EurJIC European Journal of Inorganic Chemistry

FULL PAPER

DOI: 10.1002/ejic.201200152

Synthesis, Structure and Transmetalation Activity of Various *C,Y*-Chelated Organogold(I) Compounds

Martin Hejda,[a] Libor Dostál,*[a] Roman Jambor,[a] Aleš Růžička,[a] Robert Jirásko,[b] and Jaroslav Holeček[a]

Keywords: Gold / Palladium / Platinum / Metalation / Chelates

A set of organogold(I) compounds $L^{1-4}Au(PPh_3)$, where L^1 = $[o\text{-}C_6H_4(CH{=}NC_6H_3iPr_2\text{-}2,6)]^-$ (**1**), L^2 = $\{o,o\text{-}C_6H_3[C(Me){=}NC_6H_3Me_2\text{-}2,6]_2\}^-$ (**2**), L^3 = $[o,o'\text{-}C_6H_3(CH_2OMe)(CH_2NMe_2)]^-$ (**3**), L^4 = $[o,o\text{-}C_6H_3(CH_2OMe)_2]^-$ (**4**), were synthesized by the reaction of parent organolithium derivatives $L^{1-4}Li$ with $[AuCl(PPh_3)]$ in good yields. The molecular structures of **1**–**4** were characterized by ESI mass spectrometry and ^1H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and their structures in the solid state were determined using single-crystal X-ray diffraction analyses. The transmetalation potential of **1**–**4** was tested by the reaction with either $[PdCl_2(CH_3CN)_2]$ or $[PtCl_2(Et_2S)_2]$ complexes. While the reaction of compounds **1** and **2** proceeded smoothly with the formation of the desired transition-metal complexes, i.e. $(L^1PdCl)_2$ (**5**), $L^1PtCl(Et_2S)$ (**6**) and L^2MCl [M = Pd (**7**) or Pt (**8**). In the case of the *O,C,N*- and *O,C,O*-chelated derivatives **3** and **4** only the platinum(II) compounds $L^3PtCl(PPh_3)$ (**9**) and $L^4PtCl(Et_2S)_2$ (**10**) could be isolated after the reaction, as a result of the labile behaviour of the corresponding palladium compounds. All derivatives **5**–**10** were characterized by the help of ESI mass spectrometry and ^1H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and in the case of compounds **5**–**7** and **9** using single-crystal X-ray diffraction analyses.

Introduction

The chemistry of the so called Y,C,Y (Y,Y,Y) pincer-type coordinating ligands (Y = donor atom such as N, P, O etc.) represents a rapidly developing area of chemical research in the field of organometallic chemistry and catalysis.[1] Although the chemistry of transition metals was preferred at the beginning of the research in this field,[2] later the investigation of main-group metal compounds became important and interesting findings were reported.[3] The key influence of the pincer ligand is stabilization of the central metal by two dative connections Y→M between the metal and donor atoms Y. Thus, it is necessary to metalate the pincer ligand backbone to the *ortho-ortho* position to profit from these intramolecular interactions (Figure 1, L^{2-4}). Several reaction pathways were developed for successful metalation of the pincer ligand (Scheme 1), these comprise of (i) direct *cyclometalation*,[4] which include C–H bond activation and no prefunctionalization of the ligand is necessary. (ii) *Oxidative addition*[5] of low valent metal precursors into a C–X bond (X = Br, I). (iii) *Transcyclometalation*,[6] which is the substitution of one pincer-type ligand for another. (iv) *Transmetalation*, this method requires preparation of well-defined main-group metal precursors,[7] which further react with metal halides with elimination of main-group metal halides. The transmetalation procedure is the best choice, especially for main-group metal compounds and for transition-metal complexes of N,C,N pincer-type ligands that do not undergo easy cyclometalation as do their P,C,P or S,C,S counterparts.[8] Van Koten et al. have reported on a new synthetic strategy leading to organometallic N,C,N pincer

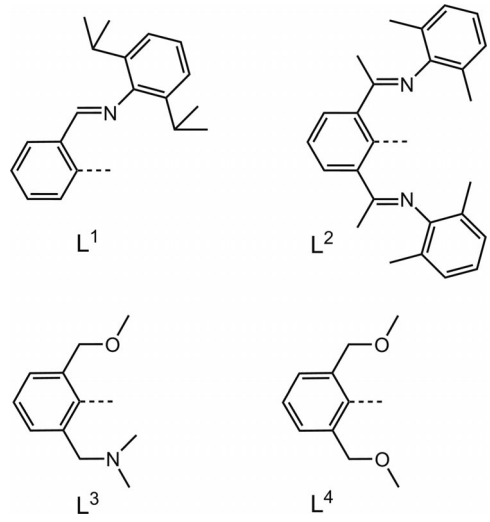
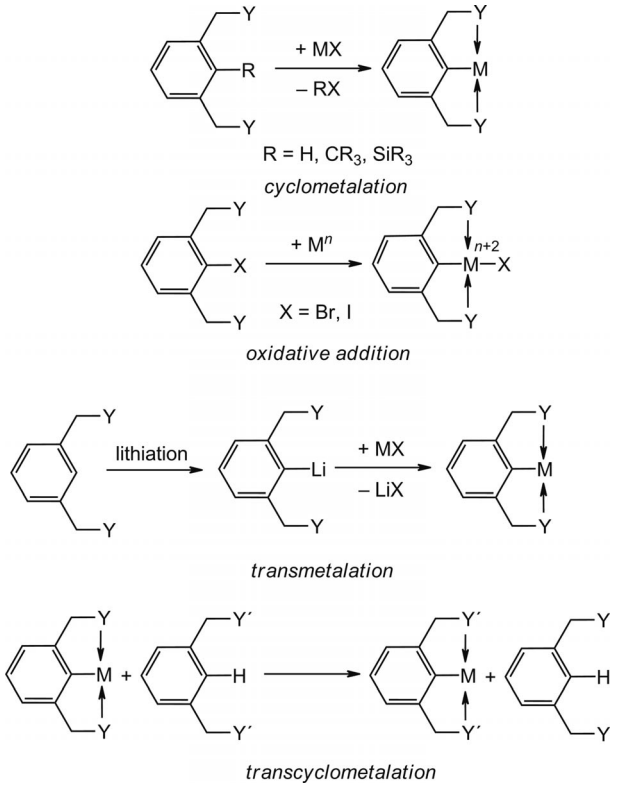


Figure 1. Ligands used in this study.

[a] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 53210 Pardubice, Czech Republic
Fax: +420-466037068
E-mail: libor.dostal@upce.cz
[b] Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 53210 Pardubice, Czech Republic

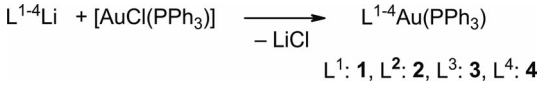
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201200152.

compounds using organogold(I) precursors[9] as the transmetalating reagents. The gold fragment AuL^+ has an isolobal relationship to Li^+, which indicates that the [RAuL] compounds could have similar transmetalating properties as the corresponding organolithium RLi reagents. These gold synthons also have several advantages in comparison with commonly used *N*,*C*,*N*-chelated organolithium compounds such as stability towards air and moisture, nontoxicity, redox stability, high yield transmetalation procedures and recycling of gold reagents. Since the first report on the transmetalation properties of organogold(I) derivatives of the classical N,C,N pincer-type ligand $\{[o,o\text{-}C_6H_4(CH_2NMe_2)_2]^-\}$,[10] the same working team has enriched this family of gold reagents to those derived from Phebox ligands. A variety of transition-metal halides (both early and late) were used as substrates for transmetalation studies.[11] It is worth noting that some silver(I) pincer compounds were used by van der Vlugt et al. for the preparation of palladium(II) complexes.[12]



Scheme 1. Synthetic strategies for metalation of the pincer ligand backbone.

We are interested in the pincer chemistry of main-group metals and during these investigations new types of O,C,O,[13] N,C,O[14] and N,C,N[15] and potentially bidentate N,C[16] ligands were introduced. Organometallic derivatives of these ligands were exclusively prepared starting from the organolithium precursors using a standard transmetalation synthetic protocol. We are interested in whether it is feasible to prepare organogold(I) derivatives of our ligands and to use them as transmetalating agents in the reactions with transition-metal halides. As the first part of these studies, we report here on the preparation of four organogold(I) compounds $L^{1-4}Au(PPh_3)$, where L^1 = $[o\text{-}C_6H_4(CH{=}NC_6H_3iPr_2\text{-}2,6)]^-$ (**1**), L^2 = $\{o,o\text{-}C_6H_3[C(Me){=}NC_6H_3Me_2\text{-}2,6]_2\}^-$ (**2**), L^3 = $[o,o'\text{-}C_6H_3(CH_2OMe)(CH_2NMe_2)]^-$ (**3**) and L^4 = $[o,o\text{-}C_6H_3(CH_2OMe)_2]^-$ (**4**) (Figure 1, Scheme 2). This set of gold(I) synthons enables us to question two basic problems, (i) is the transmetalation possible using only a bidentate ligand such as L^1, (ii) is it possible to use this synthetic protocol for ligands substituted by oxygen donor atoms ($L^{3,4}$), which are in general not well suited for coordination of late transition metals? Thus, the first attempts to use **1**–**4** as transmetaling agents using $[PdCl_2(CH_3CN)_2]$ and $[PtCl_2(Et_2S)_2]$ complexes as the substrates are described. Reported compounds were characterized by elemental analysis, electrospray mass spectrometry (ESI), multinuclear NMR spectroscopy and single-crystal X-ray diffraction analyses.



Scheme 2. Preparation of organogold(I) precursors **1**–**4**.

