

A Bis(*ortho*-amine)aryl–Gold(I) Compound as an Efficient, Nontoxic, Arylating Reagent

Maria Contel,[†] Marianne Stol,[†] Miguel A. Casado,[†] Gerard P. M. van Klink,[†]
Dianne D. Ellis,[‡] Anthony L. Spek,^{‡,§} and Gerard van Koten^{*,†}

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands, and Bijvoet Center for Biomolecular Research,
Department of Crystal and Structural Chemistry, Utrecht University,
Padualaan 8, 3584 CH Utrecht, The Netherlands

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Summary: A novel strategy for the synthesis of bis(*ortho*-amine)chelated monoanionic bisaminoaryl–metal complexes is presented. This method constitutes the exchange of a monoanionic, NCN-pincer ligand (NCN = [C₆H₃(CH₂-NMe₂)₂-2,6][−]) between a stable arylgold(I) phosphine, [Au(η¹-C-NCN)(PPh₃)] (**2**), and a transition metal halide. This transmetalation results in the quantitative formation of [M(NCN)] organometallic compounds (M = Au^{III}, Ni^{II}, Pd^{II}, Pt^{II}, Ti^{IV}, and Fe^{III}) and [AuCl(PPh₃)] as the only coproduct that can be recovered.

Introduction

Common methods to form transition metal to carbon bonds generally involve the use of organolithium¹ or -magnesium² reagents. When these reagents are not appropriate or successful, e.g., because of their reducing nature, organometallic reagents based on tin(IV), thallium(I), or mercury(II) are available for the same purpose. However, due to the considerable toxicity of these metals, there is a strong tendency to restrict the use of such reagents. Consequently, new approaches are required to complement the synthetic palette. In view of the isolobal relationship³ between AuL⁺ and Li⁺ and the inertness of gold(I), we anticipated that the transmetalating properties of organogold(I) compounds (of the type [AuRL]) could complement those of the corresponding organolithium (LiR) reagents.⁴ This new approach forms M–C bonds with the additional advantage of recovering the starting gold(I) coproduct, which subsequently can be recycled into the starting organogold(I) reagent.

Results and Discussion

Recently, we prepared a gold(I) dimer [Au(NCN)]₂ (**1**)⁵ and considered its use as a transmetalating reagent. Although preliminary results with Pd^{II} and Ni^{II} complexes were promising, the instability of **1** prevented the production of the transmetalated products in reasonable yields and purity.

It turned out, however, that [Au(NCN)(PPh₃)] (**2**) showed excellent properties in transmetalation reactions with Au^{III}, M^{II} (M = Ni, Pd, Pt), Fe^{III}, and Ti^{IV} halide-containing precursors. To our knowledge this is the first demonstration of an organogold compound to cleanly transfer its organic group to other d¹⁰, d⁸, d⁵, or d⁰ metallic centers. In all cases, the reaction afforded the corresponding [M(NCN)] organometallic compound, while [AuCl(PPh₃)] was obtained as the recyclable coproduct.

The reaction of [AuCl(PPh₃)] with [Li(NCN)]⁶ in Et₂O at −20 °C (Scheme 1) afforded the bis(*ortho*-amine)aryl–gold(I) compound [Au(NCN)(PPh₃)] (**2**) in good (68%) to excellent yields (quantitative). The gold atom in **2** is η¹-C bonded to C_{ipso} of the pincer moiety and is *trans*-coordinated to the PPh₃ ligand (Figure 1). Both *ortho*-Me₂NCH₂ ligands are noncoordinated. In contrast to [Au(NCN)]₂ (**1**),⁵ **2** is not light sensitive and is stable to prolonged heating to 100 °C. Furthermore, **2** is soluble in most organic solvents, is air and moisture stable, and can be stored as a solid for months without any noticeable decomposition.

The preparation of NCN·M complexes by this new method is outlined in Scheme 1. The use of **2** as an

* To whom correspondence should be addressed. Tel: +3130 2533120. Fax: +3130 2523615. E-mail: g.vankoten@chem.uu.nl.

[†] Debye Institute, Utrecht University.

[‡] Bijvoet Center for Biomolecular Research, Utrecht University.

[§] Address correspondence pertaining to crystallographic studies to this author. E-mail: A.L.Spek@chem.uu.nl.

