A new, easily recyclable arylating agent based on a diphosphino-digold(I) complex

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Received 26th January 2007, Accepted 3rd April 2007 First published as an Advance Article on the web 19th April 2007 DOI: 10.1039/b701271c

The synthesis of two organogold(1) complexes, $[(Au(NCN))_2(dppbp)]$ (6) and $[(Au(Phebox))_2(dppbp)]$ (9), and their application in subsequent transmetalating reactions are described. A trinuclear organogold(1) complex, $[(AuCl)_3(tdpppb)]$ (4) is also reported, which exhibits a surprisingly high solubility in dichloromethane. It was found that 6 and 9 can cleanly transfer the anionic NCN-($[C_6H_3(CH_2NMe_2)_2-2,6]^-$) or Phebox-($[2,6-bis(oxazolinyl)phenyl]^-$) moiety to Ti^{IV} and Pd^{II} centers, respectively. The coproduct $[(AuCl)_2(dppbp)]$ (3, dppbp is $[4-Ph_2PC_6H_4]_2$ (1)) formed during this transmetalation reaction, precipitates almost quantitatively from the reaction mixture (toluene) and can thus be separated by simple filtration. In comparison, $[AuCl(PPh_3)]$, formed as the coproduct in the transmetalation reaction of $[Au(NCN)(PPh_3)]$ with metal salts, has a higher solubility in apolar solvents and thus is more difficult to separate from the resultant organometallic complex. Digold complex 6 has been characterized by NMR spectroscopy and crystallographic analyses. These analyses show that the two gold units are essentially independent. The formation of a *dimetallic* transmetalating agent based on gold(1) had no effect on its transmetalating properties.

Introduction

Common methods to form transition metal-to-carbon bonds generally involve the use of organolithium¹ or -magnesium² reagents. Alternatively, methods based on tin(IV),³ thallium(I)⁴ or mercury(II)⁵ have been employed. However, due to the toxic nature of these metals and the formation of large quantities of residual metal salts from these reactions, there is a strong tendency to restrict their use. In view of the isolobal relationship⁶ between AuL⁺ (where L is a neutral 2e⁻ donor ligand) and Li⁺ and the inertness of organylgold(I) complexes toward air, moisture, and the stability of the Au^I oxidation state, it was anticipated that the transmetalating properties of organogold(I) compounds,7 [AuRL], could complement those of the corresponding organolithium (LiR) reagents.8 Recently, we have prepared a gold(I) triphenylphosphine complex bearing a monoanionic 2,6-[(dimethylamino)methyl]phenyl ligand, $[Au(NCN)(PPh_3)]$ (NCN = $[C_6H_3(CH_2NMe_2)_2-2,6]^{-}$), and showed its utility as a transmetalating reagent for various transition metal species.8 This was, to our knowledge, the first demonstrated application of an organogold(I) compound to cleanly transfer an organic group to other d⁰, d⁵, d⁸ or d¹⁰ metallic centers. In all cases, the reaction with $[MX_nL_k] (M = Ni^{II}, Pd^{II}, Pt^{II})$, Au^{III}, Ti^{IV}, Fe^{III}) afforded the corresponding $[MX_{n-1}(NCN)L_{k-2}]$ organometallic compound. The (only) coproduct, [AuCl(PPh₃)], was separated from the desired organometallic compound by precipitation from diethyl ether and could subsequently be recycled. In this paper, a scaffold is introduced which is based on 4,4'-bis(diphenylphosphino)biphenyl. The use of this scaffold for the preparation of dinuclear gold(I) complexes leads to new transmetalating reagents which, due to their solubility properties, are more easily separated from the generated organometallic compounds and thus can be more efficiently and easily recycled.

Results and discussion

Reaction of 4,4'-dibromobiphenyl with two equivalents of *n*-BuLi, followed by treatment with two equiv of CIPPh₂, afforded 4,4'-bis(diphenylphosphino)biphenyl (1, abbreviated as dppbp) in 88% yield (Scheme 1). Condensation of 4-bromoacetophenone in the presence of SiCl₄ and ethanol afforded 1,3,5-tris(4-bromophenyl)benzene,⁹ which subsequently was reacted with three equiv *n*-BuLi, followed by quenching with CIPPh₂ resulting in the formation of 1,3,5-tris[4-(diphenyl-phosphino)phenyl]benzene (**2**, abbreviated as tdpppb, Scheme 1).



