

# Ag(I) and Au(I) complexes of sterically crowded cyclic phosphinimine ligands†

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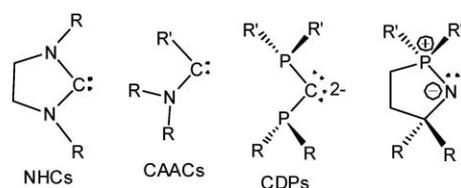
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Cyclic phosphinimines are strong bases with structural similarities to carbene ligands. The cyclic phosphinimines  $R_2PNCPh_2(CH_2CH(CO_2Me))$  ( $R = Ph$  **4**, *i*-Pr **5**, Me **6**),  $R_2PNCPh_2(CCOMe)_2$  ( $R = Ph$  **7**, *i*-Pr **8**) and  $Ph_2PNCPh_2(CH_2CH(CN))$  **9** are readily prepared *via* cycloaddition of the compounds  $R_2PNCPh_2$  ( $R = Ph$  **1**, *i*-Pr **2**, Me **3**) and olefins or alkynes. In the case of **4** this phosphinimine proved to be moisture sensitive, converting to  $Ph_2C(NH_2)CH(CO_2Me)CH_2P(O)Ph_2$  **10** upon hydrolysis. Nonetheless, the Ag(I) and Au(I) complexes  $[(Ph_2PNCPh_2(CH_2CH(CO_2Me))_2Ag][NO_3]$  **11** ( $Ph_2PNCPh_2(CH_2CH(CO_2Me))AuCl$  **12** and  $(Ph_2PNCPh_2(C(CO_2Me)_2)AuCl$  **13**) were prepared and characterized. Compounds **1**, **2** and **7–13** have been characterized crystallographically.

## Introduction

The advent of N-heterocyclic carbene (NHCs) ligands (Scheme 1) has had a dramatic impact on inorganic and organometallic chemistry.<sup>1</sup> These ligands have allowed access to unique coordination geometries and, in some cases, the generation of remarkably reactive catalysts.<sup>2</sup> The steric and electronic features of NHCs are unique. For example, the strong sigma bonding nature of carbenes is well understood to play a role in stabilizing reactive metal species. In addition, judicious choice of substituents permits the tuning of the steric and stereochemical environment proximal to the metal. Variants of these ligands have been described. For example, Bertrand *et al.* have described complexes of alkylaminocarbenes (CAACs) (Scheme 1).<sup>3</sup> In addition, carbodiphosphoranes (CDPs), (Scheme 1) which are formally dianionic at the carbon atom, have been extensively investigated as ligands in transition metal chemistry.<sup>4</sup> More recently, complexes of cyclic carbodiphosphoranes have also been described.<sup>5</sup>

With these precedents in mind, we sought to explore other ligand systems that might offer similar features. Phosphinimines are a class of donors which are known to be strongly basic.<sup>6</sup> Nonetheless, these systems are electronically distinct from carbenes in that the donor N atom formally has a filled p-orbital orthogonal to the donor pair, whereas in carbenes the orthogonal p-orbital is vacant. While anionic phosphinimide ligands have been exploited extensively as ancillary ligands,<sup>6–7</sup> phosphinimine ligand systems have drawn much less attention, although some recent work has incorporated such donors into chelating ligand systems.<sup>8</sup> The structural similarity of cyclic phosphinimines to NHCs suggests that such ligands may also combine the features of a strong donor with the additional flexibility of controlling the steric environment *via* alteration of the substituents on C and P. While cyclic phosphinimines were first prepared some 40 years ago,<sup>9</sup> to our knowledge, the ability of these systems to act as ligands has not been explored. In this paper, we explore synthetic routes



**Scheme 1** Structural similarity and electronic difference among NHCs, CAACs, CDPs and cyclic phosphinimines.

to a series of saturated and unsaturated cyclic phosphinimines and probe their viability as ligands for Ag(I) and Au(I) complexes. The implications for use of these ligands in subsequent chemistry are considered.

## Experimental section

All preparations were performed under an atmosphere of dry,  $O_2$ -free  $N_2$  employing both Schlenk line techniques and a MBraun Labmaster inert atmosphere glove box. Solvents ( $CH_2Cl_2$ ,  $Et_2O$  and pentane) were purified employing a Grubbs' type column system manufactured by Innovative Technology. 1,2-Dichloroethane was dried over  $CaH_2$  and distilled under a nitrogen atmosphere. Solvents were stored in the glove box over 4 Å molecular sieves. Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 150 °C under vacuum for 48 h prior to use. All glassware was dried overnight at 120 °C and evacuated for 1 h prior to use. The chlorophosphines were purchased from Strem Chemicals. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification.  $^1H$ ,  $^{13}C\{^1H\}$  and  $^{31}P\{^1H\}$  NMR spectroscopy spectra were recorded on Varian 400 MHz and Bruker 400 MHz spectrometers.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra are referenced to  $SiMe_4$  using the residual solvent peak impurity of the given solvent.  $^{31}P\{^1H\}$  NMR spectra were referenced to 85%  $H_3PO_4$ . Chemical shifts are reported in ppm and coupling constants in Hz.  $C_6D_6$  and  $CD_2Cl_2$  were used as the NMR solvents after being dried over Na/benzophenone ( $C_6D_6$ ) or  $CaH_2$  ( $CD_2Cl_2$ ), vacuum-transferred into Young bombs and freeze–pump–thaw degassed (three cycles). Combustion analyses were performed in-house employing a Perkin Elmer 2400 Series II CHN Analyzer.