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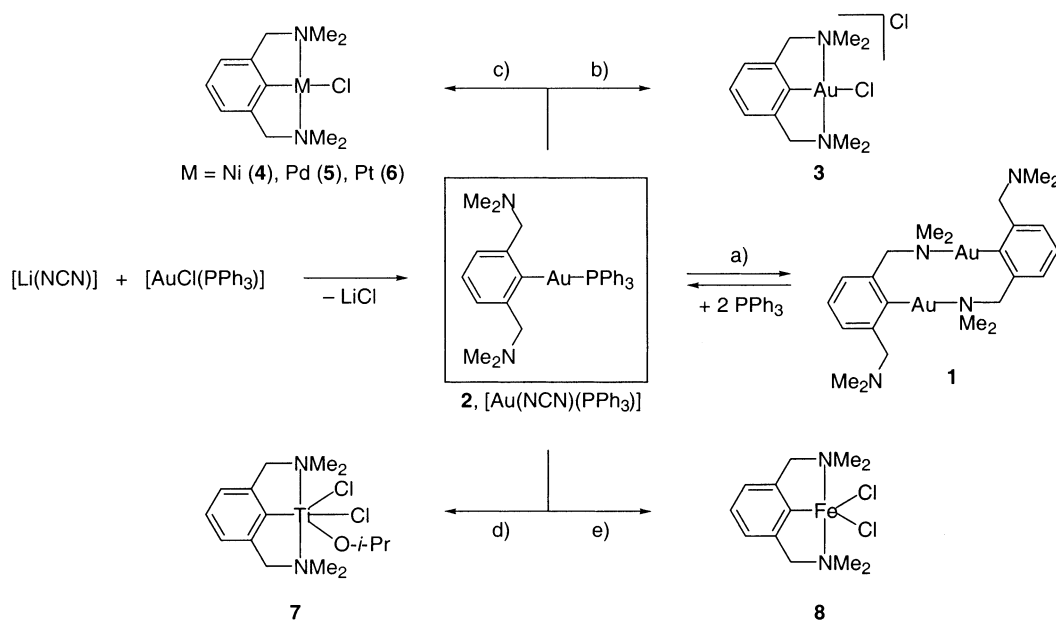
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Scheme 1. Transmetalation Reactions of [Au(NCN)(PPh₃)] (2). [AuCl(PPh₃)] Was Obtained as a Recyclable Coproduct in All Cases^a


^a Molar ratio, 1:1. (a) AuCl(tht), -tht, toluene, 0 °C; (b) AuCl₃(tht), -tht, toluene, RT; (c) **4**, [NiCl₂(PPh₃)₂], -PPh₃, toluene, RT; **5**, [PdCl₂(SEt₂)₂], -SEt₂, toluene, RT; **6**, [PtCl₂(SEt₂)₂], -SEt₂, toluene, gentle reflux, 2 h; (d) **7**, [TiCl₃(OCHMe₂)], THF, -78 °C; (e) FeCl₃ (anhydrous), toluene, RT.

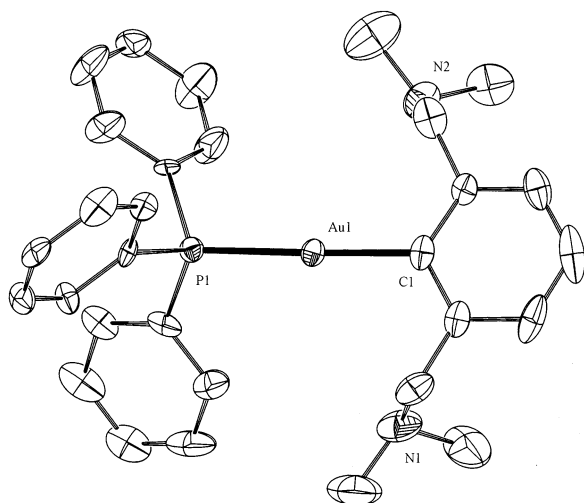


Figure 1. Displacement ellipsoid plot (50% probability) for one of the two crystallographic independent molecules of **2**. Selected bond lengths (Å) and angles (deg): Au1–C1 2.055(9), Au1–P1 2.282(2), Au2–C51 2.045(9), Au2–P2 2.287(2), C1–Au–P1 178.6(3), C51–Au2–P2 176.0(3).

