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# Coordination of a diphosphine–phosphine oxide to Au, Ag and Rh: when polyfunctionality rhymes with versatility<sup>†</sup>

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Gold, silver and rhodium complexes of the diphosphine–phosphine oxide DPPO =  $\{[o-iPr_2P-(C_6H_4)]_2P$ (O)Ph} have been prepared and characterized. Thanks to its polyfunctional character, DPPO features versatile coordination properties. According to crystallographic data, only one phosphine moiety is engaged in coordination towards (AuCl) and [RhCl(nbd)]. However, NMR data indicate fluxional behavior in solution, as the result of the exchange between the free and coordinated phosphines around the metal. Chelating coordination *via* the two phosphine sites is observed towards (Au<sup>+</sup>) and (AgCl) with PMP bite angles varying from 122° to 159°. According to X-ray and theoretical analyses, the oxygen atom of the central phosphine oxide moiety points towards the metal but does not interact significantly with it. Tridentate coordination *via* the two phosphines as well as the oxygen atom of DPPO occurs with [Rh(CO)<sup>+</sup>], leading to an original PO(P)P pincer structure.

#### Introduction

Polyfunctional ligands play a pivotal role in coordination chemistry. Their properties can be broadly modulated by variation of the stereoelectronic characteristics of the coordination sites as well as the size and rigidity of the connecting linkers. Additionally, polyfunctional systems may possess hemilabile character and/or participate actively in chemical transformations (so-called non-innocent character), which is most interesting for catalytic purposes.<sup>1</sup> Among tridentate ligands, considerable interest has been devoted over the last two decades to **PEP** frameworks in which a central p-block element E is flanked by two phosphine groups. In particular, pincer complexes derived from **PEP** ligands (E = C,<sup>2,3</sup> Si,<sup>4</sup> N,<sup>5</sup> P,<sup>6,7</sup> O,<sup>8</sup> S<sup>9</sup>) have been extensively investigated. Recently, our group has contributed to this research area by exploring original **PEP** ligands featuring a central Lewis acid moiety (E = B,<sup>10,11</sup> Al, Ga,<sup>12</sup> Si, Sn<sup>13</sup>).<sup>14</sup> These so-called ambiphilic ligands were shown to possess peculiar properties, particularly due to the ability of the Lewis acid moiety E to coordinate as a  $\sigma$ -acceptor, Z-type ligand<sup>15</sup> (M  $\rightarrow$  E interactions). We have also started to investigate the behaviour of an original diphosphine–phosphine oxide ligand referred to as DPPO 1. Upon coordination to Pd(0), an unexpected Ph–P(O) bond cleavage was observed, leading to an original PP(O)P pincer complex 2 (eqn (1)).<sup>16</sup>



Hereafter, we report on the coordination of ligand 1 to Au, Ag and Rh. In all cases, the DPPO ligand remains intact but depending on the metal fragment, it is shown to behave as a mono-, bior tri-dentate ligand. The participation or not of the central O=PPh moiety in coordination has been carefully examined by crystallographic and theoretical means and a new type of PO(P)P pincer complex has been authenticated.

## **Results and discussion**

Coordination of the diphosphine–phosphine oxide **1** to gold(1) is readily achieved upon treatment with (Me<sub>2</sub>S)AuCl (1 equiv.) in dichloromethane at room temperature. After work-up, the corresponding complex **3** is obtained as a white solid in 90% yield (Scheme 1). Crystallographic analysis (Fig. 1) revealed  $\kappa^1$ coordination of the DPPO ligand *via* one of the lateral phosphine

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**Scheme 1** Coordination of the diphosphine–phosphine oxide ligand 1 to gold(1).



**Fig. 1** Molecular view of complex **3**. Thermal ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms are omitted and isopropyl/phenyl groups at phosphorus are simplified. Selected bond lengths (Å) and bond angles (°): P3–Au 2.253(1); Cl–Au 2.287(1); P1–O1 1.483(1); P3–Au–Cl 175.68(4).

groups. The gold center adopts a quasi linear arrangement  $(P3AuCl = 175.68(4)^{\circ})$  and points away from the phosphineoxide moiety. Neutral gold(I) complexes most commonly adopt linear dicoordination,<sup>17</sup> and thus the coordination mode observed in complex 3 is in a sense nothing but expected. However, it strikingly differs from the chelating coordination systematically observed so far upon coordination of the related PEP ligands (E = B, Al, Ga, Si, Sn) to gold(1), whatever the presence or not of a central Au  $\rightarrow$  E interaction.<sup>10–13</sup> This suggests that the central P(=O)Ph moiety influences very subtly the conformational and thereby the coordination properties of ligand 1 compared with the other PEP ligands. Spectroscopic data indicate fluxional behavior for complex 3 in solution.<sup>†</sup> At room temperature, the <sup>31</sup>P and <sup>1</sup>H NMR spectra display two sets of broad signals for the coordinated and free PiPr<sub>2</sub> groups. This suggests that the two phosphines of the DPPO ligand exchange around gold relatively slowly at the NMR timescale. At 60 °C, this fluxional process occurs significantly faster and a unique set of <sup>1</sup>H NMR signals is observed for the two PiPr<sub>2</sub> groups while the corresponding <sup>31</sup>P NMR signals are further broadened.