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### Synthesis of R<sub>2</sub>PNCPh<sub>2</sub> (R = Ph 1, *i*-Pr 2, Me 3)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. A solution of benzophenone imine (9.69 g, 53.5 mmol) and Et<sub>3</sub>N (6.77 mL, 48.6 mmol) in diethyl ether (400 mL) was cooled to 0 °C before adding Ph<sub>2</sub>PCL (8.72 mL, 48.6 mmol) dropwise. The reaction mixture turned yellow and was stirred overnight. The suspension was filtered and the solvent removed *in vacuo*. Purification *via* recrystallization from acetonitrile afforded **1** as yellow crystals (12.4 g, 34.0 mmol, 70%) <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.35–7.47 (m, 20H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 175.70 (d, (Ph)<sub>2</sub>CN, <sup>2</sup>J<sub>CP</sub> = 13.7 Hz), 142.65 (<sup>2</sup>J<sub>CP</sub> = 13.7 Hz, *o*-PPh<sub>2</sub>), 140.56 (d, *o*-PPh<sub>2</sub>, <sup>1</sup>J<sub>CP</sub> = 7.5 Hz), 132.48 (Ph), 132.27 (Ph), 130.16 (Ph), 129.04 (Ph), 128.62–128.73 (m, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 36.8. C,H,N analysis calc. for C<sub>25</sub>H<sub>20</sub>NP (365.42): C, 82.17; H, 5.52; N, 3.83. Found: C, 82.02; H, 5.69; N, 3.88. **2**: orange crystals (8.52 g, 28.7 mmol, 87.5%), <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.38–7.47 (m, 10H, Ph), 1.89 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (dd, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>3</sup>J<sub>PH</sub> = 14.8 Hz), 1.00 (dd, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>3</sup>J<sub>PH</sub> = 14.8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 177.27 (d, (Ph)<sub>2</sub>CN, <sup>2</sup>J<sub>CP</sub> = 13.7 Hz), 141.04 (d, Ph, <sup>1</sup>J<sub>CP</sub> = 7.5 Hz), 129.90 (s, Ph), 129.16 (s, Ph), 129.14 (s, Ph), 128.49 (s, Ph), 27.55 (m, CH(CH<sub>3</sub>)<sub>2</sub>), 19.09 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 18.90 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 18.61 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 18.51 (s, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 68.6. C,H,N analysis calc. for C<sub>19</sub>H<sub>24</sub>NP (297.38): C, 76.74; H, 8.13; N, 4.91. Found: C, 76.75; H, 8.10; N, 5.04. X-Ray quality crystals were grown from cooling a saturated diethyl ether solution to –35 °C. **3**: orange oil <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 7.49–7.51 (m, 4H, Ph), 7.06–7.09 (m, 6H, Ph), 1.07 (d, 6H, CH<sub>3</sub>, <sup>2</sup>J<sub>PH</sub> = 4.7 Hz) <sup>1</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 27.81 (<sup>31</sup>P{<sup>1</sup>H} NMR shows 93% purity). Attempts to purify were unsuccessful, thus the crude product was used as prepared in subsequent reactions.

### Synthesis of R<sub>2</sub>PNCPh<sub>2</sub>(CH<sub>2</sub>CH(CO<sub>2</sub>Me)) (R = Ph 4, *i*-Pr 5, Me 6)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. **1** (731 mg, 2.0 mmol) was completely dissolved in diethyl ether (5 mL) before the addition of methyl acrylate (181 mg, 2.10 mmol). The yellow colour of the solution faded to a clear solution and a white precipitate formed. The solution was stirred overnight. The solution was filtered and washed with cold pentane (15 mL) to afford **4** as a white solid (772 mg, 1.71 mmol, 85.5%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.02–7.38, 7.46–7.61, 7.88–7.97 (m, 20H, Ph), 4.25–4.37 (m, 1H, CHCO<sub>2</sub>CH<sub>3</sub>), 2.93–3.03 (m, 4H, CH<sub>3</sub> and CH<sub>2</sub> *trans* to CO<sub>2</sub>Me), 2.70–2.85 (m, 1H, CH<sub>2</sub> *cis* to CO<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 173.5 (d, *J* = 6 Hz), 150.95, 148.63, 148.43, 132.26, 132.17, 131.57, 131.55, 131.11, 131.01, 130.74, 130.71, 128.22, 128.10, 128.02, 127.97, 127.91, 127.42, 127.14, 126.80, 125.92, 125.58, 82.89, 50.90, 31.85, 31.40. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 48.61. C,H,N analysis calc. for C<sub>29</sub>H<sub>26</sub>NO<sub>2</sub>P (451.51): C, 77.15; H, 5.80; N, 3.10. Found: C, 76.62; H, 5.89; N, 3.19. X-Ray quality crystals were grown by slow diffusion of pentane into a saturated dichloromethane solution. **5**: (800 mg, 2.02 mmol, 63%) white solid, <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.62–7.63 (m, 2H, Ph), 7.42–7.45 (m, 2H, Ph), 7.25 (tt, 2H, *J* = 8 Hz, Ph), 7.12–7.16 (m, 3H, Ph), 7.06 (tt, 1H, *J* = 7 Hz, Ph), 4.05–4.13 (m, 1H, CHCO<sub>2</sub>CH<sub>3</sub>), 3.08 (s, 3H, CH<sub>3</sub>), 2.45–2.54 (m, 2H, CH<sub>2</sub>), 2.08–2.18 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.63–1.68 (m, 1H,

CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (dd, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 10.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 1.34 (dd, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 10.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 0.98 (dd, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 14.7 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 0.79 (dd, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 15.5 Hz, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 73.80. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 173.97, 173.91, 152.85, 152.82, 149.56, 149.38, 127.94, 127.52, 127.28, 126.57, 125.53, 82.78, 54.58, 54.47, 53.96, 53.69, 53.42, 53.15, 52.88, 50.92, 27.53, 26.99, 26.14, 25.49, 24.41, 24.03, 17.60, 17.58, 17.14, 17.11, 16.41, 16.38, 16.34, 16.31. C,H,N analysis calc. for C<sub>23</sub>H<sub>30</sub>NO<sub>2</sub>P (383.47): C, 72.04; H, 7.89; N, 3.65. Found: C, 71.83; H, 8.05; N, 3.72. **6**: (642 mg, 1.96 mmol, 85%). Purification *via* recrystallization from dichloromethane yields colourless needles. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.48–7.54 (m, 4H, Ph), 7.22–7.26 (m, 2H, Ph), 7.12–7.18 (m, 3H, Ph), 7.06–7.10 (tt, 1H, Ph), 4.17 (m, 1H, CHCO<sub>2</sub>CH<sub>3</sub>), 3.00 (s, 3H, CH<sub>3</sub>), 2.44 (m, 1H, CH<sub>2</sub>), 2.02–2.10 (m, 1H, CH<sub>2</sub>), 1.78 (d, 3H, <sup>2</sup>J<sub>PH</sub> = 14.0 Hz, P(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, 3H, <sup>2</sup>J<sub>PH</sub> = 14.0 Hz, P(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 52.7. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 174.59, 151.56, 149.03, 148.78, 128.18, 128.08, 128.06, 127.50, 127.40, 126.32, 126.28, 82.97, 66.22, 51.45, 31.00, 30.57, 19.20, 18.62, 17.02, 16.28, 15.67. C,H,N analysis calc. for C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub>P (327.36): C, 69.71; H, 6.77; N, 4.28. Found: C, 71.09; H, 7.05; N, 4.52.