Scheme 1 Synthesis of 1 and 2.

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Subsequently, diphosphine 1 or triphosphine 2 can be reacted with two or three equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) to afford the dinuclear gold complex [(AuCl)₂(dppbp)] ($\mathbf{3}$,¹⁰ Scheme 2) and the trinuclear gold complex [(AuCl)₃(tdpppb)] ($\mathbf{4}$, Scheme 2), respectively, in quantitative yields.



Scheme 2 Synthesis of $([(AuCl)_2(dppbp)](3)$ and $([(AuCl)_3(tdppb)](4)$.

Compounds 3 and 4 are indefinitely stable toward air and moisture. Whereas 3 is only sparingly soluble in dichloromethane, 4 has a surprisingly high solubility in dichloromethane. In addition, 3 was found to be essentially insoluble in several common solvents (diethyl ether, toluene, pentane). Due to the observed solubility characteristics, gold compound 3 was anticipated to have improved recycling characteristics over [AuCl(PPh₃)]. Further research concerning the solubility properties of 4, its subsequent application under homogeneous conditions in nanofiltration membrane reactors and reaction of 4 with organolithium reagents is ongoing.

To test the reactivity of the AuCl functions, [(AuCl)₂(dppbp)] (3) was first reacted with 1 equiv of [Li(NCN)] in toluene. The ³¹P{¹H} NMR spectrum of the reaction mixture in CDCl₃ showed two signals at 34 and 45 ppm, respectively; the singlet resonance at 34 ppm corresponds to the ³¹P{¹H} NMR signal of a P-(AuCl)-unit while the singlet resonance at 45 ppm corresponds to the presence of an arylated P-(AuNCN) moiety.8 The ¹H NMR spectrum shows two singlets for the NMe₂ groups at 2.26 and 2.36 ppm with a ratio of 1 : 2, respectively. From this data it was concluded that bis(chlorogold(I)) complex 3, monoarylated 5 and bisarylated 6 were present in equal amounts. Due to the aforementioned solubility properties, the arylation of one Au center $(3 \rightarrow 5)$ resulted in the formation of a more soluble species. As such, the increased concentration resulted in enhanced reactivity of 5 as compared to 3. The similarities of the ³¹P chemical shifts for the AuNCN and AuCl functions in 5 to those in 3 (AuCl) and 6 (AuNCN) indicate that the two gold centers are essentially independent. Further reaction of this mixture with an additional equivalent of [Li(NCN)] showed complete conversion to 6 as was deduced from the single peak in the ${}^{31}P{}^{1}H$ NMR at 45 ppm, as well as from the disappearance of the signal at 34 ppm. Alternatively, direct reaction of 2 equiv of [Li(NCN)] with 3 afforded [(Au(NCN))₂(dppb)] 6, which was obtained in an isolated yield of 78% (Scheme 3).

Crystals, suitable for X-ray crystal structure determination, of 6 were obtained from a toluene-pentane solution. A top and sideon view of the molecular structure is shown in Fig. 1. A toluene molecule, which is incorporated in the crystal lattice, has been removed for clarity.

The molecular structure shows that the gold atoms are η^{1} -*C* bonded to the intra-annular C_{ipso}-atom of the pincer moieties which, in turn, are *trans*-coordinated to the diphenylphosphino



Scheme 3 Synthesis of [(Au(NCN))₂(dppbp)] (6).



Fig. 1 Displacement ellipsoid plot (50% probability) for **6**. Hydrogen atoms and toluene are omitted for clarity. Selected bond lengths (Å), bond angles (°) and torsion angle (°): Au(1)–C(1) 2.069(2), Au(1)–P(1) 2.2844(7), C(16)–C(16a) 1.491(3). C(1)–Au(1)–P(1) 177.95(9), C(15)–C(16a)–C(16a)–C(15a) 180. Symmetry code a = -x, 2 - y, 1 - z.

groups. This yields a digold complex that has a crystallographic inversion center at the $C_{Ar}-C_{Ar}$ link of the biphenyl moiety. The *trans*-disposition of ligands about the Au center is shown by the C(1)–Au(1)–P(1) angle of 177.95(9)°. In comparison, the analogous angles in two crystallographically independent molecules found in one crystal of [Au(NCN)(PPh₃)] (7)⁸ are 178.6(3) and 176.0(3)°. The Au(1)–N(1) and Au(1)–N(2) distances are 4.184(3) and 4.210(3) Å, respectively. These distances are in the range as found in 7 (3.544–4.414 Å) showing that the *ortho*-Me₂NCH₂ ligands are non-coordinated.