aryllating reagent has certain advantages over traditional organolithium or Grignard reagents. The transmetalation reactions can be performed in air and even at reflux depending on the metal involved (see Scheme 1). The NCN·M complexes formed can be easily separated from the coproduct by extraction with Et₂O (in which [AuCl(PPh₃)] is insoluble) or by using conventional fractional crystallization techniques. The reactions do not require excess transmetalating reagent and can be carried out in an exact 1:1 molar ratio. For air and moisture sensitive products, reactions at millimolar scale with [Li(NCN)] are often difficult because of the manipulation of small amounts of sensitive [Li(NCN)]. Isolated yields of **3–8** range from 65 to 95%. Due to the stability of the formal oxidation state of the Au center

in **2**, this approach does not affect the oxidation state of the metallic centers involved during the transmetalation processes. In addition, this method circumvents the use of environmentally unacceptable Hg and Tl analogues, while the [AuCl(PPh₃)] coproduct can be reused and converted back into **2**, thus making this also an atom-efficient method.

It must be noted that the known [M(NCN)L_n] compounds **1** (Au^I),⁵ **4** (Ni^{II}),⁷ **5** (Pd^{II}), and **6** (Pt^{II})⁸ have been synthesized via organolithium or Grignard reagents. However in a number of cases, alternative methods such as the use of other organometallic reagents or oxidative addition of C–X bonds (which requires the preparation of the corresponding aryl halides) to zerovalent metals are required in order to avoid reduction to metallic Ni or Pd or to prevent the formation of mixtures.⁹

Other (early) transition metals can also be incorporated by use of **2**. For example, the synthesis of titanium(IV) derivative **7**¹⁰ and iron(III) compound [FeCl₂(NCN)] (**8**)¹¹ was achieved on small scales. Moreover, using **2** only one chloride ligand can be selectively substituted.

The formation of paramagnetic **8** (from **2** and anhydrous FeCl₃ in toluene at RT, Scheme 1) was confirmed by X-ray diffraction techniques, and the spectroscopic details were in accordance with earlier results.¹¹ Using the present gold(I) route the reaction can be carried out on millimolar scale (0.55 mmol), and **8** can be obtained in good yield. Moreover, this reaction can be performed at RT, which underlines the nonreductive character of **2** giving an easy access to the formation of C–Fe^{III} bonds.

The preparation of gold(III) compound [AuCl(NCN)]Cl (**3**) is of interest, as arylgold(III) derivatives are

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commonly not accessible by organolithium or Grignard routes due to undesired reductions of gold(III) to gold(I). Existing routes involve (i) oxidation of the corresponding gold(I) compound with halogens, (ii) electrophilic substitution by gold(III) at the aromatic ring of benzene derivatives, or (iii) the use of other partly undesirable organometallic reagents based on Sn^{IV} , Zn^{II} , Tl^{I} , or Hg^{II} .¹² In case of arylgold(III) complexes with coordinating *ortho*-substituents the use of organomercury compounds is usually the only choice, as direct auration reactions toward arenes are inhibited by the presence of these substituents.^{12,13} Moreover, most of these reactions required forcing reaction conditions and prolonged times. For example, $[\text{AuCl}(\text{NCN})]\text{X}$ ($\text{X} = \text{Hg}_2\text{Cl}_6^-$) was prepared by reacting $[\text{HgCl}(\text{NCN})]$ with $\text{NH}_4[\text{AuCl}_4]$ at RT using long reaction times (48 h).¹⁴ The present method affords **3** instantaneously at RT and in high yield (95%).

An important driving force of the reactions studied (see Scheme 1) is most likely the formation of a strong Au–Cl bond in the coproduct as well as the coordination of the *ortho*-amino donor atoms in the products. Moreover, it can be envisaged that prior nitrogen–metal coordination of the free amino substituents in **2** to the metal salt assists in the transmetalation process.

