺ ions was found by DFT calculations: R = Ph (+0.32) < t-Bu (+0.36) < Me (+0.57) < H (+0.82). It is consistent with the fluoride ion affinity (FIA) scale obtained for the R₂P⁺ cations by Slattery and Hussein. The general trend in FIA was determined as follows: R = NR₂ < mesityl < SR < Ph < t-Bu < OR < C₆F₅ < I < Me < Br < Cl < F < H (increasing Lewis acidity).


