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# Copper and palladium complexes of 2-(diphenylphosphino)-N, N-dimethylbenzylamine and its selenide derivative

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#### ABSTRACT

The synthesis of 2-(diphenylphosphino)-N,N-dimethylbenzylamine, { $Ph_2P(C_6H_4CH_2NMe_2-o)$ } (1) and its chalcogenide derivatives, { $Ph_2P(E)(C_6H_4CH_2NMe_2-o)$ } (E = O, **2**; S, **3**; Se, **4**) were described. The reaction of **1** with [ $Pd(\eta^3-C_3H_5)Cl$ ]<sub>2</sub> affords a cationic complex [{ $Ph_2P(C_6H_4CH_2NMe_2-o)$ } $Pd(\eta^3-C_3H_5)$ ][OTf] (**5**) in good yield. The treatment of **1** with copper halides in 1:1 M ratio afforded complexes of the type [{ $Ph_2P(C_6H_4CH_2NMe_2-o)$ }(CuX)]<sub>2</sub> (X = Br, **6**; X = I, **7**). Similar reactions between copper halides and Ph\_2RP(Se) (**4**) produced [{ $Ph_2P(Se)(C_6H_4CH_2NMe_2-o)$ }(CuX)]<sub>2</sub> (X = Br, **8**; X = I, **9**). The copper complex **7** upon treatment with 2,2'-bipyridine and 1,10-phenanthroline produced mixed ligand complexes [{ $Ph_2P(C_6H_4CH_2NMe_2-o)$ }Cu(2,2'-bpy)]I (**10**) and [{ $Ph_2P(C_6H_4CH_2NMe_2-o)$ }Cu(1,10-phen)]I (**11**), respectively. Single crystal X-ray structures of **7** and **9** are described.

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#### 1. Introduction

The phosphorus(III) based hemilabile ligands containing N, O or S donor atoms attracted much attention in recent years mainly due to their applications in a variety of organic transformations [1]. These ligand systems were successfully employed in Suzuki-Miyaura [2,3], Mizoroki-Heck [4] cross coupling reactions, hydroformylation [5], hydrogenation [6-8] and many other catalytic reactions [9-11]. The difference in the coordination properties of two donor groups is responsible for the distinct interaction between donor atoms and the metal centers [12,13]. The soft donor atom forms stronger bond with soft metal centers, whereas the labile hard donor site provides temporarily coordinative saturation to metal centre and also detaches as and when it is required during catalytic reactions. The P,N bidentate ligands are important class of hemilabile ligands as they can exhibit either chelating mode of coordination or bind to the metal centres in a monodentate fashion *via* phosphorus leaving the nitrogen atom uncoordinated [14–17]. The coordination chemistry of 2-(diphenylphosphino)-N. N-dimethylbenzylamine is interesting due to its versatile coordination behavior [18,19]. Further, oxidation of phosphorus atom in 2-(diphenylphosphino)-N,N-dimethylbenzylamine by chalcogens can furnish N<sup>O</sup>, N<sup>S</sup> or N<sup>Se</sup> type of heterodifunctional ligands [20]. These ligand systems can coordinate to metal centre through chalcogens and pendant amine group to form seven-membered chelate complexes. Herein, we report the palladium(II) and copper(I) complexes of 2-(diphenylphosphino)-N,N-dimethylbenzylamine and its selenide derivative.

#### 2. Results and discussion

#### 2.1. Oxidation reactions of 2-(diphenylphosphino)-N,Ndimethylbenzylamine (**1**)

2-(Diphenylphosphino)-N,N-dimethylbenzylamine (1) was prepared by reacting *in situ* generated *o*-lithiated amine (LiC<sub>6</sub>H<sub>4</sub> CH<sub>2</sub>NMe<sub>2</sub>) with PPh<sub>2</sub>Cl [19,21]. The reaction of **1** with aqueous H<sub>2</sub>O<sub>2</sub> in tetrahydrofuran at room temperature gave 2-(diphenylphosphoryl)-N,N-dimethylbenzylamine (**2**). Similar reaction of **1** with elemental sulfur or selenium [22] in toluene under refluxing conditions afforded Ph<sub>2</sub>P(E)(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-*o*) (E = S, **3**; Se, **4**) in good yield. The <sup>31</sup>P NMR spectra of chalcogenides **2–4** showed sharp singlets at 33.7, 41.9 and 31.2 ppm, respectively, with the selenide derivative **4** exhibiting characteristic selenium satellite peaks with a <sup>1</sup>J<sub>PSe</sub> coupling of 724.6 Hz. The molecular composition and structures of compounds **2–4** were further confirmed by <sup>1</sup>H NMR data and HRMS analysis.