Results and Discussion

Organogold(I) Precursors: Syntheses, Characterization and Structure

Organogold(I) precursors **1**–**4** were prepared by standard procedures; treating the starting organolithium precursors $L^{1-4}Li$ with one molar equiv. of commercially available $[AuCl(PPh_3)]$ according to Scheme 2. All compounds were obtained in good yields as white or yellowish (**2**) crystalline solids, which are very soluble in both aromatic and chlorinated solvents. The identity of **1**–**4** was established by satisfactory elemental analysis and ESI mass spectrometry, where the presence of protonated molecules $[M + H]^+$ and/(or) sodium (potassium) adducts $[M + Na]^+$ or $[M + K]^+$ were detected. The ^1H NMR and ^{13}C NMR spectra of **1**–**4** revealed the expected set of signals from the ligands L^{1-4} and PPh_3 (see Exp. Section). The ^{31}P NMR spectra contained one signal for each compound (δ = 44.1 for **1**, 41.9 for **2**, 44.9 for **3** and 44.4 ppm for **4**), which are slightly shifted to lower field in comparison with the starting chlorido complex $[AuCl(PPh_3)]$ (δ = 32.7 ppm).

The molecular structures of **1**–**4** were unambiguously determined by the help of single-crystal X-ray diffraction analyses. The crystallographic data are given in the Exp. Section and the molecular structures of **1**–**4** are illustrated in Figures 2 and 3, together with the relevant structural parameters given in the figure captions. All of the molecular structures are closely related. The central gold atom is η^1-C-bonded to the C-*ipso* atom of the corresponding ligand (L^{1-4}) and the triphenylphosphane molecule is coordinated in the *trans* position [the range of the P–Au bond lengths is 2.2742(9)–2.2851(15) Å] with the bond angles P–Au–C in the range of 174.2(4)–179.21(12)° in **1**–**4**. The arms of the

donor ligands remain noncoordinated to the gold atom in all cases. The molecular structures of compounds **1**–**4** are analogous to the other organogold(I) compounds containing a *Y,C,Y*-chelating ligand reported earlier.[10,11]

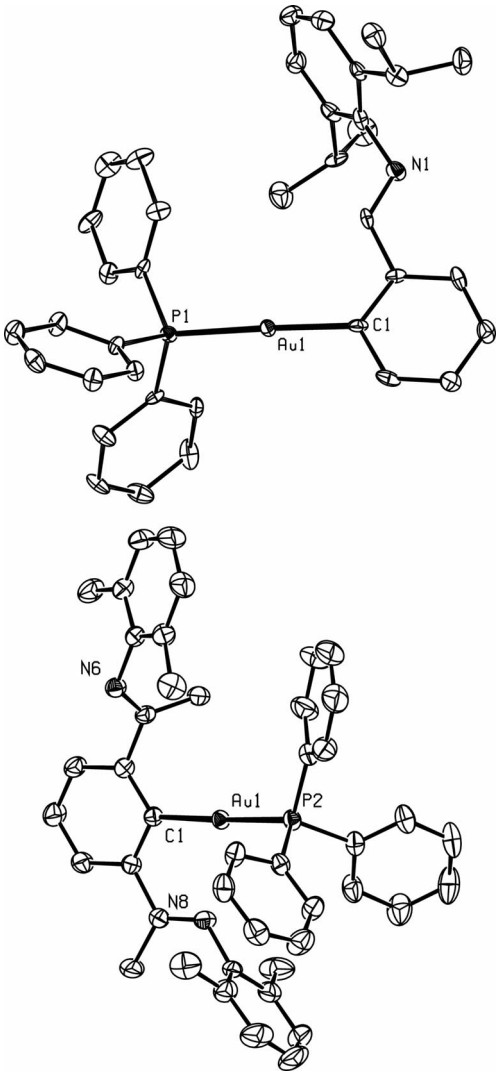


Figure 2. ORTEP diagram of compounds **1** (top) and **2** (bottom) with thermal displacement parameters at 30% probability, hydrogen atoms and the toluene molecule in the case of **2** were omitted for clarity. Selected distances [Å] and angles [°] for **1**: Au1–C1 2.019(13), Au1–P1 2.275(3), C1–Au1–P1 174.2(4). For **2**: Au1–C1 2.067(4), Au1–P2 2.2742(9), C1–Au1–P2 176.54(9).

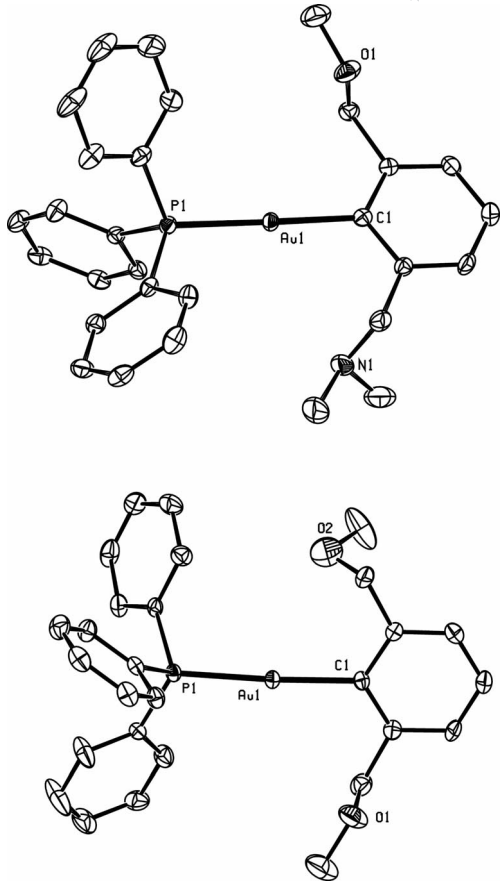
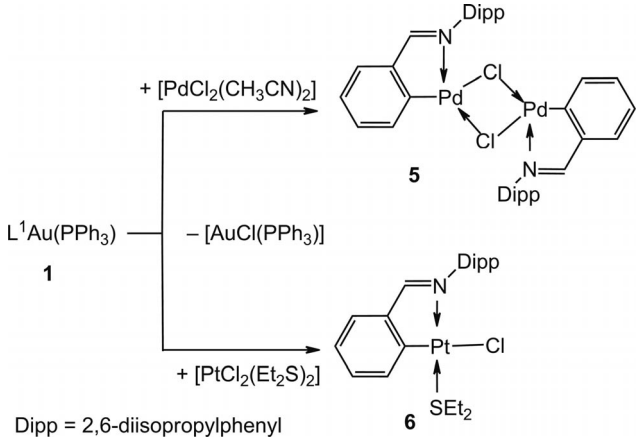


Figure 3. ORTEP diagram of compounds **3** (top) and **4** (bottom) with thermal displacement parameters at 30% probability. Selected distances [Å] and angles [°] for **3**: Au1–C1 2.042(5), Au1–P1 2.2786(14), C1–Au1–P1 179.21(12). For **4**: Au1–C1 2.053(6), Au1–P1 2.2851(15), C1–Au1–P1 175.76(16).



Scheme 3. Preparation of **5** and **6**.

Transmetalation Using Organogold(I) Compounds 1–4

The transmetalation attempts are described consecutively according to the ligand used (L^{1-4}), because the results differ substantially in most cases.

The reaction of compound **1** with both $[PdCl_2(CH_3CN)_2]$ and $[PtCl_2(Et_2S)_2]$ proceeded smoothly giving compounds $(L^1PdCl)_2$ (**5**) and $L^1PtCl(Et_2S)$ (**6**), respectively (Scheme 3). The reaction was monitored by ^{31}P NMR as well as ^1H NMR spectroscopy, which indicated essentially quantitative conversion. The ^{31}P NMR spectrum revealed only one signal at δ = 32.7 ppm for $[AuCl(PPh_3)]$ proving that all starting material was consumed. After workup, compounds **5** and **6** were isolated in 30% and 78% yield, respectively. The lower isolated yield in the case of **5** was caused mainly by a rather similar solubility of **5** and incipient $[AuCl(PPh_3)]$. Both compounds were characterized by elemental analysis and ESI mass spectrometry, where ions

$[M - Cl]^+$ or their water adducts $[M - Cl + H_2O]^+$ were detected. The ^1H NMR and ^{13}C NMR spectrum of **5** contained one set of expected signals corresponding to the ligand L^1. On the contrary, the ^1H NMR and ^{13}C NMR spectra of **6** contained, besides the signals of the ligand L^1, signals from the coordinated diethylsulfide molecule.

The presence of an intramolecular N→M interaction was reflected by the observation of two signals for the magnetically nonequivalent methyl groups of the *i*Pr moieties in the ^1H NMR and ^{13}C NMR spectra of **5** and **6**, which is consistent with the hindered rotation around the aryl–N bond. These findings indicate that the acetonitrile molecules are lost during the reaction of **1** with $[PdCl_2(CH_3CN)_2]$, on the contrary one of the diethyl sulfide molecules remains intact at the platinum centre in the case of the formation of **6** from **1** and $[PtCl_2(Et_2S)_2]$. It is also worth noting that compound **5** has recently been prepared by Chang et al. using standard cyclometalation procedures starting from L^1H, $Na_2[PdCl_4]$ and sodium acetate as the base.[17] Nevertheless, the molecular structure of **5** has not been reported.

The molecular structures of **5** and **6** were established by single-crystal X-ray diffraction analyses, the crystallographic data are given in the Exp. Section and the molecular structures are depicted in Figures 4 and 5 together with relevant structural parameters summarized in the figure captions. Compound **5** is built up as a centrosymmetric dimeric molecule with the chlorine atoms Cl1 and Cl1a located in the bridging positions. These bridges are slightly nonsymmetric as documented by the bond lengths Pd1–Cl1 2.3264(6) and Pd1–Cl1a 2.4493(6) Å. Similar dimeric units are usually formed in analogous *N,C*-chelated palladium(II) compounds.[17] The pendant arm of the ligand is coordinated to the palladium atom [the bond length Pd1–N1 is 2.0187(18) Å]. The central palladium atom is situated in a square-planar environment with the N1, Cl1 and C1, Cl1a atoms placed mutually in *trans* positions [the bond angles are C1–Pd1–Cl1a 173.07(7) and N1–Pd1–Cl1 176.19(5)°].