To favor concomitant coordination of the two phosphine sites to gold, the chloride at gold was abstracted by treating complex **3** with silver triflate (Scheme 1). The ensuing cationic complex **4** was fully characterized by multi-nuclear NMR spectroscopy. The <sup>31</sup>P NMR spectrum displays a doublet at  $\delta$  68.1 ppm and a triplet at  $\delta$  45.4 ppm ( $J_{PP} = 9.4$  Hz) with relative integrations of 2 : 1. This indicates the symmetric coordination of the two phosphines but does not infer about the participation or not of the central O=PPh moiety in coordination. Since crystals suitable for X-ray diffraction studies could not be obtained in this case, we referred to DFT calculations to shed light into the coordination mode of the DPPO ligand in complex **4**. The



Fig. 2 Optimized structure of complex 4a\*. Selected bond lengths (Å) and bond angles (°): P2–Au 2.335; P3–Au 2.324; P1–O1 1.411; P3–Au–P2 159.49.

computational study was performed on the real complex at the B3PW91/SDD+f(Pd),6-31G\*\*(other atoms) level of theory.<sup>+</sup> The global energy minimum corresponds to a dicoordinate quasi-linear gold(1) complex 4a\* (Fig. 2). The oxygen atom of the O=PPh moiety points towards gold but remains rather far away. The O…Au distance (2.613 Å) is shorter than the sum of the van der Waals radii (3.65 Å),<sup>18</sup> but exceeds the sum of the covalent radii19 by about 30%, suggesting weak, if any, interaction. This view is corroborated by NBO analysis, where only a weak donor-acceptor interaction is found from oxygen to gold  $(\Delta E_{\rm NBO} = 3.1 \text{ kcal mol}^{-1})$ . Note that another minimum 4b\* was identified 22.1 kcal mol<sup>-1</sup> higher in energy than  $4a^*$ . The two structures differ in the orientation of the central O=PPh moiety. with the Ph group instead of the O pointing towards gold in 4b\*. In addition, a gold(III) complex  $4c^*$  resulting from oxidative addition of the P(O)–Ph bond was found 12.7 kcal  $mol^{-1}$  higher in energy than 4a\*.<sup>20</sup>

The DPPO ligand was thus found to coordinate to gold(1) via one or the two phosphine sites, depending on the neutral vs. cationic character of the complex. In order to explore further its coordination properties, we then became interested in other transition metals, starting with silver(1). Treatment of 1 with a suspension of AgCl in dichloromethane led to the formation of the new complex 5 within 12 h at room temperature (Scheme 2). Colorless crystals were grown from a dichloromethane-diethyl ether (5:1) solution at -30 °C and an X-ray diffraction study was carried out. The silver center is surrounded by the two phosphines (PAg distances = 2.443(1) and 2.439(1) Å) and the chloride (ClAg = 2.482(1) Å) organized in a trigonal planar arrangement ( $\Sigma_{\alpha}Ag = 359.6^{\circ}$ ) (Fig. 3). The oxygen atom of the central P(=O)Ph moiety points towards the silver center but remains at a rather long distance (OAg = 2.640(2) Å, 25% higher than the sum of the covalent radii<sup>19</sup>). The absence of significant interaction between O and Ag was further supported by DFT computations.<sup>†</sup> The optimized geometry of 5\* fits nicely



**Scheme 2** Coordination of the diphosphine–phosphine oxide ligand **1** to silver(1).



**Fig. 3** Molecular view of complex **5**. Thermal ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms are omitted and isopropyl/phenyl groups at phosphorus are simplified. Selected bond lengths (Å) and bond angles (°): P2–Ag 2.443(1); P3–Ag 2.439(1); Cl–Ag 2.482(1); P1–O1 1.481(1); P3–Ag–P2 122.75(3); P3–Ag–Cl 120.25(3); P2–Ag–Cl 116.62(3).

with that determined crystallographically and only a very weak  $O \rightarrow Ag$  interaction was found by NBO analysis ( $\Delta E_{\text{NBO}} = 1.3 \text{ kcal mol}^{-1}$ ). According to the spectroscopic data, complex **5** adopts the same coordination mode in solution. In the <sup>31</sup>P NMR spectrum, the two phosphines are equivalent and appear at  $\delta$  18.1 ppm as a pair of doublets due to well-resolved couplings with the two isotopes of silver ( ${}^{1}J_{\text{PAg}} = 376.3 \text{ Hz for } {}^{107}\text{Ag}$  and 431.8 Hz for  ${}^{109}\text{Ag}$ ). The O=PPh moiety is associated with a signal of half intensity at  $\delta$  40.1 ppm.