Compound **1** containing both trivalent phosphorus and NMe<sub>2</sub> group is an ideal ligand for transition metal chemistry. The reaction of **1** with  $[Pd(\eta^3-C_3H_5)Cl]_2$  in a mixture of dichloromethane and acetonitrile followed by the addition of AgOTf afforded a cationic complex  $[{Ph_2P(C_6H_4CH_2NMe_2-o)}Pd(\eta^3-C_3H_5)][OTf]$  (**5**) in good





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Scheme 1.

yield (Scheme 1). The mass spectrum of **5** shows a peak at m/z 466.1 for [M–OTf] ion. The <sup>31</sup>P NMR spectrum of the complex **5** presents a sharp singlet at 21.9 ppm. The presence of coordinated allyl group was confirmed by its <sup>1</sup>H NMR spectrum.

Copper(I) halides, in particular cuprous iodide, display a wide range of structures when coordinated to phosphorus based ligands [23–27]. The reaction of copper halides with 1 in 1:1 M ratio afforded the complexes  $[{Ph_2P(C_6H_4CH_2NMe_2-o)}(CuX)]_2$  (X = Br, 6; X = I, 7) with ligand exhibiting chelating mode of coordination. The <sup>31</sup>P NMR spectra of compounds **6** and **7** consist of broad singlets at -16.2 and -14.5 ppm, respectively. The mass spectrum of complex **7** shows a molecular ion peak at m/z 1021.17, whereas **6** show a peak at m/z 845.22 due to the cation  $[M-Br]^+$ . The reaction of copper halides with 4 in 1:1 mixture of acetonitrile and dichloromethane yielded complexes of the type [ $\{Ph_2P(Se)\}$  $(C_6H_4CH_2NMe_2-o)$ }(CuX)]<sub>2</sub> (X = Br, **8**; X = I, **9**). The <sup>31</sup>P NMR spectra of compounds 8 and 9 show broad singlets at 23.2 and 26.4 ppm, respectively, with **9** showing  ${}^{1}J_{PSe}$  coupling of 650.2 Hz. Due to broad signal,  ${}^{1}J_{PSe}$  was not observed in case of **8**. The  ${}^{1}H$  NMR and elemental analysis data are consistent with the proposed structures. The structures of 7 and 9 have been confirmed by single crystal X-ray diffraction studies.

The mixed donor complexes,  $[\{Ph_2P(C_6H_4CH_2NMe_2-o)\}Cu$ (2,2'-bpy)]l (**10**) and  $[\{Ph_2P(C_6H_4CH_2NMe_2-o)\}Cu(1,10-phen)]I$ (**11**) were synthesized in good yield by the reactions of **7** with 2,2'-bipyridine or 1,10-phenanthroline in 1:2 M ratios at room temperature (Scheme 2). The yellow crystalline compounds **10** and **11** are characterized by <sup>31</sup>P, <sup>1</sup>H NMR spectra and elemental analyses. The <sup>31</sup>P NMR spectra of complexes **10** and **11** consist of broad singlets at –14.9 and –9.5 ppm, respectively.

## 2.2. Molecular structures of complexes, $[{Ph_2P(C_6H_4CH_2NMe_2-o)}(CuI)]_2$ (7) and $[{Ph_2P(Se)(C_6H_4CH_2NMe_2-o)}(CuI)]_2$ (9)

The perspective views of molecular structures of 7 and  $9^1$ along with the atom labeling schemes are shown in Figs. 1 and 2. The compounds 7 and 9 crystallize in triclinic and monoclinic crystal systems, respectively. The unit cell of binuclear copper complex 7 consists of two independent molecules with one of them possessing center of symmetry. The copper centers in 7 display a distorted tet-

rahedral geometry with internal bond angles ranging from 96.82(11) to 122.65(4)°. The Cu<sub>2</sub>I<sub>2</sub> rhombic units in both the molecules of **7** are planar. The Cu–I bond distances in asymmetric molecule are in the range of 2.5742(11) - 2.7077(10) Å, whereas in the symmetric molecule the average Cu–I bond distance is 2.640 Å. The Cu–P1, Cu2–P2 and Cu3–P3 bond distances are 2.2403(14), 2.2334(14) and 2.2349(14) Å, respectively. The Cu–N bond distances in **7** are in the range of 2.180(4) – 2.201(4) Å.

