## The Crystal and Molecular Structures of Gold(I) Complexes Containing the Electron-Rich P-Donor Ligand Ph<sub>3</sub>PNPPh<sub>2</sub>

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Dedicated to Professor Peter Klüfers on the Occasion of His 60th Birthday

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**Abstract.** The reaction of [AuCl(tht)] (tht = tetrahydrothiophene) with an equimolar amount of the electron-rich ligand *N*-diphenylphosphinotriphenylphosphinimine,  $Ph_3PNPPh_2$ , in THF afforded the new complex [AuCl( $Ph_3PNPPh_2$ )] (1) in good yield. Furthermore, the reaction of [AuHCl<sub>4</sub>] with  $Ph_3PNPPh_2$  in a molar ratio of 1:3 in dichloromethane at room temperature yielded the complex salt [Au( $Ph_3PNPPh_2$ )\_2]Cl

#### Introduction

In the last years, the interest in the chemistry of gold has grown immensely because of many applications of compounds containing this element in the fields of catalysis, materials science, and medicine. An introductory perspective in this fascinating research area was given recently by Hutchings, Brust, and Schmidbaur.<sup>[1]</sup> Current investigations show that gold species are interesting anticancer drug candidates with a mode of action different from that of well-established platinum agents. In this context, the spectrum of gold complexes described as antiproliferative compounds comprises a broad variety of different species including many phosphane complexes.<sup>[2]</sup> In addition, gold(I) compounds containing phosphane ligands are of special importance due to their characteristic luminescence as well as unique photophysical and photochemical properties.<sup>[3]</sup> Homogeneous gold catalysts are playing an increasing role in organic synthesis, whereby standard catalysts in this field are complexes of the type  $[Au(PR_3)X]$  (X = typically Cl).<sup>[4]</sup> Today there is an active interest in studies on the synthesis of such complexes using sterically demanding organophosphorus ligands, e.g.<sup>[5-7]</sup> Currently we are interested in the reaction behavior of transition metal complexes towards sterically demanding phosphane ligands such as *t*Bu<sub>2</sub>PH.<sup>[8]</sup> In this context we studied the reaction of hydrogen tetrachloridoaurate(III) hydrate with *t*Bu<sub>2</sub>PH in dichloromethane at room temperature,

 [a] Department of Chemistry Ludwig Maximilian University of Munich Butenandtstr. 5–13 (D) 81377 München, Germany product of oxidation. The molecular structures of metal complexes **1** and **2** were determined by single-crystal X-ray diffraction. Because of the bulkiness of the ligand  $Ph_3PNPPh_2$  no short intermolecular gold–gold interactions (aurophilic aggregation) could be observed in the solid-state structures.

(2) as the dichloromethane solvate beside Ph<sub>3</sub>PNPPh<sub>2</sub>Cl<sub>2</sub> as the side-

which resulted in the formation of the complex salt  $[Au(tBu_2PH)_2][HCl_2]$  in good yield.<sup>[9]</sup>

Herein we describe investigations on the reaction of a gold(I) and a gold(III) precursor compound with the electron-rich ligand *N*-diphenylphosphino-triphenylphosphinimine (Ph<sub>3</sub>PNPPh<sub>2</sub>) resulting in the new compounds [AuCl(Ph<sub>3</sub>PNPPh<sub>2</sub>)] (1) and [Au(Ph<sub>3</sub>PNPPh<sub>2</sub>)<sub>2</sub>]Cl (2), respectively, the crystal structures of which were determined by single-crystal X-ray diffraction.

#### **Results and Discussion**

#### Synthesis of Au<sup>I</sup> Complexes 1 and 2

Treatment of equimolar amounts of [AuCl(tht)] (tht = tetrahydrothiophene) with  $Ph_3PNPPh_2$  in THF afforded a clear colorless solution. During stirring for 2 h at room temperature a colorless precipitate was obtained, the amount of which increased upon further stirring overnight (Scheme 1).

$$[AuCl(tht)] + Ph_{3}PNPPh_{2} \xrightarrow{THF} [AuCl(Ph_{3}PNPPh_{2})]$$

Scheme 1. Synthesis of 1.