In the silver complex **5**, the DPPO ligand coordinates *via* the two phosphines while in the corresponding gold complex **3**, only one phosphine participates in coordination. This difference is consistent with the tendency of silver(1) to adopt higher coordination numbers than gold(1).<sup>17</sup> Cationization of the gold center (complex **4**) favors chelating coordination of DPPO as observed in the neutral silver complex **5**. However, the dicoordinate *vs.* tricoordinate nature of the metal center results in significantly different bite angles (PAuP =  $159.5^{\circ}$  in **4** *vs.* PAgP =  $122.7^{\circ}$  in **5**).

The coordination properties of DPPO towards Rh(I) fragments were then investigated. Upon reaction of 1 with half an equivalent of  $[Rh(nbd)(\mu-Cl)]_2$  (nbd = 2,5-norbornadiene), the new complex 6 was obtained in quantitative yield as an orange powder (Scheme 3). According to X-ray diffraction data (Fig. 4a), the DPPO ligand has split the chloro-bridge of the Rh precursor and coordinates to Rh by one of the phosphine sites. The Cl atom and the nbd fragment complete the coordination sphere of Rh (typical square-planar environment). <sup>31</sup>P NMR analysis of complex 6 in CDCl<sub>3</sub> gives an unexpectedly simple spectrum. The O=PPh moiety appears as a triplet at  $\delta$  43.3 ppm  $(J_{\rm PP} = 17 \text{ Hz})$  while the two phosphines give a unique signal at δ 14.8 ppm (relative integration: 2, doublet of doublet,  $J_{PP} =$  17 Hz,  $J_{PRh} = 90.4$  Hz).<sup>21</sup> The latter <sup>31</sup>P NMR chemical shift and  $J_{PRh}$  coupling constant are in between those expected for free and Rh-coordinated PiPr<sub>2</sub> fragments, suggesting rapid exchange of the two phosphines around Rh at the NMR timescale. This fluxional process is reminiscent of that observed in the neutral gold complex 3, but the exchange between the free and coordinated phosphines occurs much faster in the rhodium



Scheme 3 Coordination of the diphosphine–phosphine oxide ligand 1 to rhodium.



Fig. 4 Molecular view of complexes 6 (a) and 8 (b). Thermal ellipsoids are drawn at 50% probability. For clarity, hydrogen atoms and triflate counter-anion are omitted and isopropyl/phenyl groups at phosphorus are simplified. Selected bond lengths (Å) and bond angles (°): 6: P2–Rh 2.335(1); Cl–Rh 2.363(1); P1–O1 1.488(2); P2–Rh–Cl 91.274(2). 8: P2–Rh 2.307(2); P3–Rh 2.308(2); C3–Rh 1.802(6): O1–Rh 2.079(1); P1–O1 1.520(4); C3–Rh–O1 178.4(2); C3–Rh–P2 96.81(18); O1–Rh–P2 82.20(10); C3–Rh–P3 97.68(18), O1–Rh–P3 83.04(10); P2–Rh–P3 161.26(5).

complex 6. In this case, the two phosphines give a unique  ${}^{31}P$  NMR signal even at -80 °C.

A significantly different result was obtained when the nbd coligand at rhodium was replaced by CO. Using [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> as a precursor (0.5 equiv.), the coordination of the DPPO ligand 1 proceeds within minutes at room temperature and the reaction is accompanied by CO release. After work-up, complex 7 was isolated as a bright yellow powder in 95% yield. Despite many attempts, no X-ray quality crystals of 7 could be obtained. To circumvent this problem, we envisioned to exchange the chloride for a triflate group. Treatment of 7 with Me<sub>3</sub>SiOTf gives a new complex 8 featuring similar spectroscopic characteristics and gratifyingly, crystals of 8 could be grown in this case from an acetonitrile-diethyl ether solution (Fig. 4b). Accordingly, complex 8 adopts a discrete ion pair structure with triflate as a counter-anion. The DPPO ligand coordinates to Rh via the two phosphine sites (PRh distances = 2.308(2) and 2.307(2) Å;  $PRhP = 161.26(5)^{\circ}$ ) as well as the O atom of the central O=PPh moiety (ORh distance = 2.079(1) Å).<sup>22</sup> The P=O bond length is

substantially elongated upon coordination, from 1.48–1.49 Å in complexes **3**, **5** and **7** to 1.520(4) Å in complex **8**. The rhodium center adopts a slightly distorted square planar arrangement, with a CO molecule occupying the position *trans* to the P=O moiety. The concomitant and symmetric coordination of the two phosphine sites of DPPO is clearly apparent from the <sup>31</sup>P NMR spectrum: the corresponding signal appears at  $\delta$  52.1 ppm with a large <sup>1</sup>J<sub>PRh</sub> coupling constant (123.6 Hz) while the O=PPh moiety resonates as a triplet (J<sub>PP</sub> = 8.0 Hz) at  $\delta$  47.8 ppm. The magnitude of the O to Rh coordination was assessed theoretically.† Calculations were performed on the real complex **8**\* and NBO analysis revealed the presence of a relatively strong P(O)  $\rightarrow$  Rh interaction ( $\Delta E_{\text{NBO}} = 55.6 \text{ kcal mol}^{-1}$ ).