The complex **9** was crystallized from a mixture of dichloromethane and petroleum ether solution at room temperature. The crystal structure of **9** reveals that the copper centers are tetrahedrally coordinated to nitrogen, selenium and two bridging iodide ions. The average Cu–I bond distance is 2.630 Å which is comparable to that of complex **7**. The seven membered rings in **9** adopt the distorted chair conformations. The Cu1–Se1 bond length [2.4298(17) Å] in **9** is shorter than that found in [Ph<sub>3</sub>PSeCu ( $\mu$ -Br)NCCH<sub>3</sub>]<sub>2</sub> [2.459(2) Å] [28] and [Cu( $\kappa^2$ -P,P'-DPEphos) ( $\kappa^2$ -P,Se-DPEphos-Se)][BF<sub>4</sub>] [2.5877(6) Å] [29].

#### 3. Conclusions

Copper(I) and palladium(II) complexes of 2-(diphenylphosphino)-N,N-dimethylbenzylamine (1) have been synthesized. The binuclear copper complex upon treatment with pyridyl ligands afforded mononuclear mixed ligand complexes. The selenide **4** coordinates to the copper centre through selenium and nitrogen atoms in a chelating fashion to form a seven membered ring. Further catalytic reactions are under active investigations in our laboratory.

#### 4. Experimental section

#### 4.1. General procedures

All manipulations were performed using standard Schlenk techniques under nitrogen atmosphere unless otherwise stated. All the solvents were purified by conventional procedures and distilled prior to use. The compounds, 2-(diphenylphosphino)-N,N-dimethylbenzylamine [19],  $[Pd(\eta^3-C_3H_5)Cl]_2$  [30] and CuBr [31] were prepared according to the published procedures. Other chemicals were obtained from commercial sources and purified prior to use.

#### 4.2. Instrumentation

The NMR spectra were recorded at the following frequencies: 400 MHz (<sup>1</sup>H), and 162 MHz (<sup>31</sup>P) ( $\delta$  in ppm) using Bruker AV 400 spectrometer. The <sup>31</sup>P NMR spectra were acquired using broad band decoupling. The spectra were recorded in CDCl<sub>3</sub> (or DMSO-d<sub>6</sub>) solutions with CDCl<sub>3</sub> (or DMSO-d<sub>6</sub>) as an internal lock; chemical shifts of <sup>1</sup>H spectra are reported in ppm downfield from TMS, used

<sup>&</sup>lt;sup>1</sup> Crystal data for **7**: C<sub>42</sub>H<sub>44</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>2</sub>P<sub>2</sub>, Mw = 1019.61, Triclinic, PĪ (No. 02), *a* = 14.090(3) Å, *b* = 13.945(2) Å *c* = 18.698(2) Å *V* = 3300.7(8) Å<sup>3</sup>, *Z* = 3,  $\rho_{calc} =$ 1.539 gcm<sup>-3</sup>,  $\mu$  (Mo Kα) = 2.471 mm<sup>-1</sup>, *F*(000) = 1512, *S* = 1.17, *T* = 100 K. A total of 111650 reflections (3.0 < *h* < 25.0) were processed of which 16600, were unique ( $R_{int} = 0.044$ ). The final *wR* value was 0.111 (all data) and *R* = 0.0502 [*I* > 2*r*(*I*)]. Crystal data for **9**: C<sub>42</sub>H<sub>44</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Se<sub>2</sub>, Mw = 1177.53, Monoclinic, *P*2–1/*n* (No. 14), *a* = 12.510(5) Å, *b* = 13.372(6) Å *c* = 12.609(6) Å *V* = 2067.1(16) Å<sup>3</sup>, *Z* = 2,  $\rho_{calc} =$ 1.892gcm<sup>-3</sup>,  $\mu$  (Mo Kα) = 4.394 mm<sup>-1</sup>, *F*(000) = 1144, *S* = 0.95, *T* = 100 K. A total of 28997 reflections (3.0 < *h* < 25.0) were processed of which 4245, were unique ( $R_{int} = 0.094$ ). The final *wR* value was 0.1732 (all data), *R* = 0.0633 [*I* > 2*r*(*I*)].