After workup (see Experimental Section) colorless crystals suitable for an X-ray diffraction study were grown at room temperature from a  $CH_2Cl_2/n$ -heptane mixture by slow diffusion overnight. Elemental analysis and the NMR spectroscopic data of the new compound were consistent with the presence of the complex [AuCl(Ph<sub>3</sub>PNPPh<sub>2</sub>)] (1).

Furthermore, the reaction of solid hydrogen tetrachloridoaurate(III) hydrate with three equivalents of  $Ph_3PNPPh_2$  in di-

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chloromethane at room temperature yielded immediately a clear colorless solution. After stirring overnight to complete the reaction, a colorless solid was obtained from this solution by precipitation with *n*-heptane, which was identified by elemental analysis and spectroscopic methods as the complex salt  $[Au(Ph_3PNPPh_2)_2]Cl$  (2) (see Scheme 2, labeling scheme of complexes 1 and 2 see Figure 1).

$$[HAuCl_4] + 3 Ph_3PNPPh_2 \xrightarrow{CH_2Cl_2} r.t.$$

2

Scheme 2. Synthesis of 2.

$$R = CI (1);$$

Figure 1. Labeling scheme of complexes 1 and 2.

As outlined in the reaction scheme, during this reaction  $Au^{III}$  is reduced to  $Au^{I}$  and the excess of the organophosphorus ligand is oxidized to  $Ph_3PNPPh_2Cl_2$ . Similar observations were made in analogous reactions starting from  $AuCl_3$  and  $PPh_3$ .<sup>[10]</sup> Alternatively, complex **2** can be obtained with better yield (74 %) starting from the gold(I) complex AuCl(tht), which is reacted with two equivalents of the ligand  $Ph_3PNPPh_2$ .

### ${}^{31}P_{1}^{I}H_{1}^{I}$ and ${}^{13}C_{1}^{I}H_{1}^{I}NMR$ Spectroscopy of 1 and 2

The  ${}^{31}P{}^{1}H$  NMR spectrum of 1 in CD<sub>2</sub>Cl<sub>2</sub> exhibited two doublets at 47.3 and 19.9 ppm ( ${}^{2}J_{PP} = 23.3$  Hz). In comparison with the <sup>31</sup>P NMR spectroscopic data of the known complex [AuCl(PPh<sub>3</sub>)] ( $\delta = 33.0$ , s, CDCl<sub>3</sub><sup>[11]</sup>) a downfield shift is observed exhibiting the Ph<sub>3</sub>PNPPh<sub>2</sub> ligand as a more electron rich P-donor ligand than PPh<sub>3</sub>. The latter effect is caused by the stronger electron donating properties of the Ph<sub>3</sub>PN substituent. The presence of Ph<sub>3</sub>PNPPh<sub>2</sub>Cl<sub>2</sub> could be confirmed by us using <sup>31</sup>P NMR spectroscopy. The <sup>31</sup>P {<sup>1</sup>H} NMR spectrum of  $\mathbf{2}$  in CD<sub>2</sub>Cl<sub>2</sub> showed two triplet signals at 67.3 and 19.3 ppm  $(N = 27 \text{ Hz} = {}^{2}J_{\text{PP}} + {}^{4}J_{\text{PP}})$ . For a linear complex [Au(Ph<sub>3</sub>NPPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup> an AA'XX' spin system is expected. Due to the very small P–P coupling between the  $PR_3$  terminal phosphorus atoms and the relatively large  ${}^{2}J_{PP}$  coupling between the PPh<sub>2</sub> phosphorus atoms, the expected ten line pattern for the A (and X) part is reduced to a deceptively simple three line pattern, from which only the N value (27 Hz) can be obtained. Similarly as described for compound 1, also in this case a significant downfield shift is observed by comparison with the <sup>31</sup>P NMR spectroscopic data of [Au(PPh<sub>3</sub>)<sub>2</sub>]Cl ( $\delta$  = 39.0, s, CDCl<sub>3</sub><sup>[11]</sup>). This downfield shift is indicative of the electronrich character of the ligand  $Ph_3PNPPh_2$  (vide supra) (<sup>13</sup>C{<sup>1</sup>H} NMR spectroscopic data see Table 1).