The DPPO ligand thus behaves very differently in the rhodium complexes 6 on the one hand and 7/8 on the other hand. The presence of  $\pi$ -acceptor CO co-ligands instead of nbd favors the coordination of the two phosphines and additionally, the coordination of the central O=PPh induces ionization by displacement of the chloride.

#### Conclusion

In conclusion, gold, silver and rhodium complexes of the diphosphine–phosphine oxide DPPO are described. Depending on the metal fragment, DPPO is shown to behave as a mono-, bi- or tridentate ligand. Participation of the central O==PPh moiety in coordination eventually leads to a new type of PO(P)P pincer complex. Efforts are ongoing in our laboratory to explore further the coordination properties of diphosphine–phosphine oxide ligands and to investigate the reactivity of the ensuing complexes.

# Experimental

#### **General comments**

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were sparged with argon and dried using an MBRAUN Solvent Purification System (SPS). <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on Bruker Avance 500 or 300 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual <sup>1</sup>H (7.24 ppm) and <sup>13</sup>C (77.16 ppm) solvent signals and 85% H<sub>3</sub>PO<sub>4</sub> (0 ppm) respectively. Unless otherwise stated, NMR was recorded at 25 °C. The *N* values corresponding to 1/2[J(AX)-J(A'X)] are provided when the second-order AA'X systems were observed in <sup>13</sup>C NMR.<sup>23</sup> The same atom numbering has been used for the DPPO ligand of all compounds.<sup>24</sup> Mass spectra were recorded on a Waters LCT mass spectrometer. The DPPO ligand was prepared as previously described.<sup>16</sup>

#### Preparations

Synthesis of (DPPO)AuCl complex 3. To a Schlenk flask containing a suspension of  $AuCl(SMe_2)$  (147.3 mg, 0.50 mmol, 1 equiv.) in dichloromethane (4 mL) was added diphosphanylphenylphosphine oxide 1 (255.3 mg, 0.5 mmol, 1 equiv.) in dichloromethane (2 mL) at 0 °C. The mixture was stirred during 3 h and slowly warmed to room temperature. A clear colourless solution of (DPPO)AuCl was obtained after filtration. The solvent and SMe<sub>2</sub> were removed under vacuum. The resulting white residue was extracted with diethyl ether (10 mL) and purified by recrystallization in a mixture of dichloromethanepentane to give a (DPPO)AuCl complex (334.0 mg, 0.45 mmol, 90% yield) in 99% purity. <sup>1</sup>H NMR (300.18 MHz, 60 °C,  $C_6D_6$ ):  $\delta$  7.98 (s br, 2H, H<sub>3</sub>), 7.56 (m, 2H, H<sub>6</sub>), 7.11–6.89 (m, 7H, H<sub>4</sub>, H<sub>5</sub>, H<sub>o</sub> and H<sub>p</sub>), 6.78 (m, 2H, H<sub>m</sub>), 2.83 (s br, 4H, H<sub>7</sub>), 1.18 (dd,  ${}^{3}J_{HP} = 16.2 \text{ Hz}$ ,  ${}^{3}J_{HH} = 6.9 \text{ Hz}$ , 6H, H<sub>8</sub>), 1.02 (m, 12H, H<sub>8</sub>), 0.42 (dd,  ${}^{3}J_{\text{HP}} = 16.1 \text{ Hz}$ ,  ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}$ , 6H, H<sub>8</sub>);  ${}^{31}P\{{}^{1}\text{H}\}$ (121.47 MHz, C<sub>6</sub>D<sub>6</sub>): δ 90.8 (s br, 1P, PiPr<sub>2</sub>), 35.3 (s br, 1P, P(O)-Ph), -2.6 (s br, 1P, PiPr<sub>2</sub>);  ${}^{31}P{}^{1}H{}$  (121.47 MHz, 60 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta$  90.8 (s br, 1P, PiPr<sub>2</sub>), 35.3 (t,  ${}^{3}J_{PP} = 10.8$  Hz s, 1P, P(O)Ph), -2.6 (s br, 1P, PiPr<sub>2</sub>); HRMS (CI, CH<sub>4</sub>): exact mass (monoisotopic) calcd for C<sub>30</sub>H<sub>41</sub>OP<sub>3</sub>Au, 707.2036; found, 707.2036 (average of 3 trials); mp: 217-219 °C.