Conclusion

A general synthetic method has been developed to use stable arylgold(I) phosphine precursors as transmetalating reagents in organometallic chemistry. It represents a nontoxic method with the possibility of performing reactions at air, generally at RT, in millimolar scale without reduction of the transmetalated metal center. In addition, the $[\text{AuCl}(\text{PPh}_3)]$ coproduct can be recovered and with additional $[\text{Li}(\text{NCN})]$ transformed to starting compound **2**. The scope of this method is currently studied using various types of *ortho*-substituted arylgold(I) phosphine precursors and a range of transition metal compounds. This method complements nicely the recently reported cyclotransmetalation reactions which involve the exchange of an arene proton with a suitable metal salt cation assisted by *ortho*-chelation.¹⁵ Both methods are extremely important for the synthesis of multimetallic systems such as the metallopincher cartwheel compounds.¹⁶

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Experimental Section

General Procedures and Materials. All reactions were carried out using standard Schlenk techniques under an inert nitrogen atmosphere unless stated otherwise. Et_2O , toluene, pentane, and hexanes were carefully dried and distilled from sodium prior to use. All standard reagents were purchased from Acros or Aldrich. ^1H (300 MHz), ^{13}C (75 MHz), and ^{31}P (121 MHz) NMR spectra were recorded on a Varian 300 spectrometer at 25 °C; chemical shifts are in ppm referenced to residual solvent resonances. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Synthesis of $[\text{Au}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})(\text{PPh}_3)]$ (2**).** To a solution of 0.52 g of NCHN (1,3-bis[(dimethylamino)methyl]benzene) (2.7 mmol) in 30 mL of pentane was added by syringe 1.7 mL of a 1.6 M solution of *n*-BuLi (2.7 mmol) in hexane. After addition, stirring was continued for 16 h. The reaction mixture turned yellow and was added, at –30 °C, to a suspension of 1.33 g of $[\text{AuCl}(\text{PPh}_3)]$ (2.7 mmol) in 20 mL of diethyl ether. After addition, stirring was continued for 15 min, after which the reaction mixture was allowed to warm to room temperature and stirred for another 4.5 h and subsequently quenched with 35 mL of water. The reaction mixture was filtered over Celite, the organic fraction was separated, and the aqueous fraction was extracted with diethyl ether (2 × 35 mL). The extracts were combined, washed (water), dried (MgSO_4), filtered, and evaporated to dryness. The residual solid was washed twice with pentane (10 mL). This afforded 1.5 g (2.3 mmol, 87%) of a cream-colored solid, which was characterized as pure **2**.

^1H NMR (300 MHz, C_6D_6): δ 2.31 (s, 12H, NCH_3), 4.03 (s, 4H, ArCH_2), 6.97–7.01 (m, 9H, PArH), 7.37 (t, $^3J = 6.6$ Hz, 1H, ArH), 7.58–7.76 (m, 8H, $\text{PArH} + \text{ArH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6 , 25 °C): δ 44.9. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25 °C): δ 45.9 (CH_3), 70.8 (CH_2), 125.54, 130.83, 131.93, 132.56, 134.60, 148.05 (C_{ipso} not observed). FAB(+): m/z (%) 651 (100). Anal. Calcd for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{PAu}$: C, 55.39; H, 5.27; N, 4.31. Found: C, 55.26; H, 5.22; N, 4.25.

Synthesis of $[\text{AuCl}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})][\text{Cl}]$ (3**).** To a solution of $[\text{AuCl}_3(\text{tht})]$ (192.6 mg, 0.492 mmol) in toluene (50 mL) was added a solution of **2** (319.6 mg, 0.491 mmol) in toluene (15 mL). A pale yellow precipitate was formed readily, which was separated from the colorless solution. Pale yellow **3** was then washed with Et_2O and dried in vacuo (214.2 mg, 95% yield). The mother liquor was evaporated to dryness to afford 237.5 mg of a white precipitate, which was characterized as pure $[\text{AuCl}(\text{PPh}_3)]$ (0.480 mmol, 98%).

^1H NMR (300 MHz, C_6D_6): δ 3.29 (s, 12H, NCH_3), 4.70 (s, 4H, CH_2), 7.07 (d, 2H, ArH), 7.34 (t, $^2J = 11.7$ Hz, 1H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN): δ 55.34 (CH_3), 78.62 (CH_2), 123.29, 130.57, 143.58 (C_{ipso} not observed). FAB(+): m/z (%) 423 (50). Anal. Calcd for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{AuCl}_2$: C, 31.39; H, 4.17; N, 6.10. Found: C, 31.27; H, 4.25; N, 6.05.