### Synthesis of R<sub>2</sub>PNCPh<sub>2</sub>(CCO<sub>2</sub>Me)<sub>2</sub> (R = Ph 7, *i*-Pr 8)

These compounds were prepared in a similar fashion and thus only one preparation is detailed. Compound **1** (365 mg, 1.0 mmol) was dissolved in diethyl ether (5 mL) to which dimethyl acetylenedicarboxylate (150 mg, 1.05 mmol) dissolved in diethyl ether (5 mL) was added dropwise. The reaction turned from light yellow to light orange with a precipitate forming in 10 min. The reaction was stirred overnight. The reaction was filtered and washed with cold pentane (15 mL) to give a pure yellow powder **7** (380 mg, .75 mmol, 75%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.56–7.61 (m, 6H, Ph), 7.42–7.46 (m, 4H, Ph), 7.29–7.32 (m, 4H, Ph), 7.22–7.25 (m, 6H, Ph), 3.68 (s, 3H, CH<sub>3</sub>), 3.59 (s, 3H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 49.04. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 176.71, 176.33, 166.57, 166.33, 162.48, 162.36, 146.58, 146.51, 132.60, 132.50, 132.18, 132.16, 128.40, 128.30, 128.16, 127.36, 126.62, 88.08, 52.49, 52.28, 43.92. C,H,N analysis calc. for C<sub>31</sub>H<sub>26</sub>NO<sub>4</sub>P (507.52): C, 73.36; H, 5.16; N, 2.76. Found: C, 72.91; H, 5.59; N, 2.71. **8**: orange powder (1.20 g, 2.73 mmol, 75%). Orange crystals (8.52 g, 28.7 mmol, 88%), <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.84–7.87 (m, 2H, Ph), 7.65–7.68 (m, 2H, Ph), 7.27–7.49 (m, 6H, Ph), 4.32 (m, 1H, CHCOOCH<sub>3</sub>), 3.30 (s, 3H, CH<sub>3</sub>), 2.66–2.77 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.37 (m, 1H, CH<sub>2</sub>), 1.83–1.93 (m, 1H, CH<sub>2</sub>), 1.55–1.63 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (dd, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 15.9 Hz, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz), 1.01 (dd, 3H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>PH</sub> = 16.9 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 173.95, 152.85, 149.48, 127.94, 127.52, 127.28, 126.57, 125.53, 82.77, 54.54, 50.92, 27.27, 25.79, 24.22, 17.61, 17.34, 16.37. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 73.79. C,H,N analysis calc. for C<sub>25</sub>H<sub>30</sub>NO<sub>4</sub>P (439.48): C, 68.32; H, 6.88; N, 3.19. Found: C, 68.43; H, 6.66; N, 3.65. X-Ray quality crystals were grown by slow cooling of a saturated diethyl ether solution.

### Synthesis of R<sub>2</sub>PNCPh<sub>2</sub>(CH<sub>2</sub>CH(CN)) **9**

Compound **1** (1.096 g, 3.00 mmol) was dissolved in diethyl ether (10 mL) to which acrylonitrile (160 mg, 3.03 mmol) dissolved

in diethyl ether (5 mL) was added in addition. The reaction turned from light yellow to colourless with a white precipitate upon stirring for 12 h. The reaction volume was reduced by half *in vacuo*, filtered, and washed with cold pentane (20 mL) to give a white powder (961 mg, 2.20 mmol, 77%).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ): 7.75–7.91 (m, 4H, Ph), 7.11–7.68 (m, 16H, Ph), 4.34 (m, 1H, CH), 3.03 (m, 2H,  $\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) 46.0.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 149.00, 148.95, 148.74, 148.56, 132.82, 132.71, 132.22, 131.88, 131.78, 131.63, 130.59, 129.25, 129.12, 129.01, 128.89, 128.42, 128.29, 127.84, 127.11, 127.03, 126.85, 121.32, 81.56, 42.40, 42.27, 33.86, 33.42.

#### Synthesis of $\text{Ph}_2\text{C}(\text{NH}_2)\text{CH}(\text{CO}_2\text{Me})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ **10**