Synthesis of [(DPPO)Au]OTf complex 4. To a Schlenk flask containing a colourless solution of Ag(OTf) (100 mg, 0.40 mmol) in DCM (2 mL) was added a solution of (DPPO) AuCl 3 (300 mg, 0.40 mmol, 1 equiv.) in DCM (2 mL) at -60 °C. The resulting mixture was stirred for 1 h to give a colourless solution with a fine white precipitate. A clear colourless solution of [(DPPO)Au]OTf was obtained after filtration and the solvent was removed under vacuum. The resulting white powder was washed with pentane  $(3 \times 5 \text{ mL})$  to give [(DPPO)Au]OTf (300.0 mg, 0.34 mmol, 85% yield) in 99% purity. <sup>1</sup>H NMR (500.33 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (dd,  ${}^{3}J_{\text{HP}} = 13.5$  Hz,  ${}^{3}J_{\text{HH}} =$ 8.0 Hz, 2H, H<sub>3</sub>), 7.86-7.83 (m, 4H, H<sub>5</sub> and H<sub>6</sub>), 7.70-7.67 (m, 2H, H<sub>4</sub>), 7.56 (t,  ${}^{3}J_{HH} = 7.3$  Hz, 1H, H<sub>p</sub>), 7.46 (td,  ${}^{3}J_{HH} =$ 7.7 Hz,  ${}^{4}J_{\rm HP} = 2.8$  Hz, 2H, H<sub>m</sub>), 7.24 (dd,  ${}^{3}J_{\rm HP} = 12.4$  Hz,  ${}^{3}J_{\rm HH}$ = 7.5 Hz, 2H, H<sub>o</sub>), 3.33–3.25 (m, 2H, H<sub>7</sub>), 2.91–2.83 (m, 2H,  $H_7$ ), 1.49–1.42 (m, 18H,  $H_8$ ), 1.15–1.10 (m, 6H,  $H_8$ );  ${}^{13}C{}^{1}H{}$ NMR (125.81 MHz, CDCl<sub>3</sub>): δ 137.3-137.1 (m, C<sub>3</sub>), 136.8 (d,  ${}^{1}J_{CP} = 107.6 \text{ Hz}, C_{1}$ , 136.8 (dt,  ${}^{1}J_{CP} = 92.6 \text{ Hz}, {}^{4}J_{CP} = 6.7 \text{ Hz}$ ,  $C_i$ ), 134.8 (dd,  ${}^{1}J_{CP} = 19.4$  Hz,  ${}^{2}J_{CP} = 7.7$  Hz,  $C_2$ ), 134.6 (d,  $J_{CP}$ = 10.1 Hz, C<sub>6</sub>), 132.9–132.8 (m, C<sub>5</sub>), 132.3 (d,  ${}^{4}J_{CP}$  = 2.8 Hz,  $C_p$ ), 131.5 (d,  ${}^2J_{CP} = 9.9$  Hz,  $C_o$ ), 130.7 (d,  $J_{CP} = 12.5$  Hz,  $C_4$ ), 129.1 (d,  ${}^{3}J_{CP} = 12.1$  Hz, C<sub>m</sub>), 114.6 (br,  $\omega_{1/2} = 575$  Hz, CF<sub>3</sub>), 29.0 (AA'X, N = 14.0 Hz,  $C_7$ ), 24.0 (AA'X, N = 14.0 Hz,  $C_7$ ), 20.7 (AA'X, N = 1.2 Hz, C<sub>8</sub>), 20.6 (AA'X, N = 2.3 Hz, C<sub>8</sub>), 19.9 (AA'X, N = 5.1 Hz, C<sub>8</sub>), 18.6 (s, C<sub>8</sub>); <sup>31</sup>P{<sup>1</sup>H} (202.54 MHz, CDCl<sub>3</sub>):  $\delta$  68.1 (d,  ${}^{3}J_{PP} = 9.4$  Hz, 2P, PiPr<sub>2</sub>), 45.4 (t,  ${}^{3}J_{PP} =$ 9.4 Hz, 1P, P(O)Ph).

Synthesis of [(DPPO)AgCl] complex 5. To a Schlenk flask containing a suspension of AgCl (41.5 mg, 0.29 mmol, 1 equiv.) in dichloromethane (2 mL) was added diphosphanyl–phenylphosphine oxide 1 (150.0 mg, 0.29 mmol, 1 equiv.) in dichloromethane (2 mL) at room temperature. The mixture was stirred during 12 h. A clear colorless solution of (DPPO)AgCl was obtained after filtration and the solvent was removed under vacuum. The resulting white residue was purified by recrystallization in a mixture of dichloromethane–diethyl ether (5 : 1) to give colorless crystals at -30 °C (123.3 mg, 0.19 mmol, 65% yield) in >99% purity. <sup>1</sup>H NMR (300.18 MHz, CDCl<sub>3</sub>):  $\delta$  7.78–7.69 (m, 2H, H<sub>3</sub>), 7.61–7.52 (m, 3H, H<sub>4</sub> and H<sub>p</sub>),