<b>Table 1.</b> <sup>13</sup> C{ <sup>1</sup> H} NMR spectroscopic data of compounds	1	and	2	re-
corded in $CH_2Cl_2$ (coupling constants <sup>a)</sup> J in Hz).				

		1	<b>2</b> <sup>a)</sup>	
$\delta^{13}C$	C1	139.8	139.1	
	C2	131.4	131.0	
	C3	128.4	128.8	
	C4	130.5	130.9	
	C5	129.3	129.3	
	C6	132.7	132.3	
	C7	128.9	129.0	
	C8	132.7	132.9	
$^{1}J_{\rm PC}$	P1C1	74.6	70.7	
	P2C5	104.6	104.4	
$^{2}J_{\rm PC}$	P1C2	15.4	16.1	
	P2C6	10.4	10.5	
$^{3}J_{\rm PC}$	P1C3	12.3	11.9	
	P1C5	2.7	2.7	
	P2C1	7.6	7.5	
	P2C7	12.7	12.7	
$^{4}J_{\rm PC}$	P1C4	2.7	2.3	
	P1C6	0.6	-	
	P2C8	3.0	2.9	

a)  $N = |J_{AX} + J_{AX'}| \approx J_{AX}$ 

#### Crystal and Molecular Structures of 1 and 2

Single crystals of 1 and 2, respectively, suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-heptane into a concentrated dichloromethane solution at room temperature overnight. Complex 1 crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell. The coordination sphere at the gold atom can be considered as two-coordinate linear. A view of the molecule is shown in Figure 2, selected bond lengths and angles are given in the caption.



**Figure 2.** Molecular structure of [AuCl(Ph<sub>3</sub>PNPPh<sub>2</sub>)] (1) in the crystal (ORTEP drawing with 50 % probability ellipsoids, hydrogen atoms are omitted for clarity). Selected distances /Å and angles /°: Au1–P1 2.2334(12), Au1–Cl1 2.2928(12), P1–N1 1.621(4), P1–Cl 1.815(5), P1–C7 1.830(4), P2–N1 1.573(4), P2–Cl3 1.801(4), P2–Cl9 1.792(5), P2–C25 1.898(5); P1–Au1–Cl1 177.47(5), N1–P1–Cl 104.1(2), N1–P1–C7 104.68(19), C1–P1–C7 105.9(2), N1–P1–Au1 120.88(13), C1–P1–Au1 110.68(15), C7–P1–Au1 109.48(15), N1–P2–Cl3 114.6(2), N1–P2–Cl9 106.8(2).

The molecular structure is closely related to that of [AuCl(PPh<sub>3</sub>)].<sup>[12]</sup> For the latter the following important struc-



tural parameters were found: Au–P 2.235(3), Au–Cl 2.279(3) Å; P–Au–Cl 179.63(8)°. These data agree well with the observed ones for complex **1** (see Figure caption). Furthermore, the structural parameters of **1** are similar to the observed ones for compounds containing electron-rich organophosphorus ligand as [AuCl(PAd<sub>2</sub>*n*Bu)] (Ad = 1-adamantyl or *n*Bu = *n*-butyl)<sup>[5]</sup> and [AuCl(*t*Bu<sub>2</sub>PH)]<sup>[13]</sup> for example. Important bonding parameters of the latter species are: Au1–P1 2.2674(6), Au1–Cl1 2.3107(6) Å, P1–Au1–Cl1 177.07(2)° for [AuCl(Ad<sub>2</sub>*n*Bu)] and Au–P 2.230(2), Au–Cl 2.284(3) Å, P–Au–Cl 176.5(1)° for [AuCl(*t*Bu<sub>2</sub>PH)].