Synthesis of $[\text{NiCl}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})]$ (4**).** To a purple-red solution of $[\text{NiCl}_2(\text{PPh}_3)_2]$ (71.7 mg, 0.109 mmol) in benzene (25 mL) was added 71.3 mg (0.109 mmol) of **2**. The color of the solution changed immediately to bright yellow. After stirring for 30 min at RT, the solution was concentrated to ~10 mL. Extraction with Et_2O (10 mL) afforded a white precipitate ($[\text{AuCl}(\text{PPh}_3)]$) and an orange solution. This solution was concentrated to give 29.1 mg (0.102 mmol, 93%) of a yellow solid, which was characterized by ^1H NMR spectroscopy as pure **4**.

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^1H NMR (300 MHz, C_6D_6): δ 2.39 (s, 12H, NCH_3), 3.01 (s, 4H, ArCH_2), 6.46 (d, $^3J = 7.5$ Hz, 2H, ArH), 6.98 (t, $^3J = 7.4$ Hz, 1H, ArH). Anal. Calcd for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{NiCl}$: C, 50.89; H, 6.71; N, 9.81. Found: C, 51.06; H, 6.78; N, 9.94.

Synthesis of $[\text{PdCl}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})]$ (5**).** To a solution of 0.065 g (0.100 mmol) of **2** in toluene (10 mL) was added 0.036 g (0.10 mmol) of bright orange $[\text{PdCl}_2(\text{SEt}_2)_2]$. Almost immediately the color of the solution faded to pale yellow. The solution was stirred for 30 min at RT, after which the solution was concentrated. Upon addition of 10 mL of Et_2O , 0.45 g (97%) of a white precipitate was obtained, which was characterized as pure $[\text{AuCl}(\text{PPh}_3)]$. The solution was further concentrated and pentane added, which afforded 0.0294 g (96%) of a white compound, which was characterized by ^1H NMR spectroscopy as pure **5**.

^1H NMR (300 MHz, C_6D_6): δ 2.60 (s, 12H, NCH_3), 3.28 (s, 4H, ArCH_2), 6.55 (d, $^3J = 7.5$ Hz, 2H, ArH), 6.94 (t, $^3J = 7.6$ Hz, 1H, ArH). Anal. Calcd for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{PdCl}$: C, 43.26; H, 5.75; N, 8.41. Found: C, 43.41; H, 5.82; N, 8.47.

Synthesis of $[\text{PtCl}(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})]$ (6**).** In an NMR tube 0.0040 g (0.0061 mmol) of **2** and 0.0027 (0.006 mmol) of $[\text{PtCl}_2(\text{SEt}_2)_2]$ were combined in 0.7 mL of deuterated benzene. The solution was heated to reflux for 2 h, during which it became colorless. ^1H and ^{31}P NMR spectroscopy revealed only signals that could be ascribed to $[\text{AuCl}(\text{PPh}_3)]$, **6**, and free SEt_2 .

^1H NMR (300 MHz, C_6D_6): δ 2.69 (t, $^3J_{\text{PtH}} = 19.1$ Hz, 12H, NCH_3), 3.28 (t, $^3J_{\text{PtH}} = 22.8$ Hz, ArCH_2), 6.64 (d, $^3J = 7.5$ Hz, 2H, ArH), 7.04 (t, $^3J = 7.5$ Hz, 1H, ArH).

Synthesis of $[\text{TiCl}_2(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})(\text{OCHMe}_2)]$ (7**).** To a colorless solution of 0.045 g (0.21 mmol) of $\text{TiCl}_3(\text{OCHMe}_2)$ in toluene was added dropwise, at -78°C , 0.137 g (0.21 mmol) of **2** in 10 mL of toluene. The mixture was stirred for 30 min, after which it was allowed to warm to RT. After slight concentration, a pale yellow precipitate formed. The mixture was cooled overnight at -10°C . The precipitate was separated from the solution and characterized by ^1H and ^{31}P NMR spectroscopy as pure $[\text{AuCl}(\text{PPh}_3)]$. The mother liquor was evaporated to dryness to afford 50.4 mg (65%) of a yellow precipitate, which was characterized by ^1H NMR spectroscopy as pure **7**.