**Fig. 1.** The molecular structure of [{Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-*o*)](Cul)]<sub>2</sub> (**7**). All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond distances [Å]: Cu1–I1, 2.6000(11); Cu1–I2, 2.7077(10); Cu1–P1, 2.2403(14); Cu1–N1, 2.201(4); Cu2–I1, 2.6722(10); Cu2–I2, 2.5742(11); Cu2–P2, 2.2334(14); Cu2–N2, 2.180(4); 2.180(4); Cu3–I3, 2.6806(13); Cu3–P3, 2.2349(14); Cu3–N3, 2.186(4). Selected bond angles [°]: Cu1–I1–Cu2, 67.01(2); P1–Cu1–N1, 97.01(11); P1–Cu1–I1, 122.65(4); P1–Cu1–I2, 106.76(4); I1–Cu1–I2, 112.07(3); Cu2–P2–N2, 96.82(11); I3–Cu3–N3, 110.36(11).



**Fig. 2.** The molecular structure of  $[\{Ph_2P(Se)(C_6H_4CH_2NMe_2-o)\}(Cul)]_2$  (**9**). All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond distances [Å]: Cu1–I1, 2.6433(17); Cu1<sup>i</sup>–I1, 2.6274(16); Cu1–Se1, 2.4298(17); P1–Se1, 2.119(2); Cu1–N1, 2.145(7). Selected bond angles  $[\circ]$ : Cu1–I1–Cu1<sup>i</sup>, 59.46(3); Cu1–Se1–P1, 103.72(7); I1–Cu1–Se1, 99.76(4); I1–Cu1–N1, 108.68(18); I1–Cu1–I1<sup>i</sup>, 120.54(4); Se1–Cu1–N1, 108.65(17); I1<sup>i</sup>–Cu1–Se1, 112.15(4); Se1–P1–C1, 110.6(3).

as an internal standard. The chemical shifts of  ${}^{31}P{}^{1}H$  NMR spectra are referred to 85% H<sub>3</sub>PO<sub>4</sub> used as an external standard. The microanalyses were performed using a Carlo Erba Model 1112 elemental analyzer. Mass spectra were recorded in Waters Q-Tof micro (YA-105). The melting points were observed in capillary tubes and are uncorrected.

#### 4.3. Synthesis of $Ph_2P(O)(C_6H_4CH_2NMe_2-o)$ (2)

A 30% solution of  $H_2O_2$  (0.008 g, 0.235 mmol) in 10 mL of THF was added dropwise to solution of ligand **1** (0.07 g, 0.219 mmol) in the same solvent (6 mL) at room temperature. The reaction mixture was stirred for 10 h. The solvent was removed under vacuum,

to get product as colorless viscous liquid. Yield: 93% (0.068 g). HRMS Calc. for C<sub>21</sub>H<sub>23</sub>NPO (M+H): 336.1517. Found: 336.1515. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.43–7.00 (m, Ph, 14H), 5.03 (s, CH<sub>2</sub>, 2H), 3.29 (s, NMe<sub>2</sub>, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  33.7 (s).

#### 4.4. Synthesis of $Ph_2P(S)(C_6H_4CH_2NMe_2-o)$ (3)

A mixture of elemental sulfur (0.008 g, 0. 25 mmol) and **1** (0.077 g, 0.241 mmol) in toluene (20 mL) was refluxed for 10 h. The reaction mixture was allowed to cool to room temperature; solvent was removed under reduced pressure. The sulfide **3** was isolated as an yellow viscous liquid. Yield: 89% (0.075 g). HRMS Calc for C<sub>21</sub>H<sub>23</sub>NPS (M+H): 352.1289. Found: 352.1299. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.91–6.88 (m, Ph, 14H), 3.61 (s, CH<sub>2</sub>, 2H), 1.91 (s, NMe<sub>2</sub>, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  41.9 (s).