Complex 2 crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell. The coordination sphere at the gold atom can be considered as two-coordinate linear. A view of the cation of the complex salt  $[Au(Ph_3PNPPh_2)_2]Cl$  (2) is shown in Figure 3, selected bond lengths and angles are given in the caption.



**Figure 3.** Structure of the cation of [Au(Ph<sub>3</sub>PNPPh<sub>2</sub>)<sub>2</sub>]Cl·2CH<sub>2</sub>Cl<sub>2</sub> (**2**) in the crystal (ORTEP drawing with 50 % probability ellipsoids, hydrogen atoms are omitted for clarity). Selected distances /Å and angles /°: Au1–P1 2.320(2), Au1–P3 2.322(2), P1–N1 1.656(8), P1–C1 1.793(13), P1–C7 1.827(9), P2–N1 1.532(7), P2–C13 1.802(9), P2–C19 1.810(9), P2–C25 1.812(9), P3–N2 1.631(8), P3–C31 1.813(9), P3–C37 1.808(9), P4–N2 1.637(8), P4–C43 1.802(10), P4–C49 1.800(9), P4–C55 1.802(9); P1–Au1–P3 179.42(10), N1–P1–C1 105.9(4), N1–P1–C7 107.7(4), N1–P2–C13 113.6(4), N1–P2–C19 113.6(4), N1–P2–C25 107.3(4), C13–P2–C19 106.9(4), N1–P1–Au1 115.7(3), C1–P1–Au1 110.8(3), C7–P1–Au1 111.3(3), N2–P3–Au1 118.3(3), P1–N1–P2 125.8(5), P3–N2–P4 120.3(5).

The molecular structure of the cation of **2** is closely related to cation  $[Au(PPh_3)_2]^+$  in the compounds  $[Au(PPh_3)_2]X$  (X =  $PF_6^-$  or  $NO_3^-$ ).<sup>[14]</sup> Thus, important bonding parameters of the latter compounds agree well with the observed ones in **2**: Au– P1 2.314(2), Au–P2 2.309(2) Å, P1–Au–P2 177.4(1)° for  $[Au(PPh_3)_2]PF_6$  and Au–P1 2.312(4), Au–P2 2.311(2) Å, P1– Au–P2 171.1(2)° for  $[Au(PPh_3)_2]NO_3$ . Furthermore, the crystal structures of  $[Au(PPh_3)_2]BF_4$  and  $[Au(PPh_3)_2][C(CN)_3]$  were reported.<sup>[15]</sup> For the latter compounds the following data were found: Au–P1 2.321(3), Au–P2 2.322(3) Å, P1–Au–P2 167.3(1)° for  $[Au(PPh_3)_2]BF_4$  and Au–P 2.315(2) Å, P–Au–P' 180° for  $[Au(PPh_3)_2][C(CN)_3]$ , which are also in a good agreement with the observed data for **2**. Several other crystal structures of closely related complexes containing electron-rich organophosphorus ligands were reported:  $[Au(PAd_2Bn)_2]^+$  (Ad = 1-adamantyl, Bn = benzyl),<sup>[5]</sup>  $[Au(tBu_3P)_2]^{+[16]}$  or  $[Au(Mes_3P)_2]^+$  (Mes = mesityl).<sup>[17]</sup> Important bonding parameters of the latter compounds also agree well with the observed ones in **2**: Au1–P1 2.3348(9) Å, P1–Au–P1' 180.00° for  $[Au(Ad_2BnP)_2]^+$ , Au1–P1 2.323(2), Au1–P2 2.321(2) Å, P1–Au–P2 180.0° for  $[Au(tBu_3P)_2]^+$ , and Au–P 2.3525(10) Å, P–Au–P1' 179.72(7)° for the complex  $[Au(Mes_3P)_1]^+$ .