7.50 -7.43 (m, 4H, H<sub>o</sub> and H<sub>m</sub>), 7.42-7.35 (m, 2H, H<sub>5</sub>), 7.34-7.25 (m, 2H, H<sub>6</sub>), 2.50 (m, 4H, H<sub>7</sub>), 1.42-1.17 (m, 18H, H<sub>8</sub>), 0.87-0.73 (m, 6H, H<sub>8</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  141.1 (m, C<sub>2</sub>), 137.7 (dt, <sup>1</sup>J<sub>CP</sub> = 99.4 Hz, <sup>4</sup>J<sub>CP</sub> = 8.6 Hz, C<sub>i</sub>), 135.1 (m, C<sub>6</sub>), 134.9 (d, <sup>1</sup>J<sub>CP</sub> = 106.5 Hz, C<sub>1</sub>), 133.7 (d, <sup>2</sup>J<sub>CP</sub> = 11.8 Hz, C<sub>3</sub>), 131.9 (m, C<sub>p</sub> and C<sub>m</sub>), 130.9 (s br, C<sub>4</sub>), 128.7 (d, <sup>2</sup>J<sub>CP</sub> = 11.7 Hz, C<sub>o</sub>), 128.3 (d, J<sub>CP</sub> = 12.7 Hz, C<sub>5</sub>), 28.2 (AA'X, N = 4.6 Hz, C<sub>7</sub>), 23.1 (AA'X, N = 2.8 Hz, C<sub>7</sub>), 20.4 (AA'X, N = 5.9 Hz, C<sub>8</sub>), 19.8 (AA'X, N = 3.8 Hz, C<sub>8</sub>), 19.7 (AA'X, N = 8.7 Hz, C<sub>7</sub>), 18.7 (AA'X, N = 2.4 Hz, C<sub>8</sub>); <sup>31</sup>P{<sup>1</sup>H} (121.49 MHz, CDCl<sub>3</sub>):  $\delta$  40.1 (s, 1P, P(O)Ph), 18.1 (dd, <sup>1</sup>J<sub>P</sub><sup>109</sup><sub>Ag</sub> = 431.8 Hz, <sup>1</sup>J<sub>P</sub><sup>107</sup><sub>Ag</sub> = 376.3 Hz, <sup>3</sup>J<sub>PP</sub> = 2.7 Hz, 2P, PiPr<sub>2</sub>); HRMS (CI, CH<sub>4</sub>): exact mass (monoisotopic) calcd for C<sub>30</sub>H<sub>41</sub>OP<sub>3</sub><sup>107</sup>Ag, 617.1421; found, 617.1434 (average of 3 trials); mp: 247-250 °C.

Synthesis of (DPPO)Rh(nbd)Cl complex 6. To a Schlenk flask containing a yellow solution of [Rh(nbd)(µ-Cl)]<sub>2</sub> (115.3 mg, 0.25 mmol, 1 equiv.) in dichloromethane (2 mL) was added diphosphanyl-phenylphosphine oxide 1 (255.3 mg, 0.5 mmol, 2 equiv.) in dichloromethane (2 mL) at 0 °C. The mixture was stirred during 4 h and slowly warmed to room temperature. A clear vellow solution of (DPPO)RhCl(nbd) was obtained and the solvent was removed under vacuum. The resulting orange solid was washed with pentane  $(3 \times 5 \text{ mL})$  to give (DPPO)Rh(nbd)Cl (363.1 mg, 0.49 mmol, 98% yield) in >99% purity. Orange crystals were obtained from a dichloromethane-diethyl ether solution. <sup>1</sup>H NMR (300.18 MHz, CDCl<sub>3</sub>):  $\delta$  7.86–7.55 (m, 7H, H<sub>n</sub>, H<sub>3</sub>, H<sub>4</sub> and H<sub>5</sub>), 7.52–7.43 (m, 2H, H<sub>6</sub>), 7.42–7.33 (m, 2H, H<sub>m</sub>), 7.00–6.88 (m, 2H, H<sub>o</sub>), 4.20 (m br, 4H, CH=CH<sub>nbd</sub>), 3.80 (s br, 2H, CH<sub>nbd</sub>), 2.50 (m, 2H, H<sub>7</sub>), 2.27 (m, 2H, H<sub>7</sub>), 1.36 (s br, 2H,  $CH_{2 \text{ nbd}}$ , 1.11 (dd,  ${}^{3}J_{\text{HP}} = 13.8$  Hz,  ${}^{3}J_{\text{HH}} = 6.9$  Hz, 12H, H<sub>8</sub>), 0.99 (dd, 6H,  ${}^{3}J_{\text{HP}} = 14.8$  Hz,  ${}^{3}J_{\text{HH}} = 7.1$  Hz, H<sub>8</sub>), 0.79 (dd, 6H,  ${}^{3}J_{\rm HP} = 15.9$  Hz,  ${}^{3}J_{\rm HH} = 7.0$  Hz, H<sub>8</sub>);  ${}^{31}P{}^{1}H{}^{1}$  (121.49 MHz, CDCl<sub>3</sub>):  $\delta$  43.3 (t,  ${}^{3}J_{PP} = 17.0$  Hz, 1P, P(O)Ph), 14.8 (dd,  ${}^{1}J_{PRh} =$ 90.4 Hz,  ${}^{3}J_{PP} = 17.0$  Hz, 2P, PiPr<sub>2</sub>); HRMS (CI, CH<sub>4</sub>): exact mass (monoisotopic) calcd for C<sub>37</sub>H<sub>49</sub>OP<sub>3</sub>Rh, 705.2051; found, 705.2070 (average of 3 trials); mp: 178-180 °C.