In contrast to **5**, compound **6** retains a monomeric structure in the solid state (Figure 5), because the fourth coordination place in the square-planar environment of the central platinum atom is occupied by a diethyl sulfide donor molecule [the bond length Pt1–S1 is 2.2643(13) Å]. This ancillary ligand is coordinated in the *trans* position to the nitrogen atom N1 [bond length Pt1–N1 is 2.031(4) Å and bond angle S1–Pt1–N1 is 173.66(13)°].

Analogous to **1**, transmetalation using compound **2** substituted by the pincer-type ligand L^2 resulted in the preparation of L^2MCl [M = Pd (**7**) or Pt (**8**)], this was followed by ^{31}P NMR and ^1H NMR spectroscopy (Scheme 4). However, the isolated yields of **7** (56%) and **8** (61%) are not quantitative mainly because of the rather similar solubility with the byproduct $[AuCl(PPh_3)]$, which complicated crystallization of the products from the reaction mixtures. Both compounds displayed satisfactory elemental analysis and corresponding positive-ion full-scan ESI mass spectra showed ions $[M - Cl]^+$ or their water adducts $[M - Cl + H_2O]^+$. The ^1H NMR and ^{13}C NMR spectra of **7** and **8** contained one set of signals corresponding to the ligand L^2,

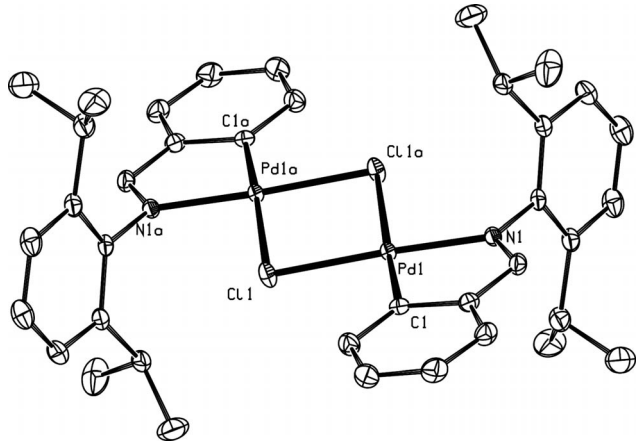


Figure 4. ORTEP diagram of compound **5** with thermal displacement parameters at 30% probability, hydrogen atoms were omitted for clarity. Symmetry operator: a = –*x*, 1 – *y*, –*z*. Selected distances [Å] and angles [°]: Pd1–C1 1.963(12), Pd1–N1 2.0187(18), Pd1–Cl1 2.3264(6), Pd1–Cl1a 2.4493(6), C1–Pd1–Cl1a 173.07(7), N1–Pd1–Cl1 176.19(5).

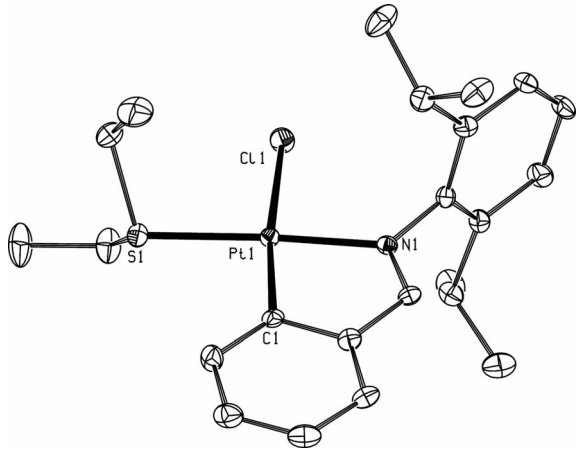
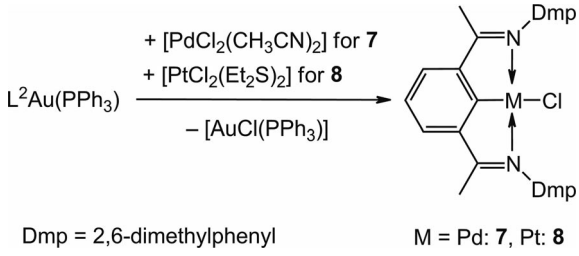


Figure 5. ORTEP diagram of compound **6** with thermal displacement parameters at 30% probability, hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Pt1–C1 1.981(5), Pt1–N1 2.031(4), Pt1–Cl1 2.3849(13), Pt1–S1 2.2643(13), C1–Pt1–Cl1 173.12(16), N1–Pt1–S1 173.66(13).



Scheme 4. Preparation of **7** and **8**.

which is consistent with a rigid tridentate NCN coordination of the ligand L^2 and square-planar environment around the central palladium or platinum atoms, which is usual in this class of compounds containing related bis(aldimine) N,C,N pincer-type ligands.[18]

The molecular structure of **7** was established by the help of single-crystal X-ray diffraction analysis; the crystallographic data are given in the Exp. Section and the molecular structure is shown in Figure 6 together with relevant structural parameters summarized in the figure caption. The molecular structure of compound **7** is closely related to other palladium(II) pincer-type complexes.[18] The pincer ligand is coordinated to the central atom in a meridional fashion through a NCN donor set with two strong N→Pd intramolecular interactions [the bond lengths are Pd1–N1 2.075(4), Pd1–N2 2.068(3) Å]. The remaining coordination position in the square-planar geometry around the central palladium atom is filled by the chlorine atom Cl1, which is situated in the *trans* position to the C-*ipso* atom of the ligand [the bond angle is 177.89(13)°].

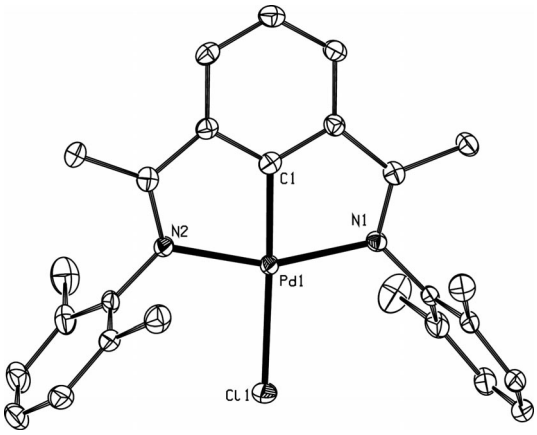
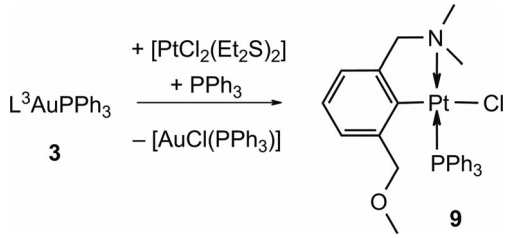


Figure 6. ORTEP diagram of compound **7** with thermal displacement parameters at 30% probability, hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Pd1–C1 1.898(4), Pd1–N1 2.075(4), Pd1–N2 2.068(3), Pd1–Cl1 2.3898(12), C1–Pd1–Cl1 177.89(13), N1–Pd1–N2 158.06(12).

The reaction of the *N*,*C*,*O*-chelated organogold(I) compound **3** with $[PdCl_2(CH_3CN)_2]$ did not afford any isolable *N*,*C*,*O*-chelated organopalladium(II) compounds, although monitoring of the reaction by ^{31}P NMR spectroscopy clearly proved that the starting material **3** was consumed and $[AuCl(PPh_3)]$ emerged in the reaction mixture. Nevertheless, the ^{1}H NMR spectrum suggested the formation of a rather complicated mixture of products, which was not separable. This result could be ascribed to the presence of a weakly coordinating oxygen functionality, which is, most probably, not able to sufficiently stabilize the incipient product.

The ^{31}P NMR spectrum of the reaction mixture after treatment of **3** with $[PtCl_2(Et_2S)_2]$ revealed two signals at δ = 32.7 ppm for $[AuCl(PPh_3)]$ together with a new signal at δ = 11.4 ppm with $^{1}J_{Pt,P}$ = 4271 Hz, and from this reaction mixture compound $L^3PtCl(PPh_3)$ (**9**) was isolated in low yield. The $^{1}J_{Pt,P}$ value of 4271 Hz in **9** is a typical value comparable to those found in related complexes.[19] The triphenylphosphane present in the structure of **9** must be moved from the incipient $[AuCl(PPh_3)]$ to the platinum centre, which caused the low yield of the reaction. This presumption was verified, because addition of one molar equiv. of PPh_3 into the reaction mixture significantly improved the yield of **9** (isolated yield 69%, Scheme 5). Compound **9** displayed satisfactory elemental analysis and its positive-ion full-scan ESI mass spectrum revealed the ion $[M - Cl]^+$ at *m*/*z* = 635. The ^{1}H NMR and ^{13}C NMR spectra of **9** contained one set of signals, which is consistent with the proposed structure and proved the presence of coordinated PPh_3 (see Exp. Section.)



Scheme 5. Preparation of **9**.

The molecular structure of **9** was established by a single-crystal X-ray diffraction analysis, the crystallographic data are given in the Exp. Section and the molecular structure is shown in Figure 7 together with relevant structural parameters summarized in the figure caption.