Compound **4** (45 mg, 0.1 mmol) was dissolved in dichloromethane (5 mL) and exposed to air for 5 min. The initially clear solution immediately formed a fine white precipitate. After 5 min. the reaction was complete, the volume reduced to 1 mL and filtered. Washing the solid with cold dichloromethane (2 mL) yields a pure white solid.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 7.62–7.74 (m, 4H, Ph), 7.41–7.51 (m, 8H, Ph), 7.28 (t, 4H, Ph), 7.13–7.20 (m, 3H, Ph), 7.06 (m, 1H, Ph), 4.10 (m, 1H,  $\text{CH}_2$ ), 2.82–2.90 (m, 1H,  $\text{CHCO}_2\text{CH}_3$ ), 2.80 (s, 3H,  $\text{CHCO}_2\text{CH}_3$ ), 2.48 (m, 1H,  $\text{CH}_2$ ), 1.70–2.30 (br, 2H,  $\text{NH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ): 29.9.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ): 174.63 (s,  $\text{CO}_2\text{CH}_3$ ), 146.00, 144.78, 133.97, 132.98, 132.15, 132.12, 132.03, 132.00, 131.53 (d,  $J = 10$  Hz), 130.90 (d,  $J = 10$  Hz), 128.97, 128.92, 128.85, 128.65, 128.53, 128.03, 128.20, 126.95, 126.68, 126.34, 63.90 (d,  $J = 13$  Hz,  $\text{C}(\text{Ph})_2(\text{NH}_2)$ ), 51.47 (s,  $\text{CO}_2\text{CH}_3$ ), 46.66 ( $\text{CHCO}_2\text{CH}_3$ ), 29.44 (d,  $J = 70$  Hz,  $\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ ). C,H,N analysis calc. for  $\text{C}_{29}\text{H}_{28}\text{NO}_3\text{P}$  (469.51): C, 74.19; H, 6.01; N, 2.98. Found: C, 73.32; H, 6.62; N, 2.97.

#### Synthesis of $[\{\text{Ph}_2\text{PNCPh}_2(\text{CH}_2\text{CH}(\text{CO}_2\text{Me}))\}_2\text{Ag}][\text{NO}_3]$ **11**

Compound **4** (226 mg, 0.50 mmol) was dissolved in dichloromethane (5 mL) and added to a slurry of silver nitrate (85 mg, 0.50 mmol, 1 eq.) in dichloromethane (3 mL). The solution was stirred for 24 h in the dark. The solution colour slowly changed from colourless to a light yellow. The solution was filtered through Celite and the solvent removed *in vacuo* to yield an off-white solid. (227 mg, 73%)  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ): 6.73–7.70 (br. m, 40H, Ph), 4.23–4.34 (br. m, 2H, CH), 3.31–3.41 (m, 2H,  $\text{CH}_2$ ), 3.08 (s, 6H,  $\text{CH}_3$ ), 2.93–3.04 (m, 2H,  $\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 52.83 (d,  $^2J_{\text{Ag-P}} = 18$  Hz), 52.58 (d,  $^2J_{\text{Ag-P}} = 18$  Hz)  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 172.18 (d,  $\text{C}=\text{O}$ ,  $J = 6$  Hz), 148.30, 145.41, 133.60, 132.3–132.8 (m, Ph), 129.21, 129.08, 128.9, 128.8, 128.4, 127.9, 127.6, 127.17, 126.75, 80.74 (d,  $\text{CHCOOCH}_3$ ,  $J = 8$  Hz), 65.7, 51.84 (s,  $\text{CH}_3$ ), 30.10. C,H,N analysis calc. for  $\text{C}_{23}\text{H}_{30}\text{NO}_2\text{P}$  (383.47): C, 72.04; H, 7.89; N, 3.65. Found: C, 71.83; H, 8.05; N, 3.72.

#### Synthesis of $(\text{Ph}_2\text{PNCPh}_2(\text{CH}_2\text{CH}(\text{CO}_2\text{Me}))\text{AuCl}$ **12** and $(\text{Ph}_2\text{PNCPh}_2(\text{C}(\text{CO}_2\text{Me}))_2\text{AuCl}$ **13**

These compounds were prepared in a similar fashion and thus only one preparation is detailed.  $(\text{Me}_2\text{S})\text{AuCl}$  (215 mg, 0.74 mmol) was dissolved in 1,2-dichloroethane (5 mL) before a 1,2-dichloroethane (5 mL) solution of **4** (345 mg, 0.75 mmol) was added dropwise. The reaction was stirred for 20 min. at which time the solvent was removed *in vacuo*. The resulting white solid was washed with pentane (10 mL) to give a white solid. Yield: 450 mg, 0.65 mmol,

89%.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ): 7.70–7.75 (m, 6H, Ph), 7.56–7.60 (m, 4H, Ph), 7.32–7.44 (m, 10H, Ph), 3.70 (s, 3H,  $\text{OCH}_3$ ), 3.58 (s, 3H,  $\text{OCH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 51.28.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 164.6, 161.35, 143.2, 134.89, 134.01, 133.90, 129.82, 129.78, 129.29, 129.02, 128.64, 86.38, 68.1, 28.1, 20.1. C,H,N analysis calc. for  $\text{C}_{29}\text{H}_{26}\text{AuNO}_2\text{P}$  (683.92): C, 50.93; H, 3.83; N, 2.05. Found: C, 50.52; H, 3.85; N, 2.31. X-Ray quality crystals were grown by slow diffusion of pentane into a saturated dichloromethane solution. **13**: Yield: 324 mg, 0.44 mmol, 82%.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ): 8.03–8.09 (m, 2H, Ph), 7.48–7.77 (m, 10H, Ph), 7.35–7.41 (m, 2H, Ph), 7.26–7.30 (m, 6H, Ph), 4.32 (m, 1H,  $\text{CHCO}_2\text{CH}_3$ ), 3.30 (m, 1H,  $\text{CH}_2$  *trans* to  $\text{CO}_2\text{CH}_3$ ), 3.17 (s, 3H,  $\text{CH}_3$ ), 2.97–3.05 (m, 1H,  $\text{CH}_2$  *cis* to  $\text{CO}_2\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 49.89.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 171.84 (d,  $\text{COOCH}_3$ ), 146.5, 146.7, 144.58, 144.47, 133.69, 132.96, 132.86, 131.82, 131.72, 129.0, 128.95, 128.83, 128.28, 128.05, 128.01, 127.57, 127.51, 127.41, 80.00, 51.9, 29.5 (d,  $\text{CH}_2$ ). C,H,N analysis calc. for  $\text{C}_{31}\text{H}_{26}\text{AuClNO}_4\text{P}$  (739.94): C, 50.32; H, 3.54; N, 1.89. Found: C, 50.82; H, 3.93; N, 1.92.