Synthesis of [(DPPO)Rh(CO)]Cl complex 7. To a Schlenk flask containing a light yellow solution of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> (290 mg, 0.75 mmol) in dichloromethane (2 mL) was added diphosphanyl-phenylphosphine oxide 1 (762 mg, 1.5 mmol, 2 equiv.) in dichloromethane (2 mL). The mixture was stirred until the effervescence ceased (~10 min). The solution was filtered to remove a black precipitate and the solvent was removed under vacuum to give a yellow oil. Trituration with pentane  $(3 \times 5 \text{ mL})$ , followed by toluene  $(3 \times 5 \text{ mL})$  wash, gave [Rh(CO)(DPPO)]Cl (960 mg, 1.4 mmol, 95% yield) as a bright yellow powder in >99% purity. <sup>1</sup>H NMR (500.33 MHz, CDCl<sub>3</sub>):  $\delta$  7.94–7.85 (m, 6H, H<sub>3</sub>, H<sub>4</sub> and H<sub>6</sub>), 7.80 (td, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz,  $J_{\rm HP} = 2.3$  Hz, 2H, H<sub>5</sub>), 7.63 (td,  ${}^{3}J_{\rm HH} = 7.7$  Hz,  ${}^{5}J_{\rm HP} = 1.2$  Hz, 2H, H<sub>p</sub>), 7.45 (td,  ${}^{3}J_{\rm HH} = 7.7$  Hz,  ${}^{4}J_{\rm HP} = 3.5$  Hz, 2H, H<sub>m</sub>), 7.12-7.05 (m, 2H, H<sub>o</sub>), 3.04-3.00 (m, 2H, H<sub>7</sub>), 2.53-2.46 (m, 2H, H<sub>7</sub>), 1.39–1.33 (m, 12H, H<sub>8</sub>), 1.32–1.28 (m, 6H, H<sub>8</sub>), 1.17–1.12 (m, 6H, H<sub>8</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.81 MHz, CDCl<sub>3</sub>):  $\delta$  192.2 (dt, <sup>1</sup>J<sub>CRh</sub> = 77.5 Hz, <sup>2</sup>J<sub>CP</sub> = 12.7 Hz, CO), 135.6–135.4 (m, C<sub>2</sub> and C<sub>3</sub>), 134.4 (d,  ${}^{4}J_{CP} = 2.4$  Hz, C<sub>p</sub>), 134.1 (m, C<sub>4</sub>), 133.1 (d,  ${}^{2}J_{CP} = 11.5$  Hz, C<sub>6</sub>), 132.9 (dt,  ${}^{1}J_{CP} = 102.9$  Hz,  ${}^{4}J_{CP}$ 

= 5.4 Hz, C<sub>i</sub>), 132.2 (d,  ${}^{2}J_{CP}$  = 11.0 Hz, C<sub>o</sub>), 130.9 (d,  $J_{CP}$  = 13.3 Hz, C<sub>5</sub>), 130.4 (d,  ${}^{1}J_{CP}$  = 110.2 Hz, C<sub>1</sub>), 129.6 (d,  ${}^{3}J_{CP}$  = 12.7 Hz, C<sub>m</sub>), 28.3 (AA'X, N = 10.6 Hz, C<sub>7</sub>), 22.5 (AA'X, N = 12 Hz, C<sub>7</sub>), 21.5 (s, C<sub>8</sub>), 18.7 (s, C<sub>8</sub>), 22.5 (AA'X, N = 4.4 Hz, C<sub>7</sub>), 18.0 (s, C<sub>8</sub>);  ${}^{31}P{}^{1}H{}$  (202.54 MHz, CDCl<sub>3</sub>):  $\delta$  51.9 (dd,  ${}^{1}J_{PRh}$  = 123.6 Hz,  ${}^{3}J_{PP}$  = 8.2 Hz, 2P, PiPr<sub>2</sub>), 47.8 (t,  ${}^{3}J_{PP}$  = 8.1 Hz, 1P, P(O)Ph); mp: 165–167 °C.