#### 4.5. Synthesis of $Ph_2P(Se)(C_6H_4CH_2NMe_2-o)$ (4)

A mixture of elemental selenium (0.02 g, 0.252 mmol) and **1** (0.1 g, 0.251 mmol) in toluene (30 mL) was refluxed for 10 h. The reaction mixture was allowed to cool to room temperature and filtered through Celite. The solvent was removed under reduced pressure to give **4** as an off-white powder. Yield: 91% (0.112 g). *Anal.* Calc. for C<sub>21</sub>H<sub>23</sub>NPSe: C, 63.14; H, 5.55; N, 3.50. Found: C, 63.28; H, 5.43; N, 3.37%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.88–6.86 (m, Ph, 14H), 3.70 (s, CH<sub>2</sub>, 2H), 2.01 (s, NMe<sub>2</sub>, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  31.2 (s, <sup>1</sup>J<sub>PSe</sub> = 724.6 Hz).

#### 4.6. Synthesis of $[{Ph_2P(C_6H_4CH_2NMe_2-0)}Pd(\eta^3-C_3H_5)](OTf)$ (5)

To a solution of  $[Pd(\eta^3-C_3H_5)Cl]_2$  (0.029 g, 0.076 mmol) in 10 mL of dichloromethane was added dropwise **1** (0.05 g, 0.158 mmol) in the same solvent (5 mL) at room temperature. The reaction mixture was stirred for 2 h. AgOTf (0.041 g, 0.159 mmol) in CH<sub>3</sub>CN (5 mL) was added to the reaction mixture and stirring was continued for another 2 h. AgCl precipitate formed was removed by filtration. The solvents were removed under vacuum to get **5** as an yellow crystalline solid. Yield: 84% (0.066 g). Mp: >120 °C (dec). *Anal.* Calc. for C<sub>25</sub>H<sub>27</sub>F<sub>3</sub>NO<sub>3</sub>PPdS: C, 48.75; H, 4.42; N, 2.27; S, 5.21. Found: C, 48.45; H, 4.43; N, 2.37; S, 4.98%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.59–6.96 (m, Ar, 14H), 6.05 (m, allyl, <sup>1</sup>H), 4.95 (br s, allyl, <sup>1</sup>H), 4.21 (br s, allyl, <sup>1</sup>H) 3.61 (s, CH<sub>2</sub>, 2H), 3.24 (m, allyl, 2H), 2.90 (s, NMe<sub>2</sub>, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  22.0 (s).

#### 4.7. Synthesis of $[{Ph_2P(C_6H_4CH_2NMe_2-o)}(CuBr)]_2$ (**6**)

To a solution of CuBr (0.0135 g, 0.094 mmol) in 10 mL of acetonitrile was added dropwise **1** (0.03 g, 0.094 mmol) in dichloromethane (5 mL) at room temperature. The reaction mixture was stirred for 4 h. The solvent was removed under reduced pressure to get **6** as a pale yellow solid. Analtyically pure product of **6** was obtained by recrystallizing the crude product in a 1:2 mixture of dichloromethane and petroleum ether. Yield: 81% (0.035 g). Mp: 158–160 °C. *Anal.* Calc. for C<sub>42</sub>H<sub>44</sub>Cu<sub>2</sub>Br<sub>2</sub>N<sub>2</sub>P<sub>2</sub>: C, 54.66; H, 4.80; N, 3.03. Found: C, 54.95; H, 4.85; N, 2.88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.52–6.83 (m, Ar, 28H), 3.50 (s, CH<sub>2</sub>, 4H), 2.42 (s, NMe<sub>2</sub>, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  –16.2 (br s). MS (EI): *m/z* 845.22 [M–Br]<sup>+</sup>.

#### 4.8. Synthesis of [{Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-o)}(CuI)]<sub>2</sub> (7)

This was synthesized by a procedure similar to that of **6** using Cul (0.04 g, 0.21 mmol) and **1** (0.067 g, 0.21 mmol). Yield: 76% (0.089 g). Mp: 216–220 °C. *Anal.* Calc. for  $C_{42}H_{44}Cu_2I_2N_2P_2$ ·2CH<sub>3</sub>CN: C, 50.18; H, 4.58; N, 5.09. Found: C, 49.98; H, 4.42; N, 5.13%. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53–6.82 (m, Ar, 28H), 3.51 (s, CH<sub>2</sub>, 4H), 2.37 (s, NMe<sub>2</sub>, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  –14.5 (br s). MS (EI): *m/z* 1021.17 [M+1]<sup>+</sup>.