#### X-Ray data collection and reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under a N<sub>2</sub> stream, thus maintaining a dry, O<sub>2</sub>-free environment for each crystal. The data for crystals of **10** were collected on a Nonius Kappa-CCD diffractometer; for crystals of **4**, **6**, **7**, and **8**, data were collected on a Bruker Apex II diffractometer. The data were collected at 150((2) K for all crystals. For crystals of **5**, data were processed with the DENZO-SMN package. For crystals of **4**, **6**, **7**, and **8**, the frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

#### Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations.<sup>10</sup> The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on  $F$ , minimizing the function  $\omega(F_o - F_c)^2$  where the weight  $\omega$  is defined as  $4F_o^2/2\sigma(F_o^2)$  and  $F_o$  and  $F_c$  are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they were bonded, assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they were bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in Table 1 and the Supporting Information.†

Table 1 Crystallographic data

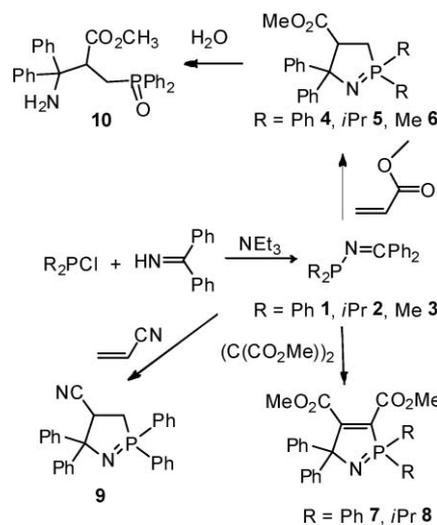
	(1)	(2)	(4)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
Formula	C <sub>22</sub> H <sub>30</sub> NP	C <sub>19</sub> H <sub>24</sub> NP	C <sub>29</sub> H <sub>36</sub> NO <sub>2</sub> P	C <sub>31</sub> H <sub>32</sub> NO <sub>4</sub> P	C <sub>35</sub> H <sub>30</sub> NO <sub>4</sub> P	C <sub>38</sub> H <sub>32</sub> N <sub>2</sub> P	C <sub>29</sub> H <sub>33</sub> NO <sub>3</sub> P	C <sub>60</sub> H <sub>56</sub> Ag <sub>2</sub> Cl <sub>4</sub> N <sub>4</sub>	C <sub>29</sub> H <sub>36</sub> AuCl <sub>3</sub> N	C <sub>33</sub> H <sub>36</sub> AuCl <sub>3</sub> N
Formula wt	365.39	297.36	451.48	655.93	439.47	418.45	469.49	1412.57	766.81	909.77
Cryst. syst.	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	P2 <sub>1</sub>	Triclinic	Triclinic	Monoclinic
Space grp	P2 <sub>1</sub> /c	P1	P1	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub>	P1	P1	P2 <sub>1</sub> /c
a (Å)	14.9681(5)	10.0312(11)	6.1469(12)	8.6024(6)	15.8375(8)	18.1088(15)	5.8622(12)	11.2357(9)	9.8098(3)	8.9595(7)
b (Å)	18.5680(6)	16.5830(19)	12.962(3)	18.0080(11)	8.0078(3)	5.9338(4)	17.456(4)	11.5055(9)	12.3568(3)	14.3413(11)
c (Å)	6.9944(2)	10.7114(11)	15.073(3)	21.0067(14)	19.2830(9)	20.6934(14)	11.936(2)	13.2632(11)	12.9623(3)	27.391(2)
α (°)	85.977(3)	90.32(3)	90.32(3)	96.638(4)	110.237(3)	96.973(5)	103.83(3)	112.819(4)	107.066(1)	98.231(5)
β (°)	90.314(2)	77.378(3)	93.83(3)	96.638(4)	110.237(3)	96.973(5)	103.83(3)	109.495(4)	102.188(2)	98.231(5)
γ (°)	1943.91(11)	1734.4(3)	1183.9(4)	3232.4(4)	2294.58(19)	2207.1(3)	1186.0(4)	91.874(4)	94.728(1)	3483.2(5)
V (Å <sup>3</sup> )	4	4	2	4	4	4	2	1	2	4
Z	4	4	2	4	4	4	2	1	2	4
Temp (K)	150	150	150	150	150	150	150	150	150	150
d(calc) g cm <sup>-3</sup>	1.248	1.139	1.226	1.348	1.272	1.259	1.315	1.603	1.756	1.735
R(int)	0.0565	0.0565	0.0344	0.0582	0.1036	0.1262	0.0299	0.0331	0.0522	0.0705
μ (cm <sup>-1</sup> )	0.150	0.153	0.143	0.372	0.151	0.142	0.148	0.969	5.431	4.691
Total data	19952	28715	20194	29348	40834	47239	1144	12144	11621	17636
Data used	5334	7894	5301	7927	5264	7699	4825	10212	34679	4915
Variables	244	379	298	388	280	280	306	373	347	403
R (>3σ)	0.0470	0.0515	0.0662	0.0410	0.0399	0.0509	0.0641	0.0412	0.0356	0.0439
R <sub>w</sub>	0.1231	0.1142	0.1712	0.0906	0.1022	0.1484	0.1446	0.1232	0.1135	0.0866
GOF	1.051	0.993	0.997	0.865	1.043	0.996	1.027	1.002	0.744	1.052

Data collected with Mo Kα radiation (λ = 0.71069 Å), <sup>a</sup>R = Σ(F<sub>o</sub> - F<sub>c</sub>)/ΣF<sub>o</sub>, <sup>b</sup>R<sub>w</sub> = {Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)]/Σ[w(F<sub>o</sub>)]}