As a result of the inversion center in the C(16)-C(16a) bond, the biphenylene moiety is flat with the torsion angle C(15)-C(16)-C(16a)-C(15a) amounting to 180°. The C-C bond length (1.491(3) Å) between the arenes (C(16)-C(16a)) is that of a single $C(sp^2)-C(sp^2)$ bond, which restricts electronic communication between the gold centers (cf. $[(Ru^{III})_2(4,4'-\{C_6H_2(CH_2NMe_2)_2 (2,6)_2$ (terpy)₂]⁴⁺ (CuCl₂⁻)₄).¹¹ The biphenylene moiety is rotated with respect to the plane defined by C(1)-Au(1)-P(1)-C(13)-C(16) (largest deviation from the LS-plane = 0.0099(7) Å for P(1)) by 44.73(12)°. The Au(1)–C(1) and Au(1)–P(1) bond lengths of 2.069(2) and 2.2844(7) Å, respectively, compare well to those lengths in the mono-NCN gold structure 7 (2.055(9), 2.045(9) and 2.282(2), 2.287(2) Å, respectively).8 The observations are in agreement with the ³¹P chemical shifts of the P(AuCl) groupings in 3 and 5, as well as those found for the ³¹P chemical shifts of the P(AuNCN) groupings in 5 and 6.

Following the same procedure, **3** was reacted with two equivalents of [Li(Me,Me-Phebox)] (**8**), affording [(Au(Phebox))₂-(dppbp)] (**9**) in 93% yield (Scheme 4). The ¹H NMR spectrum of **9** in C₆D₆ shows the same chemical shifts for the Phebox moieties as in the ¹H NMR spectrum of [Au(Me,Me-Phebox)(PPh₃)] (**10**).¹² For example, the methyl and methylene signals for **10** are 1.08 and 3.73 ppm, compared to 1.09 and 3.74 ppm, respectively, for **9**. As in **10**, the oxazoline ligands do not coordinate to the Au center (X-ray crystal structure determination)¹² it is obvious that these ¹H and ³¹P{¹H} NMR data point to the presence of non-coordinated oxazoline ligands in **9**. In the same way, the structural features of **7** and **10** are similar with δ ³¹P data of 41.4 ppm *vs* 41.8 ppm.



Scheme 4 Synthesis of [(Au(Me,Me-Phebox))₂(dppbp)] (9).

In contrast to the low solubility of 3 in common organic solvents, the bis(NCN)gold(I) complexes 6 and 9 are soluble in most organic solvents (toluene, diethyl ether, acetonitrile, dichloromethane). To test the transmetalating properties of the new digold reagents and the recyclability of the mutual coproduct 3, 6 was reacted with [TiCl₃(OiPr)] while 9 was reacted with $[PdCl_2(SEt_2)_2]$ (Scheme 5). In contrast to transmetalation reactions with organolithium reagents, the reaction with $[PdCl_2(SEt_2)_2]$ could be performed in air without further precautions affording 12 in almost quantitative yield after filtration. The reaction with [TiCl₃(O*i*Pr)] still had to be performed under an inert atmosphere as the resulting (NCN)Ti-complex 11 is air sensitive. The use of 6 as the transmetalating agent resulted in a higher yield of the transmetalated product (84%) as compared with reactions in which either the gold monomer 7 or [Li(NCN)] was used for 11 (658 and 74%¹³ yield, respectively). Obviously, the lower solubility of the gold coproduct 3 as compared with that of $[AuCl(PPh_3)]$ is the



Scheme 5 Transmetalation experiments

main reason for these higher yields. In the transmetalation reaction between [Li(NCN)] and [TiCl₃(OiPr)] the product is formed along with side-products due to the redox properties of the Li-reagent. Separation of these side-products from the Ti^{IV}-product resulted in considerable losses of product. By using **6** these side-reactions are avoided due to the inertness of the gold-centers in **6** and **7**⁹

Although complexes **11** and **12** have been synthesized before using the corresponding organolithium reagents,^{13,14} especially for the synthesis of the Phebox complexes of type **12**, alternative methods such as direct cyclometalation¹⁵ or oxidative addition of C–X bonds to zerovalent Pd¹⁶ have been used to avoid the inherent problems arising from reduction of the Pd^{II} by the organolithium reagents. Also, higher yields of **12** were obtained by reacting the organogold(1) compound **9** with [PdCl₂(SEt₂)₂].