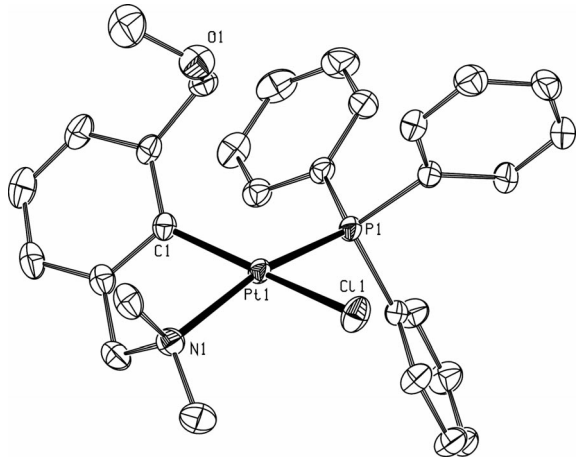
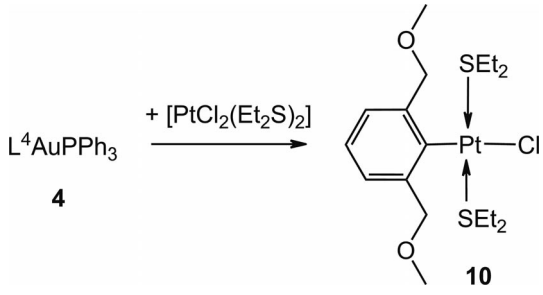


Figure 7. ORTEP diagram of compound **9** with thermal displacement parameters at 30% probability, hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Pt1–C1 2.007(4), Pt1–N1 2.150(3), Pt1–P1 2.2307(9), Pt1–Cl1 2.3997(9), Pt1–O1 3.778(3), C1–Pt1–Cl1 165.12(12), N1–Pt1–P1 161.53(14).

The potentially terdentate N,C,O pincer-type ligand is coordinated to the central platinum atom only in a N,C bidentate fashion and the oxygen-containing ligand arm remains pendant. The coordination sphere of the platinum atom is completed by the chlorine atom and triphenylphosphane donor. In the square planar array, the N1, P1 and C1, Cl1 are placed mutually in *trans* positions. The oxygen atom-containing donor arm is orientated above the platinum atom, which most probably causes a slight defor-

mation of the bonding angles C1–Pt1–Cl1 165.12(12) and N1–Pt1–P1 161.53(14)° from the ideal value of 180°. However, the oxygen donor atom remains outside the primary coordination sphere of the central platinum atom as demonstrated by the bond length Pt1–O1 3.778(3) Å. This observation seems to be a bit more questionable in solution. The ^{13}C NMR spectra of this compound showed the coupling between the carbon atom of the CH_2N groups and the platinum atom as well as the phosphorus atom from the Ph_3P moiety [with the values of $^2J_{Pt,C}$ = 53 Hz and $^3J_{P,C}$ = 4 Hz], interestingly, rather similar coupling was also observed for the CH_2O groups ($^2J_{Pt,C}$ = 54 Hz, $^3J_{P,C}$ = 6 Hz, see also Supporting Information). This observation indicates that the O→Pt interaction in solution for compound **9** is most probably not negligible. Interestingly, it has been recently demonstrated that in the closely related palladium(II) P,C,O pincer-type compounds the oxygen functionality is involved in an intramolecular O→Pd coordination.[20] In this regard, the concept of hemilabile coordination[21] of the oxygen donor group taking place in the case of **9** may be considered.

Finally, the reaction between compound **4** and $[PdCl_2(CH_3CN)_2]$ did not result in any isolable palladium(II) compounds and the situation and reaction mixture closely resembles this described in the case of the reaction of **3** and $[PdCl_2(CH_3CN)_2]$ vide supra. Nevertheless, the reaction between **4** and $[PtCl_2(Et_2S)_2]$ proceeded smoothly and quantitatively, according to the ^1H NMR and ^{31}P NMR spectra, to produce compound $L^4PtCl(Et_2S)_2$ (**10**), which was isolated in 79% yield after workup (Scheme 6). Compound **10** displayed satisfactory elemental analysis and ESI mass spectra, where ions $[M - Cl]^+$, $[M - Cl - Et_2S]^+$, $[M - Cl - 2Et_2S]^+$ or $[M - Cl - Et_2S - HCOH]^+$ were observed in the positive-ion full-scan mass spectrum. The ^1H NMR spectrum contained, besides signals of the ligand L^4, signals at δ = 0.98 and 2.61 ppm, corresponding to the coordinated $S(CH_2CH_3)_2$ molecules. The ^{13}C NMR spectra proved the presence of two *trans*-coordinated diethyl sulfides by the observation of the signals at δ = 13.2 and 29.2 ppm. Although many attempts were made to determine the solid-state structure of **10** using single-crystal X-ray diffraction analysis, the molecular structure could not be refined completely because of an extensive disorder of the backbone of the ligand.



Scheme 6. Preparation of **10**.

Conclusions

In conclusion, four novel organogold(I) compounds **1**–**4** were prepared, characterized and their transmetalation potential was tested in the reactions with $[PdCl_2(CH_3CN)_2]$ and $[PtCl_2(Et_2S)_2]$. It turned out that compounds **1** and **2** are useful starting materials and transmetalation using them proceeded smoothly regardless of whether a potentially bidentate (L^1) or terdentate (L^2) ligand was employed. On the contrary, it is evident that using precursors containing oxygen-donor functionalities **3** and **4** (L^3 and L^4) is not possible for the clean synthesis of palladium(II) complexes and only more kinetically stable platinum(II) complexes were isolated. It is worth mentioning that in both cases the oxygen atoms remain noncoordinated in the product and stabilization by additional ancillary soft ligands such as Et_2S or Ph_3P is necessary. It is most probably a consequence of highly unfavourable intramolecular O→Pd(Pt) interactions, which lead to the decomposition of the products in the case of the palladium compounds. Of importance is also the further investigation of reactions of compounds **1** and **3** with other transition-metal halides, which is currently underway in our labs.

Experimental Section

General Procedures: All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube techniques. All solvents were dried by standard procedures and distilled prior to use. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker 400 spectrometer using a 5-mm tunable broadband probe. Appropriate chemical shifts in the ^1H NMR and ^{13}C NMR spectra were related to the residual signals of the solvent [C_6D_6: $\delta(^1H)$ = 7.16 ppm, $\delta(^{13}C)$ = 128.39 ppm]. The starting ligands L^{1-4} were prepared according to literature procedures.[5c,13,14,22] All other chemicals were purchased from commercial suppliers and were used as delivered. Positive-ion electrospray ionization (ESI) mass spectra were measured with an Esquire 3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the range *m*/*z* = 50–1200. Samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 5 μL/min. The ion source temperature was 300 °C, the flow rate and the pressure of nitrogen were 4 L/min and 10 psi, respectively.

[*o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)]AuPPh$_3$ (1): *n*BuLi (2.5 mL, 4.1 mmol, 1.6 M solution in hexane) was added to a solution of [*o*-C_6H_4(CH=NC_6H_3*i*Pr_2-2,6)]Br (1.40 g, 4.1 mmol) in diethyl ether (20 mL) at –70 °C and stirred for 30 min at this temperature. A suspension of [AuCl(PPh$_3$)] (2.01 g, 4.1 mmol) in diethyl ether (30 mL), precooled to –70 °C, was added to the resulting yellow-orange suspension of the lithium compound. The obtained orange mixture was allowed to reach room temp. and stirred overnight. The insoluble material was filtered off in the air and the filtrate volume was reduced to ca. one third. Hexane (10 mL) was added to this solution and the mixture was left standing for crystallization at 5 °C for several days. The obtained air-stable colourless crystals of compound **1** were decanted from the solution and dried in vacuo. Compound **1** was stable in air for a long time (several months); yield 2.50 g, 85%; m.p. 82 °C. Positive-ion ESI-MS: *m*/*z* (%) = 1182 [M + AuPPh$_3$]$^+$, 762 [M + K]$^+$, 746 [M + Na]$^+$, 724 [M + H]$^+$, 100. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.09 [d, 12 H, CH(CH_3)$_2$], 3.38 [sept, 2 H, C*H*(CH$_3$)$_2$], 6.88 (m, 6 H, *m*-*H*-

PPh$_3$), 6.97 (m, 3 H, *p*-*H*-PPh$_3$), 7.16 (m, 3 H, C$_6$*H*$_3$*i*Pr$_2$-2,6), 7.27 (d, 2 H, C$_6$*H*$_4$), 7.45 (m, 6 H, *o*-*H*-PPh$_3$), 8.20 (d, 1 H, C$_6$*H*$_4$), 8.33 (d, 1 H, C$_6$*H*$_4$), 9.13 (s, 1 H, C*H*=N) ppm. ^{13}C NMR (100.61 MHz, C$_6$D$_6$, 25 °C): δ = 24.1 [s, CH(*C*H$_3$)$_2$], 28.8 [s, *C*H(CH$_3$)$_2$], 123.6 (s, Ar-*C*), 124.1 (s, Ar-*C*), 126.5 (s, Ar-*C*), 128.9 (s, Ar-*C*), 129.4 (d, $^3J_{P,C}$ = 11 Hz, PPh$_3$-*C*), 130.8 (s, Ar-*C*), 131.3 (s, PPh$_3$-*C*), 131.8 (d, $^1J_{P,C}$ = 48 Hz, PPh$_3$-*C*), 134.9 (d, $^2J_{P,C}$ = 14 Hz, PPh$_3$-*C*), 138.7 (s, Ar-*C*), 141.5 (s, Ar-*C*), 145.7 (s, Ar-*C*), 151.9 (s, Ar-*C*), 169.0 (s, *C*H=N) ppm, (Ar-*ipso*-*C*) not observed. ^{31}P NMR (161.97 MHz, C$_6$D$_6$, 25 °C): δ = 44.1 ppm. C$_{37}$H$_{37}$AuNP (723.65): calcd. C 61.4, H 5.2; found C 61.5, H 5.4.