## Results and discussion

## Ligand synthesis

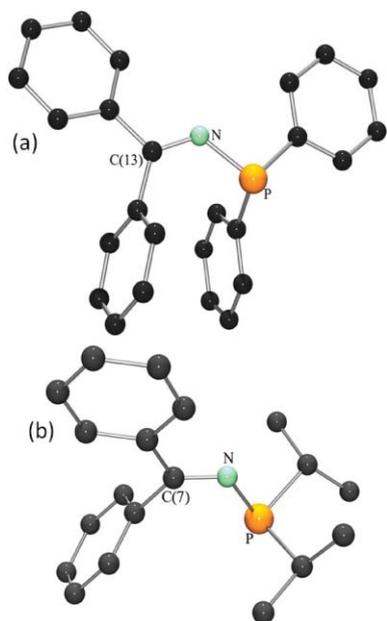
A convenient synthesis of cyclic phosphinimines was established by Schmidpeter *et al.*<sup>9</sup> in the 1970s. While these researchers examined the cycloaddition chemistry of these systems, the utility of such compounds in metal complex chemistry has not been explored. Thus, we began with the synthesis of a series of ligands using the Schmidpeter methodology. To this end, the compounds R<sub>2</sub>PNCPh<sub>2</sub> (R = Ph **1**, *i*-Pr **2**, Me **3**) were prepared *via* the reaction of benzophenone-imine with the corresponding chlorophosphine in the presence of base as per literature precedent (Scheme 2). The NMR data was consistent with the formulations and crystallographic data was obtained for **1** and **2** which confirmed the formulations (Fig. 1). The metric parameters within the two molecules were unexceptional with P–N bond distances of 1.7203(14) and 1.7419(17) Å, respectively, and N=C bond lengths of 1.282(2) Å.



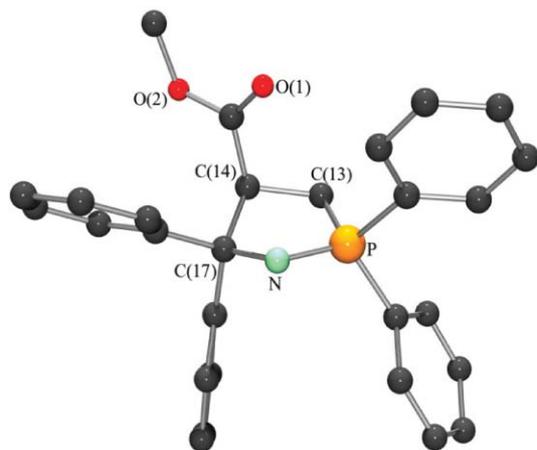
Scheme 2 Synthesis of compounds 1–10.

Cycloaddition of **1–3** to methyl acrylate affords the phosphinimines R<sub>2</sub>PNCPh<sub>2</sub>(CH<sub>2</sub>CH(CO<sub>2</sub>Me)) (R = Ph **4**, *i*-Pr **5**, Me **6**) in 86, 63 and 85% yields, respectively. The NMR data were as expected with <sup>31</sup>P{<sup>1</sup>H} chemical shifts of 48.6, 73.8 and 52.7 ppm, respectively. The crystal structure of **4** (Fig. 2) confirmed the formation of a puckered five-membered PNC<sub>3</sub> ring. The ester substituent adopts an axial position with respect to the ring, presumably minimizing steric conflict with the phenyl substituents on the adjacent carbon. The P–N and P–C bond distances within the ring are found to be 1.573(3) Å and 1.823(3) Å, respectively; while the N–C distance and the C–C distance within the ring were 1.471(4) Å and 1.536(4) Å, respectively. The corresponding P–N–C angle in **4** was found to be 109.0(2)°.

Attempts to effect similar cyclizations with more electron-rich alkynes such as PhCCPh, *t*BuCCPh, Me<sub>3</sub>SiCCPh, PhCCH were unsuccessful. However, the corresponding reactions of **1** and **2** with dimethyl acetylenedicarboxylate affords the related cyclized products R<sub>2</sub>PNCPh<sub>2</sub>(CCOMe)<sub>2</sub> (R = Ph **7**, *i*-Pr **8**) in approximately 80% yields.

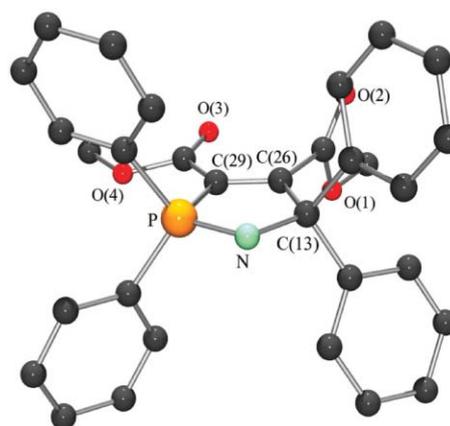


**Fig. 1** POV-ray depictions (a): **1**, (b): one of the two molecules in the asymmetric unit of **2**, hydrogen atoms are omitted for clarity.

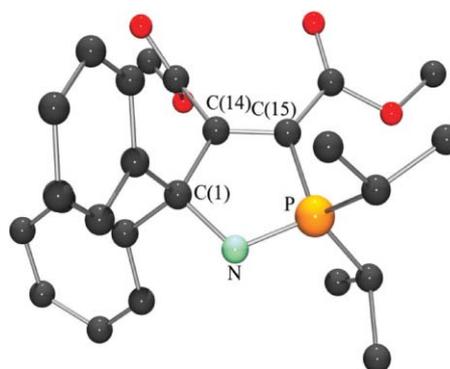


**Fig. 2** POV-ray depiction of **4**, hydrogen atoms are omitted for clarity.

These five-membered phosphinimine species retain a C=C double bond in the ring and are essentially planar. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data were as expected while the  $^{31}\text{P}\{^1\text{H}\}$  chemical shifts of **7** and **8** were 49.0 ppm and 73.8 ppm, respectively. Whereas compound **7** has been previously reported, X-ray crystallographic data for **7** confirmed the cyclic nature and revealed P–N, P–C, N–C and C=C bond lengths of 1.5749(15) Å, 1.7998(17) Å, 1.457(2) Å and 1.331(2) Å in the heterocyclic ring (Fig. 3). The C–N–P angle was found to be 111.98(11)°. The increase in the C–N–P angle in comparison to that in **4** is consistent with the rigidity resulting from the planarity of the five-membered ring. In a similar fashion, the crystallography study of **8** (Fig. 4) revealed a planar structure where P–N and N=C bond distances were found to be 1.5801(13) Å and 1.4618(19) Å, respectively, while the corresponding C–N–P angle was 112.21(9)°. These structural perturbations are consistent with the presence of a more electron-rich P centre in **8**.