Conclusions

Due to the easy separation of coproduct 3 and the mild transmetalating properties (non-reducing nature, inertness of the gold(I)centers) of 9, pure 12 could be isolated. These results show that the introduction of a rigid diphosphine (1) leads to the preparation of dinuclear gold(I) transmetalating agents with excellent arylating properties.

Experimental

All experiments were carried out under a dry, oxygen free, nitrogen atmosphere, using standard Schlenk techniques unless stated otherwise. Solvents were dried and distilled from sodium (pentane, toluene), Na-benzophenone (diethyl ether) or CaH₂ (CH₂Cl₂), prior to use. n-BuLi (1.6 M in hexane) was obtained from Acros and used as received. ¹H and ¹³C{¹H} NMR spectra were recorded on a Varian Inova 300 spectrometer. ${}^{31}P{}^{1}H{}$ (81 MHz) NMR experiments were recorded on a Varian Mercury 200 spectrometer. Benzene- d_6 was purchased from Cambridge Isotope Laboratories, distilled from Na and stored in a nitrogen filled M-Braun glove box. CD₂Cl₂ was used as received. ¹H and ${}^{13}C{}^{1}H$ NMR chemical shifts (δ) are reported in ppm relative to the residual solvent signal as an internal standard. ${}^{31}P{}^{1}H$ NMR chemical shifts are referenced externally to H_3PO_4 . [AuCl(tht)],¹⁷ [Li(NCN)]₂⁸ and [Li(Phebox)]₂¹⁸ were synthesized according to literature procedures. All other chemicals were purchased from either Acros or Aldrich and used as received. Elemental analysis were performed by Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr, Germany.

Synthesis of 4,4'-bis(diphenylphosphino)biphenyl (dppbp) (1)

A solution of *n*-BuLi (6.3 mL, 10 mmol, 1.6 M in hexanes) was added to a solution of 4,4'-dibromobiphenyl (1.56 g, 5.0 mmol) in THF (60 mL) at -78 °C. After 2 h, ClPPh₂ (1.8 mL, 10 mmol) was added dropwise *via* a syringe. The reaction mixture was warmed to room temperature and stirred overnight. The light yellow solution was quenched with a degassed, saturated aqueous solution of NH₄Cl (60 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were dried with MgSO₄, filtered and dried *in vacuo*. The residual solid was washed with pentane (10 mL). This afforded 1 as a white, air stable solid (2.30 g, 88%). ¹H NMR (200 MHz,

 $\begin{array}{l} C_{6}D_{6}): \delta \ 7.02 \ (m, \ 12H), \ 7.38 \ (m, \ 16H). \ ^{13}C\{^{1}H\} \ NMR \ (75 \ MHz, \\ C_{6}D_{6}): \delta \ 127.4 \ (d, \ ^{3}J_{P-C} = 7 \ Hz), \ 128.8, \ 129.0 \ (d, \ ^{3}J_{P-C} = 3 \ Hz), \\ 134.2 \ (d, \ ^{2}J_{P-C} = 19 \ Hz), \ 134.8 \ (d, \ ^{2}J_{P-C} = 19 \ Hz), \ 137.4 \ (d, \ ^{1}J_{P-C} = \\ 15 \ Hz), \ 138.0 \ (d, \ ^{1}J_{P-C} = 12 \ Hz), \ 141.1. \ ^{31}P\{^{1}H\} \ NMR \ (81 \ MHz, \\ C_{6}D_{6}): \delta - 5 \ (s). \ Anal. \ Calcd \ for \ C_{36}H_{28}P_{2}: \ C, \ 82.74; \ H, \ 5.40. \ Found: \\ C, \ 82.53; \ H, \ 5.48. \end{array}$

Synthesis of 1,3,5-tris[4-(diphenylphospino)phenyl]-benzene (tdpppb) (2)