#### 4.9. Synthesis of $[{Ph_2P(Se)(C_6H_4CH_2NMe_2-o)}(CuBr)]_2$ (8)

A solution of CuBr (0.0173 g, 0.12 mmol) in 10 mL of acetonitrile was added dropwise to a solution of **4** (0.048 g, 0.12 mmol) in 10 mL of dichloromethane at room temperature. The reaction mixture was stirred for 4 h. The solvent was removed under reduced pressure to obtain **8** as a brown crystalline solid. Yield: 82% (0.054 g). Mp: >195 °C (dec). *Anal.* Calc. for C<sub>42</sub>H<sub>44</sub>Cu<sub>2</sub>Br<sub>2</sub>N<sub>2</sub>P<sub>2-</sub>Se<sub>2</sub>·CH<sub>3</sub>CN: C, 46.99; H, 4.21; N, 3.74. Found: C, 46.77; H, 4.10; N, 3.79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73–7.02 (m, Ar, 28H), 3.43 (s, CH<sub>2</sub>, 4H), 2.46 (s, NMe<sub>2</sub>, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  23.2 (br s).

#### 4.10. Synthesis of $[{Ph_2P(Se)(C_6H_4CH_2NMe_2-o)}(CuI)]_2$ (9)

This was synthesized by a procedure similar to that of **8** using Cul (0.029 g, 0.151 mmol) and **4** (0.06 g, 0.151 mmol). Yield: 76% (0.068 g). Mp: >219 °C (dec). *Anal.* Calc. for  $C_{42}H_{44}Cu_2I_2N_2P_2Se_2$ : C, 42.79; H, 3.77; N, 2.38. Found: C, 42.54; H, 3.76; N, 2.43%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.82–7.06 (m, Ph, 28H), 3.50 (s, CH<sub>2</sub>, 4H), 2.40 (s, NMe<sub>2</sub>, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  26.1 (br s, <sup>1</sup>J<sub>PSe</sub> = 650.2).

#### 4.11. Synthesis of [{Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-0)}Cu(2,2'-bpy)]I (**10**)

To a suspension of **7** (0.0304 g, 0.029 mmol) in dichloromethane (10 mL), was added 2,2'-bipyridine (0.0093 g, 0.059 mmol) also in dichloromethane (5 mL). After 4 h, the clear yellow solution was dried under reduced pressure to afford **10** as an yellow solid. Yield: 78% (0.031 g). Mp: 150–152 °C. *Anal.* Calc. for C<sub>31</sub>H<sub>30</sub>CulN<sub>3</sub>P·CH<sub>2</sub>-Cl<sub>2</sub>: C, 51.26; H, 4.30; N, 5.60. Found: C, 51.15; H, 4.24; N, 5.48%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.55–6.98 (m, Ar, 22H), 3.54 (s, CH<sub>2</sub>, 2H), 2.39 (s, NMe<sub>2</sub>, 6H).<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  –14.9 (br s).

#### 4.12. Synthesis of [{Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>-o)}Cu(1,10-phen)]I (**11**)

This was synthesized by a procedure similar to that of **10** using **7** (0.034 g, 0.033 mmol) and 1,10-phenanthorline (0.012 mg, 0.066 mmol). Yield: 75% (0.0345 g). Mp: 197–200 °C. *Anal.* Calc. for  $C_{33}H_{30}$ CulN<sub>3</sub>P·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 54.93; H, 4.27; N, 5.74. Found: C, 54.67; H, 4.46; N, 5.83%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67–6.92 (m, Ar, 22H), 3.61 (s, CH<sub>2</sub>, 2H), 2.29 (s, NMe<sub>2</sub>, 6H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  –9.5 (br s).

#### 4.13. X-ray Crystallography

Crystals of each of the compounds **7** and **9** suitable for X-ray crystal analysis were mounted on a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected using three sets of 606 scans in  $\omega$  (0.3° per scan) at  $\varphi$  = 0, 120, and 240° using the SMART [32] software package, or the APEX2 program suite. The raw data were reduced to F2 values using the SAINT + software [33], and a global refinement of unit cell parameters, using about 2332–2779 reflections chosen from the full data set, were performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (sADABS [34]). The structure of **7** was solved by direct methods, whereas the positions of the heavy atoms were obtained from a sharpened Patterson function in case of compound **9**.

Both the structures were refined by full matrix least-squares procedures using the SHELXTL program package [35]. Hydrogen atoms attached to carbon were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for phenyl hydrogen and 1.5 times for CH<sub>3</sub>.

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#### Appendix A. Supplementary data

CCDC 938540 and 938541 contain the supplementary crystallographic data for **7** and **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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