The Au···Au separations in both complexes are quite large (greater than 5 Å). This suggests that there are no attractive interactions between the gold atoms in the solid state since the organophosphorus ligands appear to be too bulky to allow the metal atoms to associate.

#### Conclusions

A convenient synthesis for the new compounds  $[AuCl(Ph_3PNPPh_2)]$  (1) and  $[Au(Ph_3PNPPh_2)_2]Cl$  (2) were developed and their molecular structures were confirmed by X-ray crystal structure analysis. In the solid state, for both compounds no attractive interactions between the gold atoms (aurophilic aggregation) could be observed presumably because of the bulkiness of the used organophosphorus ligands.

#### **Experimental Section**

**General:** All manipulations were carried out under dry argon using standard Schlenk techniques. Solvents were dried according to standard procedures and stored under nitrogen. Hydrogen tetrachloroaurate(III) hydrate was purchased from ABCR. Complex [AuCl(tht)]<sup>[18]</sup> and ligand Ph<sub>3</sub>PNPPh<sub>2</sub><sup>[19]</sup> were prepared according to literature procedures. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded with Jeol Eclipse 270 and Jeol EX 400 instruments operating at 270 and 400 MHz (<sup>1</sup>H), at 68 and 100 MHz (<sup>13</sup>C), and at 109 and 161 MHz (<sup>31</sup>P), respectively. Elemental analyses (C, H, N, Cl) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, with a Heraeus Elementar Vario El instrument. Melting Points were measured in sealed capillaries under argon with a Büchi B540 instrument.

**X-ray Crystal Structure Determination:** Single crystals of **1** and **2**, respectively, were placed on perfluorinated oil. A suitable crystal was selected by means of a polarization microscope and mounted on the tip of a glass fiber. Data collection was performed with an Oxford XCalibur diffractometer using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by Direct Methods (SIR97)<sup>[20]</sup> and refined by full-matrix least-squares calculations on  $F^2$  (SHELXL-97).<sup>[21]</sup> Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details of crystal data, data collection, structure solution, and refinement parameters of **1** and **2** are summarized in Table 2.

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-748585 (1) and CCDC-748586 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk).

Synthesis of [AuCl(Ph<sub>3</sub>PNPPh<sub>2</sub>)] (1) from [AuCl(tht)]: To a slurry of [AuCl(tht)] (321 mg, 1 mmol) in THF (20 mL) the ligand

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Table 2. Details of the X-ray data	ollection and refinement for 1 and 2
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	1	2
Formula	C <sub>30</sub> H <sub>25</sub> AuClNP <sub>2</sub>	C <sub>62</sub> H <sub>54</sub> AuCl <sub>5</sub> N <sub>2</sub> P <sub>4</sub>
M <sub>r</sub>	693.9	1325.2
Temperature /°C	200	200
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_{1}/c$
a /Å	10.3451(2)	18.9172(4)
b /Å	14.6615(3)	13.0705(2)
c /Å	17.7018(4)	24.4936(5)
$\beta$ /deg	97.367(2)	106.822(2)
$V/\text{\AA}^3$	2662.75(10)	5797.1(2)
Ζ	4	4
$D_{\rm calcd}$ /g·cm <sup>-3</sup>	1.731	1.518
$\mu$ (Mo- $K_a$ ) /mm <sup>-1</sup>	5.765	2.920
<i>F</i> (000), e	1352	2656
$\theta$ range for data		
collection /deg	3.69 to 26.00	3.80 to 25.50
hkl range	$-12 \le h \le 12$	$-22 \le h \le 13$
	$-18 \le k \le 11$	$-15 \le k \le 15$
	$-21 \le l \le 16$	$-29 \le l \le 29$
Reflections collected/		
independent	5166/3569	10734/7228
Parameters/restraints	310/0	849/0
$R_1 [I \ge 2\sigma(I)]$	0.0624	0.0858
$wR_2$ (all data)	0.0517	0.1362
Goodness-of-fit on $F^2$	0.887	1.209
Largest diff.		
peak/hole /e·Å <sup>-3</sup>	0.963/-0.946	2.178/-3.072