{*o*,*o*-C$_6$H$_3$[C(Me)=NC$_6$H$_3$Me$_2$-2,6]$_2$}AuPPh$_3$ (2): *n*BuLi (1.5 mL, 2.4 mmol, 1.6 M solution in hexane) was added to a solution of [*o*,*o*-C$_6$H$_3$(C(Me)=NC$_6$H$_3$Me$_2$-2,6)$_2$]Br (522 mg, 1.2 mmol) in diethyl ether (20 mL) at –70 °C and stirred for 30 min at this temperature. A suspension of [AuCl(PPh$_3$)] (578 mg, 1.2 mmol) in diethyl ether (30 mL) precooled to –70 °C was added to the resulting orange suspension of the lithium compound. The obtained orange mixture was allowed to reach room temp. and stirred for an additional 48 h. The insoluble material was filtered off and the filtrate volume was reduced to ca. half. Hexane (20 mL) was added into this solution and the mixture was left for crystallization at –30 °C for several days. The obtained honey-yellow crystals of compound **2** were decanted from solution and dried in vacuo. Compound **2** is stable in air for a long time (several months); yield 815 mg, 85%; m.p. 208 °C. Positive-ion ESI-MS: *m*/*z* (%) = 865 [M + K]$^+$, 849 [M + Na]$^+$, 827 [M + H]$^+$, 100. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 2.05 [s, 12 H, C$_6$H$_3$(C*H*$_3$)$_2$-2,6], 2.20 [s, 6 H, C(C*H*$_3$)=N], 6.91 [m, 15 H, *m*,*p*-*H*-PPh$_3$ and C$_6$*H*$_3$(CH$_3$)$_2$-2,6], 7.30 (t, 1 H, C$_6$H$_4$-*H4*), 7.34 (m, 6 H, *o*-*H*-PPh$_3$), 7.94 (d, 1 H, C$_6$H$_4$-*H3*,*5*) ppm. ^{13}C NMR (100.61 MHz, C$_6$D$_6$, 25 °C): δ = 19.0 [s, C$_6$H$_3$(*C*H$_3$)$_2$-2,6], 22.0 [s, C(*C*H$_3$)=N], 122.8 (s, Ar-*C*), 125.7 (s, Ar-*C*), 126.8 (s, Ar-*C*), 128.5 (s, Ar-*C*), 129.3 (d, $^3J_{P,C}$ = 11 Hz, PPh$_3$-*C*), 131.1 (d, $^4J_{P,C}$ = 5 Hz, PPh$_3$-*C*), 132.5 (d, $^1J_{P,C}$ = 49 Hz, PPh$_3$-*C*), 134.8 (d, $^2J_{P,C}$ = 15 Hz, PPh$_3$-*C*), 151.2 (s, Ar-*C*), 151.4 (s, Ar-*C*), 172.6 (s, Ar-*C*), 172.7 (s, *C*H=N) ppm. ^{31}P NMR (161.97 MHz, C$_6$D$_6$, 25 °C): δ = 41.9 ppm. C$_{44}$H$_{42}$AuN$_2$P (826.78): calcd. C 63.9, H 5.1; found C 64.3, H 5.3.

[*o*,*o*′-C$_6$H$_3$(CH$_2$NMe$_2$)(CH$_2$OMe)]AuPPh$_3$ (3): *n*BuLi (2.5 mL, 4.0 mmol, 1.6 M solution in hexane) was added to a solution of *o*,*o*′-C$_6$H$_4$(CH$_2$NMe$_2$)(CH$_2$OMe) (708 mg, 4.0 mmol) in hexane (20 mL) at room temp. and stirred for 2 h. The orange solution of the lithium compound was added to a suspension of [AuCl(PPh$_3$)] (1.95 g, 4.0 mmol) in diethyl ether (30 mL) and precooled to –70 °C. The obtained creamy mixture was allowed to reach room temperature and stirred for an additional 24 h. The resulting suspension was filtered in the air over Celite. The insoluble material was washed with diethyl ether and the filtrate was left to slowly evaporate at room temp. giving colourless crystals within several hours. The obtained air stable colourless crystals of compound **3** were collected by filtration and washed by hexane and dried in vacuo. Compound **3** is stable in air for a long time (several months); yield 1.41 g, 56%; m.p. 124 °C. Positive-ion ESI-MS: *m*/*z* (%) = 676 [M + K]$^+$, 660 [M + Na]$^+$, 638 [M + H]$^+$, 100, 178 [L]$^+$. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 2.28 [s, 6 H, N(C*H*$_3$)$_2$], 3.38 (s, 3 H, OC*H*$_3$), 3.96 (s, 2 H, NC*H*$_2$), 5.15 (s, 2 H, OC*H*$_2$), 7.03 (m, 9 H, *m*,*p*-*H*-PPh$_3$), 7.35 (dd, 1 H, C$_6$*H*$_4$), 7.60 (m, 6 H, *o*-*H*-PPh$_3$), 7.65 (d, 1 H, C$_6$*H*$_4$), 7.76 (d, 1 H, C$_6$*H*$_4$) ppm. ^{13}C NMR (100.61 MHz, C$_6$D$_6$, 25 °C): δ = 46.4 [s, N(*C*H$_3$)$_2$], 58.0 (s, O*C*H$_3$), 71.0 (s, N*C*H$_2$), 80.5 (s, O*C*H$_2$), 126.1 (s, Ar-*C*), 126.7 (s, Ar-*C*), 128.6 (s, Ar-*C*), 129.5 (d, $^3J_{P,C}$ = 11 Hz, PPh$_3$-*C*), 131.5 (d, $^4J_{P,C}$ = 2 Hz, PPh$_3$-*C*), 132.3 (d, $^1J_{P,C}$ = 48 Hz, PPh$_3$-*C*), 134.9 (d, $^2J_{P,C}$ = 14 Hz, PPh$_3$-*C*), 147.6 (s, Ar-*C*), 148.7 (s, Ar-*C*) ppm, (Ar-*ipso*-*C*) not observed. ^{31}P NMR (161.97 MHz, C$_6$D$_6$, 25 °C): δ = 44.9 ppm. C$_{29}$H$_{31}$AuNOP (637.51): calcd. C 54.6, H 4.9; found C 54.8, H 5.1.

[*o*,*o*-C$_6$H$_3$(CH$_2$OMe)$_2$]AuPPh$_3$ (4): *n*BuLi (1.9 mL, 3.1 mmol, 1.6 M solution in hexane) was added to a solution of [*o*,*o*-C$_6$H$_3$(CH$_2$OMe)$_2$]Br (749 mg, 3.1 mmol) in diethyl ether (20 mL) at –78 °C and stirred for 3 h. A suspension of [AuCl(PPh$_3$)] (1.51 g, 3.1 mmol) in diethyl ether (20 mL) precooled to –70 °C was added to the resulting suspension of the lithium compound. The obtained yellow mixture was allowed to reach room temperature and stirred for an additional 2 h. The insoluble material was filtered off in air, then washed with diethyl ether and the filtrate volume was reduced to ca. half. Hexane (5 mL) was added to this solution and the mixture was left for crystallization at –30 °C for several days. Obtained colourless crystals of compound **4** were decanted from solution and dried in vacuo. Compound **4** was stored under an argon atmosphere and very slow decomposition to a black material was noticed after several months at 5 °C; yield 965 mg, 51%; m.p. 118 °C. Positive-ion ESI-MS: *m*/*z* (%) = 1083 [M + AuPPh$_3$]$^+$, 1053 [M + AuPPh$_3$ – HCOH]$^+$, 663 [M + K]$^+$, 647 [M + Na]$^+$, 100, 625 [M + H]$^+$. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 3.36 (s, 6 H, OC*H*$_3$), 5.10 (s, 2 H, OC*H*$_2$), 7.00 (m, 9 H, *m*,*p*-*H*-PPh$_3$), 7.37 (t, 1 H, C$_6$*H*$_4$-*H4*), 7.55 (m, 6 H, *o*-*H*-PPh$_3$), 7.75 (d, 2 H, C$_6$*H*$_4$) ppm. ^{13}C NMR (100.61 MHz, C$_6$D$_6$, 25 °C): δ = 57.9 (s, O*C*H$_3$), 80.4 (s, O*C*H$_2$), 126.4 (s, Ar-*C*), 127.5 (s, Ar-*C*), 129.5 (d, $^3J_{P,C}$ = 11 Hz, PPh$_3$-*C*), 131.5 (d, $^4J_{P,C}$ = 2 Hz, PPh$_3$-*C*), 132.1 (d, $^1J_{P,C}$ = 49 Hz, PPh$_3$-*C*), 134.9 (d, $^2J_{P,C}$ = 14 Hz, PPh$_3$-*C*), 147.6 (s, Ar-*C*) ppm, (Ar-*ipso*-*C*) not observed. ^{31}P NMR (161.97 MHz, C$_6$D$_6$, 25 °C): δ = 44.4 ppm. C$_{28}$H$_{28}$AuO$_2$P (624.27): calcd. C 53.9, H 4.5; found C 53.7, H 4.7.

{[*o*-C$_6$H$_4$(CH=NC$_6$H$_3$*i*Pr$_2$-2,6)]PdCl}$_2$ (5): A solution of [PdCl$_2$(CH$_3$CN)$_2$] (66 mg, 0.25 mmol) in acetonitrile (15 mL) was added to a stirred solution of **1** (183 mg, 0.25 mmol) in benzene (20 mL) in a small round-bottom flask. The resulting mixture was heated to 70 °C for 2 h. The obtained yellow-green solution was evaporated in vacuo. The reaction mixture was characterized by ^{1}H NMR and ^{31}P NMR spectroscopy proving that the reaction proceeded almost quantitatively (see Results and Discussion). The residue was extracted by a mixture of dichloromethane/hexane (10:1) and the traces of insoluble material were filtered off. The filtrate was left to crystallize by slow evaporation at room temp. The obtained ginger crystals of **5** were decanted, washed with hexane and dried in vacuo; yield 31 mg, 30%; m.p. 205 °C (dec.). Positive-ion ESI-MS: *m*/*z* (%) = 411 [M – Cl + CH$_3$CN]$^+$, 100, 388 [M – Cl + H$_2$O]$^+$. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ = 0.96 [d, 6 H, CH(C*H*$_3$)$_2$], 1.39 [d, 6 H, CH(C*H*$_3$)$_2$], 3.58 [sept, 2 H, C*H*(CH$_3$)$_2$], 6.64 (dd, C$_6$*H*$_4$), 6.70 (dd, C$_6$*H*$_4$), 6.75 (dd, C$_6$*H*$_4$), 7.07 (m, 3 H, C$_6$*H*$_3$*i*Pr$_2$-2,6), 7.12 (s, 1 H, C*H*=N), 7.54 (d, 1 H, C$_6$*H*$_4$) ppm. Other NMR spectroscopic data in CDCl$_3$ were consistent with those published.[16] C$_{38}$H$_{44}$Cl$_2$N$_2$Pd$_2$ (812.5): calcd. C 56.2, H 5.5; found C 56.5, H 5.7.