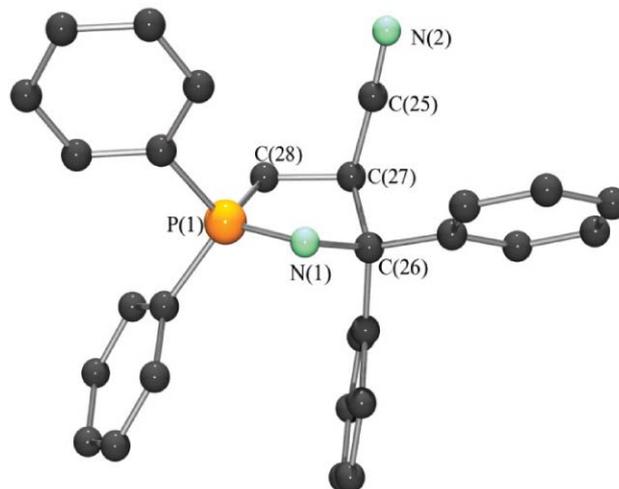
**Fig. 3** POV-ray depiction of **7**, hydrogen atoms are omitted for clarity.



**Fig. 4** POV-ray depiction of **8**, hydrogen atoms are omitted for clarity.

Reaction of **1** with acrylonitrile results in the isolation of the white solid in 77% yield. This product **9** was formulated as  $\text{Ph}_2\text{PNCPh}_2(\text{CH}_2\text{CH}(\text{CN}))$ . The spectroscopic data are similar to the cyclic phosphinimines described above, with a  $^{31}\text{P}\{^1\text{H}\}$  NMR resonance at 46.0 ppm. The infrared spectrum was also consistent with the presence of the nitrile fragment exhibiting a C≡N stretch at 2240  $\text{cm}^{-1}$ .

Once again, crystallographic data confirmed the formulation unambiguously (Fig. 5). Similar to **4**, the ring conformation



**Fig. 5** POV-ray depiction of **9**, hydrogen atoms are omitted for clarity.

is puckered with the nitrile substituent adopting an axial position. The P–N and N–C bond distances were found to be 1.5892(13) Å and 1.4802(19) Å, respectively, while the C–N–P angle was determined to be 107.81(9)°. The comparatively long P–N and N–C bonds, together with the small angle at N are consistent with the electron-withdrawing nature of the nitrile substituent.

These phosphinimines proved to be moisture sensitive. In the case of **4**, exposure to H<sub>2</sub>O resulted in the hydrolytic ring opening of the phosphinimine. This results in the cleavage of the P–N bond and formation of the corresponding amine-phosphine-oxide species Ph<sub>2</sub>C(NH<sub>2</sub>)CH(CO<sub>2</sub>Me)CH<sub>2</sub>P(O)Ph<sub>2</sub> **10**. This species is isolated as a white solid, The <sup>1</sup>H NMR spectrum reveals a resonance at 1.70–2.30 attributable to the NH<sub>2</sub> fragment, while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a resonance at 29.9 ppm, typical of phosphine oxides. The formulation of this hydrolysis product was confirmed crystallographically (Fig. 6). The structure reveals the open chain nature of this species with a P–O bond distance of 1.490(3) Å.

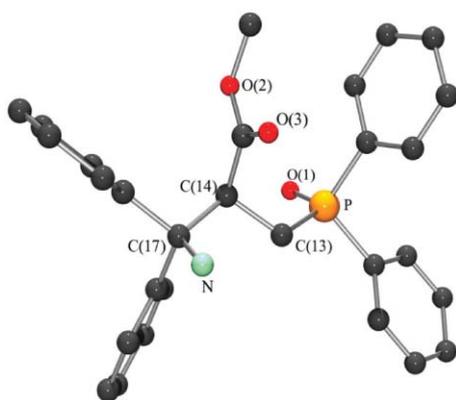


Fig. 6 POV-ray depiction of **10**, hydrogen atoms are omitted for clarity.

## Complexation

In examining the potential of these cyclic phosphinimines as ligands, the reactions of **4** with Ag(NO<sub>3</sub>) was first performed. Employing a 1 : 1 ligand : silver stoichiometry, crystals of a new species were isolated in 73% yield. While the NMR data was consistent with the complexation of the ligand, the nature of the product **11** was only unambiguously confirmed *via* X-ray diffraction methods. These experiments revealed the formulation of **11** to be [(Ph<sub>2</sub>PNCPh<sub>2</sub>(CH<sub>2</sub>CH(CO<sub>2</sub>Me))<sub>2</sub>Ag) [(NO<sub>3</sub>)<sub>2</sub>Ag] (Fig. 7, Scheme 3). The anion is a linear Ag ion, in which two nitrate groups bind *via* one oxygen atom to the Ag centre with a Ag–O distance of 2.223(3) Å. The cation of this salt is a two-coordinate pseudo-linear Ag ion coordinated to the N of two phosphinimine ligands. The Ag–N distance was determined to be 2.0675(17) Å, while the linearity of the N–Ag–N vector was crystallographically imposed. This distance is similar to the distances reported for a series of Ag-carbene complexes of the form LAgCl where the Ag–C distances range from 2.094(6) to 2.060(19) Å.<sup>11</sup> The geometry of the cation of **11** is similar to that seen in the bis-carbene complex [(C<sub>6</sub>H<sub>4</sub>(NEt)<sub>2</sub>C)<sub>2</sub>Ag][AgBr<sub>2</sub>]<sup>12</sup> although the Ag–N distance in **11** is slightly shorter than that reported for this carbene species (2.073(26) Å).