A solution of 1,3,5-tris(p-bromophenyl)benzene (827 mg, 1.52 mmol) in THF (60 mL) at -78 °C was added dropwise to a solution of n-BuLi (3.2 mL, 5.1 mmol, 1.6 M in hexanes) in THF (20 mL) at -78 °C under vigorous stirring. When the addition was complete, the reaction mixture was diluted with THF (50 mL) and the turbid light yellow mixture was stirred for 1 h at -78 °C after which ClPPh₂ (0.90 mL, 5.0 mmol) was added. The resulting clear solution was warmed to room temperature and then stirred overnight. The light yellow solution was quenched with a degassed aqueous solution of NH₄Cl (100 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried with MgSO₄ and filtered. All volatiles were evaporated and the residue was washed with pentane $(4 \times 5 \text{ mL})$, after which 2 was obtained as a white, air-stable solid (1.05 g, 80%). ¹H NMR (C6D6, 200 MHz): *δ* 7.10 (m, 18H), 7.47 (m, 24H), 7.69 (s, 3H). 13C NMR (CDCl3, 300 MHz): δ 125.4, $127.4 (d, 3J_{P-C} = 6.1 Hz), 128.7 (d, 3J_{P-C} = 6.7 Hz), 128.9, 133.9 (d, 3J_{P-C} = 6.7 Hz), 138.9, 138.9 Hz)$ $2J_{P-C} = 19$ Hz), 134.4 (d, $2J_{P-C} = 20$ Hz), 136.9 (d, $1J_{P-C} = 11$ Hz), 137.2 (d, $1J_{P-C} = 11$ Hz), 141.3, 141.9. ³¹P-NMR (C6D6, 81 MHz): δ -5. Anal. Calcd for C₆₀H₄₅P₃: C, 83.90; H, 5.28; Found: C, 83.26; H, 5.43.

Synthesis of [(AuCl)₂(dppbp)] (3)

A solution of dppbp (1) (575 mg, 1.10 mmol) in CH₂Cl₂ (40 mL) was added to a solution of [AuCl(tht)] (706 mg, 2.20 mmol) in CH₂Cl₂ (30 mL) at room temperature. After 16 h the solution was separated from the minor precipitate by a cannula and the precipitate was extracted with warm CH₂Cl₂ (20 mL). The CH₂Cl₂ was removed from the solution by evaporation *in vacuo*. The residue, thus obtained, was suspended in toluene (15 mL) and stirred for 5 min. The toluene was removed *in vacuo*, which afforded **3** as a white air stable solid (1.09 g, 100%). ¹H NMR (CD₂Cl₂, 200 MHz): δ 7.50–7.65 (m, 24H), 7.70–7.75 (m, 4H). ¹³C{¹H} NMR (CD₂Cl₂, 50 MHz): δ 128.1 (d, ³J_{P-C} = 13 Hz), 129.5 (d, ³J_{P-C} = 12 Hz), 132.3, 134.3 (d, ²J_{P-C} = 14 Hz), 134.9 (d, ²J_{P-C} = 14 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 81 MHz): δ 34 (s). Anal. Calcd for C₃₆H₂₈Au₂Cl₂P₂: C, 43.79; H, 2.86; Found: C, 43.81; H, 2.95.

Synthesis of [(AuCl)₃(tdpppb)] (4)

A solution of tdpppb (2) (414 mg, 0.48 mmol) in CH₂Cl₂ (30 mL) was added to a solution of [AuCl(tht)] (465 mg, 1.45 mmol) in CH₂Cl₂ (30 mL) at room temperature. After 16 h the reaction mixture was filtered over Celite and the solvent removed from the solution by evaporation *in vacuo*. The residue, thus obtained, was suspended in pentane (10 mL) and stirred for 5 min. The pentane was removed *in vacuo* which afforded **4** as a white air stable solid (746 mg, 100%). ¹H NMR (CD₂Cl₂, 200 MHz): δ 7.48–7.86 (m,

42 H), 7.89 (s, 3H). ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 81 MHz): δ 34 (s). Anal. Calcd for C₆₀H₄₅Au₃Cl₃P₃: C, 46.31; H, 2.91; Found: C, 46.34; H, 3.06.