Synthesis of [(DPPO)Rh(CO)]OTf complex 8. 0.9 mmol of (Me<sub>3</sub>Si)OTf (16 µL, 1.0 equiv.) were added to a Schlenk flask containing a yellow solution of Rh(CO)(DPPO)Cl 7 (61.71 mg, 0.09 mmol, 1 equiv.) in dichloromethane (2 mL) at room temperature. The resulting mixture was stirred for 1 h to give a yellow solution of [Rh(CO)(DPPO)]OTf. The solvent was removed under vacuum and the resulting yellow powder was washed with pentane  $(3 \times 2 \text{ mL})$  to give [Rh(CO)(DPPO)]OTf (64.0 mg, 0.08 mmol, 90% yield) as a bright yellow powder in >99% purity. Crystals suitable for X-ray diffraction studies were obtained from an acetonitrile-diethyl ether solution. <sup>1</sup>H NMR (300.18 MHz, CDCl<sub>3</sub>): δ 7.95-7.68 (m, 2H, H<sub>6</sub>), 7.83-7.65 (m, 6H, H<sub>3</sub>, H<sub>4</sub> and H<sub>5</sub>), 7.60 (t br,  ${}^{3}J_{HH} = 7.7$  Hz, 2H, H<sub>p</sub>), 7.42 (td,  ${}^{3}J_{\rm HH} = 7.7$  Hz,  ${}^{4}J_{\rm HP} = 2.9$  Hz, 2H, H<sub>m</sub>), 7.11–7.00 (m, 2H, H<sub>o</sub>), 2.95 (m, 2H, H<sub>7</sub>), 2.45 (m, 2H, H<sub>7</sub>), 1.41-1.20 (m, 18H, H<sub>8</sub>), 1.19–1.05 (m, 6H, H<sub>8</sub>);  ${}^{31}P{}^{1}H{}$  (121.49 MHz, CDCl<sub>3</sub>):  $\delta$  52.1  $(dd, {}^{1}J_{PRh} = 123.2 \text{ Hz}, {}^{3}J_{PP} = 8.0 \text{ Hz}, 2P, PiPr_{2}), 48.3 (t, {}^{3}J_{PP} =$ 8.0 Hz, 1P, P(O)Ph); HRMS (CI, CH<sub>4</sub>): exact mass (monoisotopic) calcd for C<sub>31</sub>H<sub>41</sub>O<sub>2</sub>P<sub>3</sub>Rh, 641.1374; found, 641.1365 (average of 3 trials); mp: 216-218 °C.

#### Crystallographic data for complexes 3, 6 and 8

Crystallographic data were collected at 193 K on a Bruker-AXS APEX-II QUAZAR diffractometer equipped with an air-cooled microfocus source (5 and 8) or on Bruker-AXS SMART APEX-II (3 and 6), using Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). Semi-empirical absorption corrections were employed.<sup>25</sup> The structures were solved by direct methods (SHELXS 97),<sup>26</sup> and all non-hydrogen atoms were refined anisotropically using the least-squares method on  $F^{2,27}$  The crystallographic data for the structures are given in Table 1.

### **Computational details**

Calculations were carried out with the Gaussian 03 program<sup>28</sup> at the DFT level of theory using the hybrid functional B3PW91.<sup>29</sup> B3PW91 is Becke's 3 parameter functional, with the non-local correlation provided by the Perdew 91 expression. Au, Ag and Rh were treated with the Stuttgart-Dresden set-RECP (relativistic effective core potential) in combination with its adapted basis set.<sup>30</sup> The latter has been augmented by a set of f polarization functions.<sup>31</sup> All the other atoms (C, H, O, P, Cl) have been described with a 6-31G(d,p) double- $\zeta$  basis set.<sup>32</sup> Geometry optimizations were carried out without any symmetry restrictions, the nature of the extrema was verified with analytical frequency calculations. Electronic structure of the different complexes was studied using Natural Bond Orbital analysis (NBO-5 program).<sup>33</sup> The Natural Localized Molecular Orbital (NLMO) obtained from the second-order NBO analysis was plotted by using the molecular graphic package Molekel.<sup>34</sup>

	3	5	6	8
Empirical formula	C <sub>30</sub> H <sub>41</sub> AuClOP <sub>3</sub>	C <sub>30</sub> H <sub>41</sub> AgClOP <sub>3</sub>	C37H49ClOP3Rh	C <sub>31</sub> H <sub>41</sub> O <sub>2</sub> P <sub>3</sub> Rh, CF <sub>3</sub> O <sub>3</sub> S
Formula weight	742.96	653.86	741.03	790.54
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	Pbca	$P2_1/n$	$P\bar{1}$	$P\overline{1}$
a/Å	15.4329(3)	8.832(4)	10.4107(2)	8.1191(5)
b/Å	15.7352(3)	18.830(8)	10.5382(2)	19.9268(12)
c/Å	25.7359(5)	18.315(8)	17.9760(3)	23.3037(15)
$\alpha/^{\circ}$	90	90	75.4240(10)	68.072(3)
$\beta^{\circ}$	90	97.935(10)	74.6830(10)	85.812(3)
$\gamma/^{\circ}$	90	90	71.3380(10)	85.295(3)
$V/Å^3$	6249.7(2)	3017(2)	1771.69(6)	3482.0(4)
Ζ	8	4	2	4
$Density_{calcd}/mg m^{-3}$	1.579	1.44	1.389	1.508
$\mu/\text{mm}^{-1}$	4.968	0.937	0.721	0.742
Reflections collected	103 280	20 202	40 865	52 047
Independent reflection	9682	5976	10 728	14 095
$R_1 \left[ \hat{I} > 2\sigma(I) \right]$	0.0344	0.0325	0.0255	0.0602
wR <sub>2</sub>	0.0929	0.0766	0.0707	0.1396
$(\Delta/r)$ max/e Å <sup>-3</sup>	1.549 and -0.79	0.357 and -0.355	0.753 and -0.491	1.047 and -0.887
T	193(2)	193(2)	193(2)	193(2)

Table 1Crystallographic data for compounds 3, 5, 6 and 8

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