[*o*-C$_6$H$_4$(CH=NC$_6$H$_3$*i*Pr$_2$-2,6)]PtCl(Et$_2$S) (6): A solution of [PtCl$_2$(Et$_2$S)$_2$] (129 mg, 0.29 mmol) in benzene (15 mL) was added to a stirred solution of **1** (209 mg, 0.29 mmol) in benzene (20 mL) in a small round-bottom flask. The resulting mixture was heated to 70 °C for 2 h. The obtained orange solution was evaporated in vacuo. The reaction mixture was characterized by ^{1}H NMR and ^{31}P NMR spectroscopy proving that the reaction proceeded quantitatively (see Results and Discussion). The residue was extracted by diethyl ether and the insoluble material {[AuCl(PPh$_3$)]} was filtered off. The filtrate volume was reduced to ca. half, and a small amount of hexane was added and the resulting mixture was left to crystallize at 5 °C. Obtained orange crystals of **6** were decanted from the solution and dried in vacuo; yield 100 mg, 78%; m.p. 200 °C

(dec.). Positive-ion ESI-MS: *m/z* (%) = 623 [M + K]$^+$, 607 [M + Na]$^+$, 549 [M – Cl]$^+$, 100. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.09 [m, 12 H, overlap of CH(C*H*$_3$)$_2$ and S(CH$_2$C*H*$_3$)$_2$], 1.56 [d, 6 H, CH(C*H*$_3$)$_2$], 2.30 [m, 2 H, S(C*H*$_2$CH$_3$)$_2$], 3.17 [m, 2 H, S(C*H*$_2$CH$_3$)$_2$], 3.58 [sept, 2 H, C*H*(CH$_3$)$_2$], 6.94 (m, 2 H, C_6H_4), 7.00 (dd, 1 H, C_6H_4), 7.17 (m, 3 H, C_6H_3*i*Pr$_2$-2,6), 7.63 (s, $^3J_{Pt,H}$ = 119 Hz, 1 H, C*H*=N), 7.90 (d, $^3J_{Pt,H}$ = 45 Hz, 1 H, C_6H_4) ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 13.3 [s, $^2J_{Pt,C}$ = 32 Hz, S(CH$_2$*C*H$_3$)$_2$], 23.7 [s, CH(*C*H$_3$)$_2$], 24.8 [s, CH(*C*H$_3$)$_2$], 28.7 [s, *C*H(CH$_3$)$_2$], 32.1 [s, $^1J_{Pt,C}$ = 20 Hz, S(*C*H$_2$CH$_3$)$_2$], 123.5, 123.8, 130.0, 132.0, 133.4, 142.5, 145.3, 147.0, 148.7, 180.8 (s, $^2J_{Pt,C}$ = 91 Hz, *C*H=N) ppm, (Ar-*ipso*-*C*) not observed. $C_{23}H_{32}ClNPtS$ (585.13): calcd. C 47.2, H 5.5; found C 47.5, H 5.7.

{*o*,*o*-C$_6$H$_3$[C(Me)=NC$_6$H$_3$Me$_2$-2,6]$_2$}PdCl (7): A solution of [PdCl$_2$(CH$_3$CN)$_2$] (35 mg, 0.14 mmol) in acetonitrile (15 mL) was added to a stirred solution of **2** (111 mg, 0.14 mmol) in benzene (20 mL) in a small round-bottom flask. The resulting mixture was heated to 70 °C for 4 h. The obtained dirty-yellow solution was evaporated in vacuo. The reaction mixture was characterized by ^{1}H NMR and ^{31}P NMR spectroscopy proving that the reaction proceeded quantitatively (see Results and Discussion). The residue was extracted by a mixture of dichloromethane/hexane (10:1) and traces of insoluble material were filtered off. The filtrate was left to crystallize by slow evaporation at room temp. The obtained pale-yellow crystals of **7** were decanted from solution and dried in vacuo; yield 38 mg, 56%; m.p. 294 °C (dec.). Positive-ion ESI-MS: *m/z* (%) = 985 [2M – 2Cl + K]$^+$, 547 [M + K]$^+$, 491 [M – Cl + H$_2$O]$^+$, 473 [M – Cl]$^+$, 100. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.47 [s, 6 H, C(C*H*$_3$)=N], 2.21 [s, 12 H, C_6H_3(C*H*$_3$)$_2$-2,6], 6.86 (m, 3 H, C_6H_4), 6.94 [s, 6 H, C_6H_3(CH$_3$)$_2$-2,6] ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 15.9 [s, C(*C*H$_3$)=N], 19.2 [s, C_6H_3(*C*H$_3$)$_2$-2,6], 123.0, 127.0, 128.7, 130.4, 145.7, 145.8, 184.1, 186.0 (s, *C*H=N and Ar-*C*) ppm. $C_{26}H_{27}ClN_2Pd$ (509.37): calcd. C 61.3, H 5.3; found C 61.5, H 5.4.

{*o*,*o*-C$_6$H$_3$[C(Me)=NC$_6$H$_3$Me$_2$-2,6]$_2$}PtCl (8): A solution of [PtCl$_2$(Et$_2$S)$_2$] (60 mg, 0.14 mmol) in benzene (15 mL) was added to a stirred solution of **2** (111 mg, 0.14 mmol) in benzene (20 mL) in a small round-bottom flask. The resulting mixture was heated to 70 °C for 24 h. The obtained honey-coloured solution was evaporated in vacuo. The reaction mixture was characterized by ^{1}H NMR and ^{31}P NMR spectroscopy proving that the reaction proceeded quantitatively (see Results and Discussion). The residue was extracted by a mixture of dichloromethane/hexane (10:1) and the insoluble material was filtered off. The filtrate was left to crystallize by free evaporation at room temp. The obtained orange crystals of **8** were decanted from solution and dried in vacuo; yield 49 mg, 61%; m.p. 205 °C (dec.). Positive-ion ESI-MS: *m/z* (%) = 580 [M – Cl + H$_2$O]$^+$, 100, 562 [M – Cl]$^+$. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.48 [s, $^4J_{Pt,H}$ = 8 Hz, 6 H, C(C*H*$_3$)=N], 2.14 [s, 12 H, C_6H_3(C*H*$_3$)$_2$-2,6], 6.94 (m, 3 H, C_6H_4), 7.08 [m, 6 H, C_6H_3(CH$_3$)$_2$-2,6] ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 16.1 [s, $^2J_{Pt,C}$ = 58 Hz, C(*C*H$_3$)=N], 18.6 [s, C_6H_3(*C*H$_3$)$_2$-2,6], 121.1, 127.4, 128.5, 128.7, 131.2, 143.6, 145.9, 176.2, 186.1 (s, *C*H=N and Ar-*C*) ppm. $C_{26}H_{27}ClN_2Pt$ (598.06): calcd. C 52.2, H 4.6; found C 52.5, H 4.9.

[*o*,*o*′-C$_6$H$_3$(CH$_2$NMe$_2$)(CH$_2$OMe)]PtPPh$_3$ (9): A solution of [PtCl$_2$(Et$_2$S)$_2$] (233 mg, 0.52 mmol) in benzene (15 mL) was added to a stirred solution of **3** (333 mg, 0.52 mmol) in benzene (20 mL) in a small round-bottom flask. Finally triphenylphosphane (137 mg, 0.52 mmol) was added. The resulting mixture was heated to 70 °C for 2 h. The obtained pale-orange suspension was evaporated in vacuo. The reaction mixture was characterized by the help of ^{1}H NMR and ^{31}P NMR spectroscopy proving that the reaction proceeded almost quantitatively (see Results and Discussion). The residue was washed by diethyl ether and the insoluble material was filtered. The insoluble material was dried in vacuo and extracted by benzene. The extract was left to crystallize by slow evaporation at room temp. The obtained yellow crystals of **9** were decanted from solution and dried in vacuo; yield 241 mg, 69%; m.p. 180 °C (dec.). Positive-ion ESI-MS: *m/z* = 635 [M – Cl]$^+$, 100. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 2.44 [s, 6 H, N(C*H*$_3$)$_2$], 3.07 (s, 3 H, OC*H*$_3$), 3.59 (s, $^3J_{Pt,H}$ = 31 Hz, 2 H, NC*H*$_2$), 3.92 (s, 2 H, OC*H*$_2$), 6.98 (m, 9 H, *m*,*p*-*H*-PPh$_3$), 7.05 (dd, 1 H, C_6H_4), 7.10 (m, 2 H, C_6H_4), 7.88 (m, 6 H, *o*-*H*-PPh$_3$) ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 50.3 [s, N(*C*H$_3$)$_2$], 57.5 (s, O*C*H$_3$), 75.7 (d, $^2J_{Pt,C}$ = 53, $^3J_{P,C}$ = 4 Hz, N*C*H$_2$), 79.7 (d, $^2J_{Pt,C}$ = 54, $^3J_{P,C}$ = 6 Hz, O*C*H$_2$), 121.7 (s, Ar-*C*), 124.5 (s, Ar-*C*), 127.5 (s, Ar-*C*), 128.3 (d, $^3J_{P,C}$ = 11 Hz, PPh$_3$-*C*), 130.8 (s, $^4J_{P,C}$ = 2 Hz, PPh$_3$-*C*), 135.9 (d, $^2J_{P,C}$ = 11 Hz, PPh$_3$-*C*), 143.6 (s, Ar-*C*), 146.0 (d, $^1J_{P,C}$ = 7 Hz, PPh$_3$-*C*) 147.0 (Ar-*C*) ppm, (Ar-*ipso*-*C*) not observed. ^{31}P NMR (161.97 MHz, C_6D_6, 25 °C): δ = 11.4 ($^1J_{Pt,P}$ = 4271 Hz) ppm. $C_{29}H_{31}ClNOPPt$ (671.09): calcd. C 51.9, H 4.7; found C 51.6, H 5.0.