Synthesis of [(Au(NCN))₂(dppbp)] (6)

A previously prepared solution of [Li(NCN)] (4.0 mL, 0.80 mmol, 0.2 M in toluene) was added to a suspension of [(AuCl)₂(dppbp)] (3) (401 mg, 0.41 mmol) in toluene (35 mL) and the reaction mixture was stirred for 16 h. The mixture was centrifuged, the solvent removed and the residue was extracted with toluene (5 mL). The volume of the combined toluene extracts was reduced in vacuo to ~ 10 mL after which the product was precipitated with pentane. The mixture was centrifuged and the solvent decanted to yield the product as a white air stable solid characterized as the toluene solvate of 6 (344 mg, 78%). ¹H NMR (C₆D₆, 300 MHz): δ 2.34 (s, 24H), 4.06 (s, 8H), 7.08 (m, 12H), 7.36 (m, 6H), 7.69–7.74 (m, 16H). ¹³C{¹H} NMR (C₆D₆, 75 MHz): δ 46.0, 70.9, 125.7, 127.8, 127.9 (d, ${}^{3}J_{P-C} = 7$ Hz), 129.2 (d, ${}^{3}J_{P-C} = 11$ Hz), 131.1, 132.2 (d, ${}^{1}J_{P-C} = 48$ Hz), 134.7 (d, ${}^{2}J_{P-C} = 14$ Hz), 135.3 (d, ${}^{2}J_{P-C} = 14$ Hz), 142.5, 148.1, 176.0, 177.5. ³¹P{¹H} NMR (C₆D₆, 81 MHz): δ 44 (s). Anal. Calcd for C₆₀H₆₆Au₂N₄P₂·C₇H₈: C, 57.84; H, 5.36; N, 4.03 Found: C, 57.64; H, 5.27; N, 3.86.

Synthesis of [(Au(Me,Me-Phebox))₂(dppbp)] (9)

A solution of [Li(Phebox)] (241 mg, 0.87 mmol) in toluene (10 mL) was added to a suspension of [(AuCl)₂(dppbp)] (**3**) (425 mg, 0.43 mmol) in toluene (20 mL). The flask was rinsed with an additional portion of toluene (10 mL). After stirring overnight, the reaction mixture was filtered over Celite and the filtrate was dried *in vacuo*. The residue was washed with pentane (3×6 mL) and dried *in vacuo* to yield **9** as an air stable off-white solid (580 mg, 93%). ¹H NMR (C₆D₆, 300 MHz): δ 1.09 (s, 24H), 3.74 (s, 8H), 7.08 (m, 12H), 7.18 (t, ³J_{H-H} = 8.1 Hz), 7.41 (d, 4H, ³J_{H-H} = 6.9 Hz), 7.81–7.90 (m, 12H), 8.48 (d, ³J_{H-H} = 7.8 Hz). ¹³C{¹H} NMR (C₆D₆, 75 MHz): δ 28.7, 68.1, 79.0, 125.1, 125.6, 126.1, 126.6, 129.0 (d, ³J_{P-C} = 10.3 Hz), 130.9, 131.6 (d, ³J_{P-C} = 5.4 Hz), 132.9 (d, ¹J_{P-C} = 48.8 Hz), 135.1 (d, ²J_{P-C} = 14.2 Hz), 135.7 (d, ²J_{P-C} = 14.2 Hz), 139.0, 167.6. ³¹P{¹H} NMR (C₆D₆, 81 MHz): δ 41 (s). Anal. Calcd for C₆₈H₆₆Au₂N₄O₄P₂: C, 55.97; H, 4.56; Found: C, 56.11; H, 4.51.

Synthesis of [TiCl₂(NCN)(O*i*Pr)] (11)