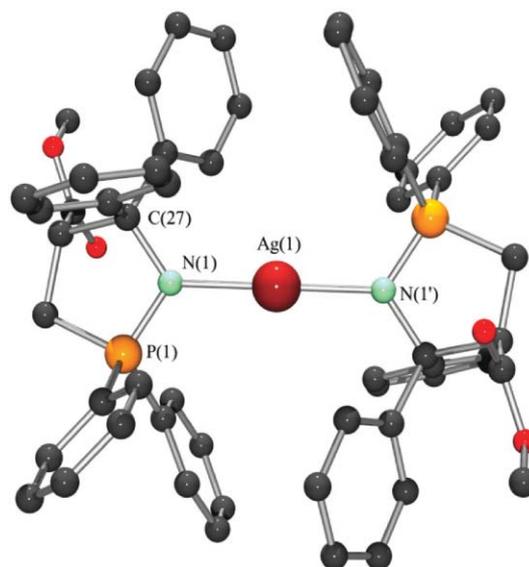
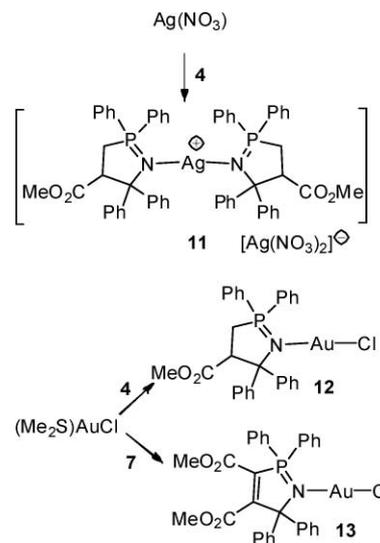


Fig. 7 POV-ray depiction of the cation of **11**, hydrogen atoms are omitted for clarity.



Scheme 3 Synthesis of compounds **11**–**13**.

In reactions conducted in a similar fashion, the cyclic phosphinimines **4** and **7** were reacted with (Me<sub>2</sub>S)AuCl. This resulted in the isolation of Ph<sub>2</sub>PNCPh<sub>2</sub>(CH<sub>2</sub>CH(CO<sub>2</sub>Me)AuCl **12** and (Ph<sub>2</sub>PNCPh<sub>2</sub>(C(CO<sub>2</sub>Me)<sub>2</sub>)AuCl **13**, respectively, in yields of 89 and 82%. While coordination to Au was inferred by the observation of a complexation shift of the NMR resonances, X-ray crystallography was employed to confirm the formulations (Fig. 8, 9, Scheme 3). In both cases these molecules were linear Au(I) complexes in which the N of the cyclic phosphinimine was coordinated to a AuCl fragment. The Au–N distances in **12** and **13** were determined to be 2.0253(13) and 2.010(7) Å, with corresponding Au–Cl distances of 2.2612(4) and 2.257(2) Å, and N–Au–Cl angles of 177.07(4)° and 179.7(2)°, respectively.

The Au–N distances in **12** and **13** are slightly longer than those observed for Au–C bond lengths in related NHC-carbene-AuCl complexes,<sup>13</sup> which range from 1.965(5) Å to 2.018(3) Å, and slight shorter than those seen in the CAAC complex cations of

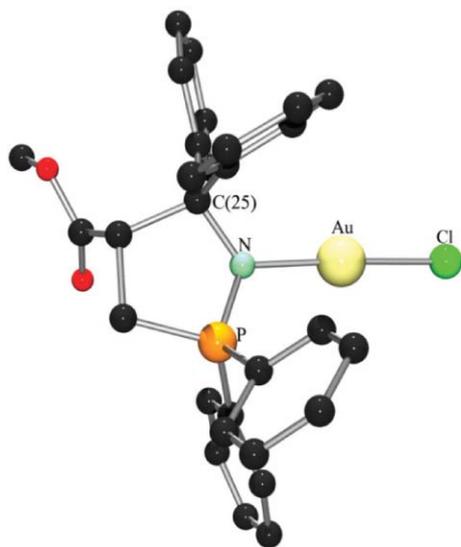


Fig. 8 POV-ray depiction of **12**, hydrogen atoms are omitted for clarity.

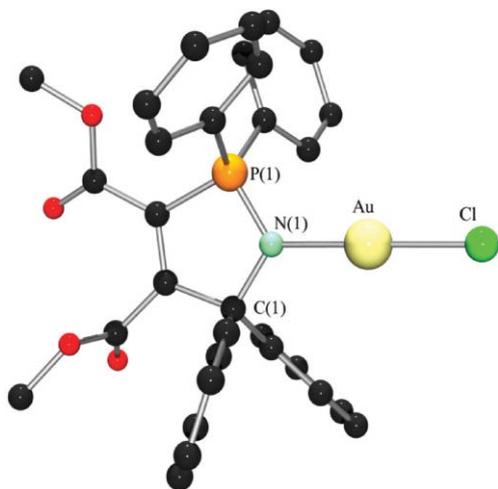


Fig. 9 POV-ray depictions of **13**, hydrogen atoms are omitted for clarity.

the form  $[L_2Au]^+$  (2.0321(11) 2.033(4) Å).<sup>3b</sup> Consequently the Au–Cl distances in **12** and **13** are slightly shorter as the Au–Cl in the related carbene complexes range from 2.2698(11) to 2.3061(11) Å.

While the structural features of these cyclic phosphinimine ligands are reminiscent of that of carbene ligands the data presented herein is consistent with the anticipated strong donor ability of these ligands. The metric data suggest that these ligands exhibit similar sigma donor abilities to N-heterocyclic carbenes, however the geminal substitution at the P and C adjacent to N generates a donor environment that is even more sterically encumbered than that in bulky N-heterocyclic carbenes.

## Conclusions

In conclusion, in this initial study in this area, we have described the facile syntheses of a number of cyclic phosphinimines, which

allows for ready derivatization of the substitution on P and on the backbone of the ring. In addition, we have shown that these species act as strong sigma donor ligands for Ag(I) and Au(I), while providing a highly sterically encumbered donor environment. The utility of these attributes in subsequent chemistry and catalysis are under study and will be reported in due course.

## Acknowledgements

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