[*o*,*o*-C$_6$H$_3$(CH$_2$OMe)$_2$]PtCl(Et$_2$S)$_2$ (10): A solution of [PtCl$_2$(Et$_2$S)$_2$] (216 mg, 0.48 mmol) in benzene (15 mL) was added to a stirred solution of **4** (302 mg, 0.48 mmol) in benzene (20 mL) in a small round-bottom flask. The resulting mixture was heated to 70 °C for 2 h. The obtained pale-orange suspension was evaporated in vacuo The reaction mixture was characterized by ^{1}H NMR and ^{31}P NMR spectroscopy proving that the reaction proceeded quantitatively (see Results and Discussion). The residue was extracted by diethyl ether and the insoluble material {[AuCl(PPh$_3$)]} was filtered off. The filtrate volume was reduced to half, then a small amount of hexane was added and the resulting solution was left to crystallize at 5 °C. The obtained yellow crystals of **10** were decanted from solution and dried in vacuo; yield 220 mg, 79%; m.p. 88 °C. Positive-ion ESI-MS: *m/z* (%) = 540 [M – Cl]$^+$, 510 [M – Cl – HCOH]$^+$, 450 [M – Cl – Et$_2$S]$^+$, 100, 420 [M – Cl – Et$_2$S – HCOH]$^+$, 360 [M – Cl – 2Et$_2$S]$^+$. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.98 [t, 6 H, S(CH$_2$C*H*$_3$)$_2$], 2.61 [m, 4 H, S(C*H*$_2$CH$_3$)$_2$], 3.36 [s, 6 H, O(C*H*$_3$)], 5.01 [s, 2 H, O(C*H*$_2$)], 7.08 (t, 1 H, C_6H_4-*H4*), 7.37 (d, 2 H, C_6H_4) ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 13.2 [s, $^2J_{Pt,C}$ = 45 Hz, S(CH$_2$*C*H$_3$)$_2$], 29.2 [s, S(*C*H$_2$CH$_3$)$_2$], 58.8 (s, O*C*H$_3$), 79.5 (s, O*C*H$_2$), 124.8, 127.8, 143.3 (s, Ar-*C*) ppm, (Ar-*ipso*-*C*) signal not observed. $C_{18}H_{33}ClO_2PtS_2$ (576.1): calcd. C 37.5, H 5.8; found C 37.7, H 5.7.

X-ray Crystallography: The suitable single crystals of the studied compounds were mounted on glass fibres with an oil and measured with a four-circle diffractometer KappaCCD with CCD area detector by monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 150(1) K. The numerical[23] absorption corrections from the crystal shapes were applied for all crystals. The structures were solved by the direct method (SIR92)[24] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97).[25] Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors H_{iso}(H) = 1.2 U_{eq} (pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H bond lengths of 0.96, 0.97 and 0.93 Å for methyl, methylene and hydrogen atoms in the aromatic ring, respectively. The final difference maps displayed no peaks of chemical significance as the highest peaks and holes are in close vicinity (ca. 1 Å) of heavy atoms. The crystal structure of **9** was determined at room temperature because the single crystal of this compound undergoes a phase transformation at 150 K. Some of the carbon atoms of the solvent (toluene) in **2** were disordered but attempts made to split these gave no better data set.

CCDC-863055 (for **4**), -863056 (for **2**), -863057 (for **3**), -863058 (for **1**), -863059 (for **6**), -863060 (for **9**), -863061 (for **7**), -863062 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic Data for 1: $C_{37}H_{37}AuNP$, M_r = 723.61 g/mol, monoclinic, $P2_1$, a = 13.4191(3) Å, b = 6.8730(4) Å, c = 16.9638(10) Å, β = 90.329(4)°, V = 1564.54(13) Å^3, Z = 2, T = 150(1) K, 7491 total reflections, 5064 independent [R_{int} = 0.061, R_1 (obsd. data) = 0.058, wR_2 (all data) = 0.148].

Crystallographic Data for 2: $C_{44}H_{42}AuN_2P\cdot(C_7H_8)$, M_r = 918.87 g/mol, triclinic, $P\bar{1}$, a = 11.9179(9) Å, b = 14.6980(9) Å, c = 14.8970(4) Å, α = 113.629(5)°, β = 96.618(4)°, γ = 111.699(6)°, V = 2112.3(2) Å^3, Z = 2, T = 150(1) K, 41956 total reflections, 9653 independent [R_{int} = 0.031, R_1 (obsd. data) = 0.027, wR_2 (all data) = 0.056].

Crystallographic Data for 3: $C_{29}H_{31}AuNOP$, M_r = 637.48 g/mol, monoclinic, $P2_1/c$, a = 14.9700(12) Å, b = 8.5400(5) Å, c = 22.7451(15) Å, β = 116.593(6)°, V = 2600.2(3) Å^3, Z = 4, T = 150(2) K, 21703 total reflections, 5949 independent [R_{int} = 0.044, R_1 (obsd. data) = 0.034, wR_2 (all data) = 0.062].

Crystallographic Data for 4: $C_{28}H_{28}AuO_2P$, M_r = 624.44 g/mol, monoclinic, $P2_1/c$, a = 10.9530(8) Å, b = 8.2310(3) Å, c = 28.9221(15) Å, β = 107.298(6)°, V = 2489.5(3) Å^3, Z = 4, T = 150(1) K, 17305 total reflections, 5668 independent [R_{int} = 0.041, R_1 (obsd. data) = 0.043, wR_2 (all data) = 0.081].

Crystallographic data for 5: $C_{38}H_{44}Cl_2N_2Pd_2$, M_r = 812.45 g/mol, monoclinic, $P2_1/c$, a = 11.0470(2) Å, b = 10.2780(5) Å, c = 16.5011(11) Å, β = 105.359(3)°, V = 1806.64(15) Å^3, Z = 2, T = 150(1) K, 13857 total reflections, 4027 independent [R_{int} = 0.025, R_1 (obsd. data) = 0.022, wR_2 (all data) = 0.049].

Crystallographic Data for 6: $C_{23}H_{32}ClNPtS$, M_r = 585.10 g/mol, orthorhombic, $P2_12_12_1$, a = 11.1509(3) Å, b = 14.0480(10) Å, c = 15.1001(14) Å, V = 2365.4(3) Å^3, Z = 4, T = 150(1) K, 21005 total reflections, 5415 independent [R_{int} = 0.054, R_1 (obsd. data) = 0.028, wR_2 (all data) = 0.060].

Crystallographic Data for 7: $C_{26}H_{27}ClN_2Pd$, M_r = 509.35 g/mol, orthorhombic, $P2_12_12_1$, a = 12.7667(10) Å, b = 12.7910(8) Å, c = 14.3100(8) Å, V = 2336.8(3) Å^3, Z = 4, T = 150(1) K, 10469 total reflections, 5063 independent [R_{int} = 0.044, R_1 (obsd. data) = 0.035, wR_2 (all data) = 0.066].

Crystallographic Data for 9: $C_{29}H_{31}ClNOPPt$, M_r = 671.06 g/mol, triclinic, $P\bar{1}$, a = 9.6100(3) Å, b = 10.0341(5) Å, c = 14.6610(8) (Å), α = 87.121(4)°, β = 71.029(3)°, γ = 77.209(4)°, V = 1303.40(11) Å^3, Z = 2, T = 300(1) K, 27455 total reflections, 5937 independent [R_{int} = 0.028, R_1 (obsd. data) = 0.026, wR_2 (all data) = 0.060].

Supporting Information (see footnote on the first page of this article): H- and C-NMR spectra of compound **9**.

Acknowledgments

The authors thank the Czech Republic, Grant Agency (project number P207/10/0215) and the Ministry of Education of the Czech Republic (project number MSM0021627501) for financial support. R. J. acknowledges support sponsored by the Ministry of Education, Youth and Sports of the Czech Republic (grant project number MSM0021627502).

[1] a) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781; b) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792; c) D. Morales–Morales, C. M. Jensen, *The chemistry of pincer compounds*, Elsevier, Amsterdam, **2007**; d) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602; e) S. Schneider, J. Meiners, B. Askevold, *Eur. J. Inorg. Chem.* **2012**, 412–429; f) J. I. van der Vlugt, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, 8990; *Angew. Chem. Int. Ed.* **2009**, *48*, 8832–8846.

[2] For early examples see: a) C. J. Moulton, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1976**, 1020–1024; b) G. van Koten, K. Timmer, J. G. Noltes, A. L. Spek, *J. Chem. Soc., Chem. Commun.* **1978**, 250–252; c) C. S. Creaser, W. C. Kaska, *Inorg. Chim. Acta* **1978**, *30*, L325–L326; G. van Koten, *Pure Appl. Chem.* **1989**, *61*, 1681.