A solution of **6** (930 mg, 0.84 mmol) in toluene (7 mL) was added to a solution of [TiCl₃(O*i*Pr)] (358 mg, 1.68 mmol) in toluene (10 mL). The flask was rinsed with an additional portion of toluene (7 mL). The reaction mixture was stirred overnight after which it was centrifuged and separated. The residue was extracted with toluene (15 mL). The residue was characterized as pure **3** (797 mg, 96%). Anal. Calcd for C₃₆H₂₈Au₂Cl₂P₂: C, 43.79; H, 2.86; Found: C, 43.71; H, 2.93. The mother liquor was evaporated to dryness to afford **9** (521 mg, 84%) as an air sensitive yellow solid. ¹H NMR (C₆D₆, 200 MHz): δ 1.8 (d, 6H, ³J_{H-H} = 4.8 Hz), 2.1 (s, 6H), 2.6 (d, 2H, ³J_{H-H} = 12 Hz), 2.8 (s, 6H), 4.7 (s, 2H), 5.8 (septet, 1H, ³J_{H-H} = 6 Hz), 6.6 (d, 2H, ³J_{H-H} = 7 Hz), 6.9 (t, 1H, ³J_{H-H} = 7 Hz). Anal. Calcd for C₁₅H₂₆Cl₂N₂OTi: C, 48.80; H, 7.10; N, 7.59; Found: C, 48.62; H, 6.88; N, 7.37. In air, a solution of **9** (218.5 mg, 0.15 mmol) in toluene (15 mL) was added to a solution of $[PdCl_2(SEt_2)_2]$ (107 mg, 0.3 mmol) in toluene (5 mL). The flask was rinsed with an additional portion of toluene (3 mL). The reaction mixture was stirred overnight after which it was centrifuged and separated. The residue was extracted with 6 mL toluene. After removal of the solvent the residue was characterized as pure **3** (146.7 mg, 100%) Anal. Calcd for $C_{36}H_{28}Au_2Cl_2P_2$: C, 43.79; H, 2.86; Found: C, 43.93; H, 2.76. The mother liquor was evaporated to afford **12** (122 mg, 100%) as an air stable light yellow solid. ¹H NMR (C_6D_6 , 300 MHz): δ 1.49 (s, 12H), 3.60 (s, 4H), 6.67 (t, 1H, ${}^{3}J_{H-H} = 7.7$ Hz), 7.05 (d, 2H, ${}^{3}J_{H-H} = 7.8$ Hz). ${}^{13}C{}^{1}H{}$ NMR (C_6D_6 , 75 MHz): δ 27.9, 66.0, 82.8, 123.7, 126.5, 130.7, 169.2, 172.5. Anal. Calcd for $C_{16}H_{19}ClN_2O_2Pd$: C, 46.51; H, 4.63; N, 6.78; Found: C, 46.42; H, 4.69; N, 6.63.

Crystal structure determination of [(Au(NCN))₂(dppbp)] (6)

 $C_{60}H_{66}Au_2N_4P_2 \cdot C_7H_8$, $M_r = 1391.18$, colorless, irregular crystal cut from a larger aggregate (approximate dimensions 0.2 \times 0.3×0.3 mm), triclinic, space group P $\overline{1}$ (no. 2) with a =10.6883(10), b = 11.8062(10), c = 13.7445(10) Å, a = 104.35(3), $\beta = 90.04(4), \gamma = 115.51(4)^{\circ}, V = 1505.0(2)\text{Å}^3, Z = 1, \mu(\text{Mo-}$ $K\alpha$) = 4.964 mm⁻¹. 43053 Reflections were measured, 6878 of which were independent, $R_{int} = 0.0423$, $R_{\sigma} = 0.0243$, $1.54^{\circ} < \theta <$ 27.45°, T = 150 K, Mo-Ka radiation, graphite monochromator, $\lambda = 0.71073$ Å. Data were collected on a Nonius Kappa CCD area detector on rotating anode and corrected for absorption by a multi-scan method (PLATON/MULABS,19 T-range 0.238-0.368). The structure was solved by Patterson methods (DIRDIF-99)²⁰ and refined on F^2 using SHELXL-97-2.²¹ The unit cell contains a toluene molecule, disordered over a crystallographic inversion centre. Mild distance restraints were applied to enforce a reasonable geometry of the solvent molecule. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement was described with a fixed isotropic parameter linked to the value of the equivalent isotropic parameter of their carrier atoms. Final wR2 (= { $\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]$ }^{1/2}) = 0.0527, $w = 1/[\sigma^2(F_0^2) + (0.0253P)^2 + 1.20P]$, where $P = (\max(F_0^2, 0) + 1.20P)$ $2F_{c}^{2}/3$, R1 (= $\Sigma ||F_{o}| - |F_{c}|/\Sigma ||F_{o}|$) = 0.0208 (for 6469 I > $2\sigma(I)$, S = 1.088, 336 refined parameters, $-1.32 < \Delta \rho < 1.04 \text{ e} \text{ Å}^{-3}$ (near Au).

CCDC reference numbers 254665 for compound 6.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701271c

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