^1H NMR (300 MHz, C_6D_6): δ 1.21 (d, $^3J = 7.41$ Hz, 6H, $\text{OCH}(\text{CH}_3)$), 2.1 (bs, 6H, NCH_3), 2.6 (bs, 2H, ArCH_2), 2.8 (bs, 6H, NCH_3), 4.7 (bs, 2H, ArCH_2), 5.88 (septet, $^3J = 6.22$ Hz, 1H, OCH), 6.61 (d, $^3J = 7.40$ Hz, 2H, ArH), 6.88 (t, $^3J = 7.41$ Hz, 1H, ArH). Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{N}_2\text{Cl}_2\text{OTi}$: C, 48.80; H, 7.10; N, 7.59. Found: C, 48.91; H, 7.13; N, 7.52.

Synthesis of $[\text{FeCl}_2(\text{C}_6\text{H}_3\{\text{CH}_2\text{NMe}_2\}_2\text{-2,6})]$ (8**).** To a dark green solution of 0.090 g of FeCl_3 (anhydrous) (0.56 mmol) in degassed, dry toluene (10 mL) was added a solution of 0.322 g of **2** (0.56 mmol) in 5 mL of toluene. The color of the solution slowly changed to dark orange. After 5 h stirring at RT the toluene was removed in vacuo. Extraction with degassed, dry Et_2O (15 mL) afforded a white precipitate $[\text{AuCl}(\text{PPh}_3)]$ and a light red solution that was transferred to another flask by cannula. This solution was concentrated to ca. 5 mL, and subsequent cooling (-20°C) afforded **8** as dark brown needles (0.14 g, 79%). Confirmation of the structure of **8** was obtained by an X-ray diffraction study. The crystallographic data were in agreement with a previously reported X-ray of **8**.¹¹

Crystal Structure Determination of **2.** A colorless block-shaped crystal measuring (0.50 \times 0.44 \times 0.25 mm) was mounted under a nitrogen stream (150 K) on an Enraf-Nonius CAD4 diffractometer with a graphite monochromator ($\lambda = 0.71073$ Å) and a rotating anode source. The unit cell dimensions were determined from the setting values of 25 accurately centered reflections in the range $11.56^\circ < \theta < 13.76^\circ$. The stability of the crystal was monitored by measuring the intensities of three standard reflections every hour. Data were corrected for Lorentz, polarization, and absorption effects, the

Table 1. Crystal Data and Details of Structure Refinement for **2**

Crystal Data	
formula	$\text{C}_{30}\text{H}_{34}\text{AuN}_2\text{P}$
fw	650.53
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, b, c [Å]	9.2074(8), 21.4351(15), 28.801(4)
α, β, γ [deg]	90, 108.511(9), 90
V [Å ³]	5390.1(10)
Z	8
$D(\text{calc})$ [g/cm ³]	1.603
$\mu(\text{Mo K}\alpha)$ [1/mm]	5.538
$F(000)$	2576
cryst size [mm]	0.25 \times 0.44 \times 0.50
Data Collection	
temperature [K]	150
radiation [Å]	Mo K α 0.71073
$\theta(\text{min-max})$ [deg]	0.8, 27.5
dataset	-3: 11; -27: 27; -37: 35
no. tot., uniq. data, $R(\text{int})$	26 342, 12 339, 0.089
no. obsd data [$I > 2.0\sigma(I)$]	8541
Refinement	
$N_{\text{ref}}, N_{\text{par}}$	12339, 627
R, wR_2, S	0.0529, 0.1032, 0.99
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	
max. and av. shift/error	0.00, 0.00
min. and max. resd dens [$e/\text{Å}^3$]	-1.64, 1.41

latter using an empirical correction based on ΔF values (with routine DELABS incorporated in PLATON).¹⁷ The structure was solved with the DIRDIF97 program¹⁸ and refined with SHELXL-97 using full matrix least-squares on F^2 .¹⁹ Data were initially collected in the $P2_1/n$ setting (β angle of 90.13°). The structure was twinned along the a axis, thus a TWIN matrix $\{-1\ 0\ 0 \mid 0\ 1\ 0 \mid 0\ 0\ 1\}$ was applied with a BASF parameter that refined to 0.269(1). The N3 and C59 displacement ellipsoids in one of the two crystallographically independent molecules are large and were modeled being disordered across two sites in a ratio 65(1):35(1). The packing of the molecules mimics $Pbcn$ symmetry. Crystallographic data (excluding structure factors) for **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 165228. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Details of the X-ray crystal structure analysis of compound **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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