[3] For example see Group 13: a) A. H. Cowley, F. P. Gabbäi, D. A. Atwood, *J. Am. Chem. Soc.* **1994**, *116*, 1559–1560; b) A. H. Cowley, R. A. Jones, M. A. Mardones, J. Ruiz, J. L. Atwood, S. G. Bott, *Angew. Chem.* **1990**, *102*, 1169; *Angew. Chem. Int. Ed. Engl.* **1990**, *102*, 1150–1151; c) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, I. Císařová, J. Holeček, *J. Organomet. Chem.* **2006**, *691*, 35–44; Group 14: d) R. Jambor, B. Kašná, K. N. Kirschner, M. Schürmann, K. Jurkschat, *Angew. Chem.* **2008**, *120*, 1674; *Angew. Chem. Int. Ed.* **2008**, *47*, 1650–1653; e) M. Mehring, I. Vrasidas, D. Horn, M. Schürmann, K. Jurkschat, *Organometallics* **2001**, *20*, 4647–4653; f) M. Henn, M. Schürmann, B. Mahieu, P. Zanello, A. Cinquantini, K. Jurkschat, *J. Organomet. Chem.* **2006**, *691*, 1560–1572; g) M. Bouška, L. Dostál, F. de Proft, A. Růžička, A. Lyčka, R. Jambor, *Chem. Eur. J.* **2011**, *17*, 455–459; h) E. Bonnefille, S. Mazières, C. Bibal, N. Saffon, H. Gornitzka, C. Couret, *Eur. J. Inorg. Chem.* **2008**, 4242–4424; Group 15: i) L. Balázs, H. J. Breunig, E. Lork, A. P. Soran, C. Silvestru, *Inorg. Chem.* **2006**, *45*, 2341–2346; j) L. Dostál, R. Jambor, A. Růžička, J. Holeček, *Organometallics* **2008**, *27*, 2169–2171; k) L. Dostál, R. Jambor, A. Růžička, M. Erben, R. Jirásko, Z. Černošková, J. Holeček, *Organometallics* **2009**, *28*, 2633–2636; l) K. Peveling, M. Schurmann, S. Herres-Pawlis, C. Silvestru, K. Jurkschat, *Organometallics* **2011**, *30*, 5181–5187; m) I. J. Casely, J. W. Ziller, B. J. Mincher, W. J. Evans, *Inorg. Chem.* **2011**, *50*, 1513–1520; n) R. Thirumoorthi, T. Chivers, I. Vargas-Baca, *Dalton Trans.* **2011**, *40*, 8086–8088; o) C. D. Martin, P. J. Ragogna, *Inorg. Chem.* **2012**, DOI: 10.1021/ic202213x.

[4] a) A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403–424; b) P. Steenwinkel, R. A. Gossage, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 759–762.

[5] a) D. M. Grove, G. van Koten, H. J. C. Ubbels, R. Zoet, A. L. Spek, *Organometallics* **1984**, *3*, 1003–1009; b) J. A. M. van Beek, G. van Koten, M. J. Ramp, N. C. Coenjaarts, D. M. Grove, K. Goublitz, M. C. Zoutberg, C. H. Stam, W. J. J. Smeets, A. L. Spek, *Inorg. Chem.* **1991**, *30*, 3059–3068; c) M. Stol, D. J. M. Snelders, M. D. Godbole, R. W. A. Havenith, D. Haddleton, G. Clarkson, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten, *Organometallics* **2007**, *26*, 3985–3994.

[6] a) P. Dani, M. Albrecht, G. P. M. van Klink, G. van Koten, *Organometallics* **2000**, *19*, 4468–4476; b) M. Albrecht, P. Dani, M. Lutz, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2000**, *122*, 11822–11833; c) M. Albrecht, S. L. James, N. Veldman, A. L. Spek, G. van Koten, *Can. J. Chem.* **2001**, *79*, 709–718; d) F. Maassarani, M. F. Davidson, I. C. M. Wehman-Ooyevaar, D. M. Grove, M. A. van Koten, W. J. J. Smeets, A. L. Spek, G. van Koten, *Inorg. Chim. Acta* **1995**, *235*, 327–338; e) P. Dani, T. Karlen, R. A. Gossage, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1997**, *119*, 11317–11318.

[7] a) R. A. Gossage, J. T. B. H. Jastrzebski, G. van Koten, *Angew. Chem.* **2005**, *117*, 1472; *Angew. Chem. Int. Ed.* **2005**, *44*, 1448–1454; b) P. A. Chase, M. Lutz, A. L. Spek, R. A. Gossage, G. van Koten, *Dalton Trans.* **2008**, 5783–5790; c) R. Jambor, L. Dostál, A. Růžička, I. Císařová, J. Holeček, *Inorg. Chim. Acta*

2005, *358*, 2422–2426; d) M. Mehring, M. Schürmann, K. Jurkschat, *Organometallics* **1998**, *17*, 1227–1236.

[8] a) W. Gao, D. Cui, *J. Am. Chem. Soc.* **2008**, *130*, 4984–4991; b) J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, M. C. Zoutberg, D. Heijdenrijk, *Organometallics* **1989**, *8*, 1373–1375; c) A. Růžička, R. Jambor, I. Císařová, J. Holeček, *Chem. Eur. J.* **2003**, *9*, 2411–2418; d) M. R. Meneghetti, M. Grellier, M. Pfeffer, A. De Cian, J. Fischer, *Eur. J. Inorg. Chem.* **2000**, 1539–1547; e) J. A. M. Brandts, R. A. Gossage, J. Boersma, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 2642–2648; f) A. A. H. van der Zeijden, G. van Koten, R. A. Nordemann, B. Kojic-Prodic, A. L. Spek, *Organometallics* **1988**, *7*, 1957–1966.

[9] M. Contel, D. Nobel, A. L. Spek, G. van Koten, *Organometallics* **2000**, *19*, 3288–3295.

[10] M. Contel, M. Stol, M. A. Casado, G. P. M. van Klink, D. D. Ellis, A. L. Spek, G. van Koten, *Organometallics* **2002**, *21*, 4556–4559.

[11] a) A. V. Chuchuryukin, R. Huang, M. Lutz, J. C. Chadwick, A. L. Spek, G. van Koten, *Organometallics* **2011**, *30*, 2819–2830; b) M. Stol, D. J. M. Snelders, H. Kooijman, A. L. Spek, G. P. M. van Klink, G. van Koten, *Dalton Trans.* **2007**, 2589–2593; c) A. V. Chuchuryukin, R. Huang, E. E. van Faassen, G. P. M. van Klink, M. Lutz, J. C. Chadwick, A. L. Spek, G. van Koten, *Dalton Trans.* **2011**, *40*, 8887–8895.

[12] J. I. van der Vlugt, M. A. Siegler, M. Janssen, D. Vogt, A. L. Spek, *Organometallics* **2009**, *28*, 7025–7032 and references cited therein.

[13] a) R. Jambor, L. Dostál, A. Růžička, I. Císařová, J. Brus, J. Holeček, *Organometallics* **2002**, *21*, 3996–4004; b) M. Chovancová, R. Jambor, A. Růžička, R. Jirásko, I. Císařová, L. Dostál, *Organometallics* **2009**, *28*, 1934–1941.

[14] a) J. Vrána, R. Jambor, A. Růžička, J. Holeček, L. Dostál, *Collect. Czech. Chem. Commun.* **2010**, *75*, 1041–1050; b) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, J. Holeček, F. De Proft, *Dalton Trans.* **2011**, *40*, 8922–8934.

[15] P. Šimon, F. De Proft, R. Jambor, A. Růžička, L. Dostál, *Angew. Chem. Int. Ed.* **2010**, *49*, 5468–5471.

[16] L. Dostál, R. Jambor, A. Růžička, P. Šimon, *Eur. J. Inorg. Chem.* **2011**, 2380–2386.

[17] Y. Jiang, Y. Guo, X. Zhu, D. Song, Y. Wang, X. Song, F. Verpoort, X. Chang, *Inorg. Chim. Acta* **2011**, *376*, 144–151.

[18] For recent examples of related palladium and platinum bisaldimine NCN pincer compounds see: a) J. S. Fossey, M. L. Russell, K. M. A. Malik, C. J. Richards, *J. Organomet. Chem.* **2007**, *692*, 4843–4848; b) K. Takenaka, M. Minakawa, Y. Uozumi, *J. Am. Chem. Soc.* **2005**, *127*, 12273–12281; c) J. S. Fossey, C. J. Richards, *Organometallics* **2002**, *21*, 5259–5264; d) J. S. Fossey, C. J. Richards, *Tetrahedron Lett.* **2003**, *44*, 8773–8776.

[19] a) A. Capapé, M. Crespo, J. Granell, M. Font-Bardía, X. Solans, *Dalton Trans.* **2007**, 2030–2039; b) M. D. Meijer, A. W. Kleij, M. Lutz, A. L. Spek, G. van Koten, *J. Organomet. Chem.* **2001**, *640*, 166–169.

[20] G. R. Fulmer, W. Kaminsky, R. A. Kemp, K. I. Goldberg, *Organometallics* **2011**, *30*, 1627–1636.

[21] a) R. Lindner, B. van der Bosch, M. Lutz, J. N. H. Reek, J. I. van der Vlugt, *Organometallics* **2011**, *30*, 499–510; b) P. G. Alsabeh, R. McDonald, M. Stradiotto, *Organometallics* **2012**, *31*, 1049–1054; c) J. I. van der Vlugt, M. M. P. Grutters, A. M. Mills, H. Kooijman, A. L. Spek, D. Vogt, *Eur. J. Inorg. Chem.* **2003**, 4361–4369; d) P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702; *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699; e) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27–110.

[22] D. Zhao, W. Gao, Y. Mu, L. Ye, *Chem. Eur. J.* **2010**, *16*, 4394–4401.

[23] P. Coppens, *Crystallographic Computing* (Eds.: F. R Ahmed, S. R. Hall, C. P. Huber), Copenhagen, Munksgaard, **1970**, pp. 255–270.

[24] A. Altomare, G. Cascarone, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. J. Camalli, *Appl. Crystallogr.* **1994**, *27*, 1045.

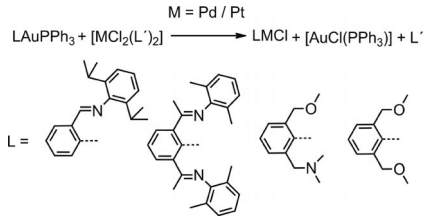
[25] G. M. Sheldrick, *SHELXL-97, A Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received: February 14, 2012
Published Online: ■

EurJIC European Journal of Inorganic Chemistry

Gold(I) Compounds

Organogold(I) compounds $LAu(PPh_3)$ were prepared and characterized. Their reactions with $[PdCl_2(CH_3CN)_2]$ and $[PtCl_2(Et_2S)_2]$ complexes were investigated and they showed promising potential for utilization as transmetalating reagents.



Keywords: Gold / Palladium / Platinum / Metalation / Chelates