Ph<sub>3</sub>PNPPh<sub>2</sub> (462 mg, 1 mmol) was added at room temperature. The solution became clear immediately. After stirring for about 2 h, compound 1 precipitated from the solution as colorless powder. The mixture was stirred overnight to complete the reaction. During this time the product precipitated from the solution in nearly quantitative yield. The colorless crystals were filtered off, washed three times with *n*-pentane (10 mL portions) and dried in vacuo. Yield 652 mg (94 %), Mp: 210–215 °C dec. <sup>31</sup>P{<sup>1</sup>H} **NMR** (109 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 47.3 (d, <sup>2</sup>*J*<sub>PP</sub> = 23.3 Hz, *P*Ph<sub>2</sub>), 19.9 (d, <sup>2</sup>*J*<sub>PP</sub> = 23.3 Hz, *P*Ph<sub>3</sub>). <sup>1</sup>H **NMR** (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.78 (m, 4 H, *o*-H, PPh<sub>2</sub>), 7.34 (m, 6 H, *m*-H, *p*-H, PPh<sub>2</sub>), 7.67 (m, 6 H, *o*-H, PPh<sub>3</sub>), 7.47 (m, 6 H, *m*-H, PPh<sub>3</sub>), 7.59 (m, 3 H, *p*-H, PPh<sub>3</sub>). C<sub>30</sub>H<sub>25</sub>AuClNP<sub>2</sub> (693.87): calcd. C 51.93, H 3.63, N 2.02, Cl 5.11 %; found C 52.33, H 3.26, N 2.25, Cl 4.78 %.

Synthesis of [Au(Ph<sub>3</sub>PNPPh<sub>2</sub>)<sub>2</sub>]Cl (2) from [AuHCl<sub>4</sub>]: To a slurry of [AuHCl<sub>4</sub>] (180 mg, 0.5 mmol, monohydrate) in dichloromethane (20 mL), Ph<sub>3</sub>PNPPh<sub>2</sub> (693 mg, 1.5 mmol) was added at room temperature The color of the solution changed immediately from yellow to colorless and the solution became clear immediately. The mixture was stirred at room temperature overnight to complete the reaction. After removal of the solvent to dryness in vacuo, the residue was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-heptane (1:10) as colorless crystals. The compound was filtered off, washed three times with *n*-pentane (10 mL portions) and dried in vacuo. Yield 266 mg (46 %, related to Au), Mp: 255–260 °C dec. <sup>31</sup>P{<sup>1</sup>H} NMR (109 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 67.3 (t, PPh<sub>2</sub>), 19.3 (t, PPh<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.50 (m, 20 H, *o*-H, PPh<sub>2</sub>), 7.30 (m, 30 H, *m*-H and *p*-H, PPh<sub>2</sub> and PPh<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): see Table 1. C<sub>60</sub>H<sub>50</sub>AuClN<sub>2</sub>P<sub>4</sub> (1155.38): calcd. C 62.37, H 4.36, N 2.42, Cl 3.07 %; found C 62.17, H 4.03, N 2.14, Cl 2.87 %.

Synthesis of [Au(Ph<sub>3</sub>PNPPh<sub>2</sub>)<sub>2</sub>]Cl (2) from [AuCl(tht)]: To a solution of [AuCl(tht)] (160 mg, 0.5 mmol) in dichloromethane (30 mL),

Ph<sub>3</sub>PNPPh<sub>2</sub> (462 mg, 1 mmol) was added at room temperature and the mixture was stirred overnight. The resulting colorless solution was evaporated to dryness in vacuo. The remaining residue was crystallized from  $CH_2Cl_2/n$ -heptane (1:10) as colorless crystals. The precipitate was filtered off, washed three times with *n*-pentane (10 mL portions) and dried in vacuo. Yield 428 mg (74 %).

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