Gold(I)-Mediated Rearrangement of **1,2-Diphenylhydrazine to Semidines**

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Summary: Reaction of 1,2-diphenylhydrazine with the gold oxo complex $[(PPh_3Au)_3(\mu-O)]BF_4$ gives a mixture of $[(Ph_3PAu)_3(\mu-N-1,4-C_6H_4-NHPh)]BF_4$ (1; 82%) and $[(Ph_3PAu)_3(\mu - N - 1, 2 - C_6H_4 - NHPh)]BF_4$ (2; 18%) in CH_2 - Cl_2 at ambient temperature. A crossover experiment using a 1:1 mixture of 1,2-diphenylhydrazine and 1,2*diphenylhydrazine-d*₁₀ *indicates that the rearrangement* process is intramolecular.

Introduction

The rearrangement of hydrazo aromatics, collectively called benzidine rearrangement, has been known for over 100 years. Among the most extensively studied is the rearrangement of 1,2-diphenylhydrazine (Figure 1). Acid-catalyzed rearrangement of 1,2-diphenylhydrazine gives about 70% benzidine and 30% diphenyline,^{1,2} while thermal rearrangement at 150 °C gives mainly psemidine and o-semidine.³ The acid-catalyzed rearrangement of 4-substituted hydrazobenzenes also give mainly *p*-semidines and *o*-semidines.⁴ Here we report the facile rearrangement of 1,2-diphenylhydrazine to *p*-semidine and *o*-semidine mediated by Au(I).

Results and Discussion

Reaction of 1.2-diphenylhydrazine with the gold oxo complex $[(Ph_3PAu)_3(\mu-O)]BF_4$ in CH_2Cl_2 gives in 4 h a mixture of the imido complexes [(Ph₃PAu)₃(µ-N-1,4- $C_{6}H_{4}$ -NHPh)]BF₄ (1; 82%) and [(Ph₃PAu)₃(μ -N-1,2-C₆H₄-NHPh)]BF₄ (2; 18%) (eq 1). The ³¹P NMR spec-



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Figure 1. Rearrangement products of 1,2-diphenylhydrazine

Diphenvline

o-Semidine

Table 1. Crystallographic and Data Collection
Parameters for
$[(Ph_3PAu)_3(\mu-N-1,4-C_6H_4-NHPh)]BF_4\cdot1.5CH_2Cl_2$
(1·1.5CH ₂ Cl ₂)

formula	$C_{67.5}H_{58}Au_3BCl_3F_4N_2P_3$
fw	1774.13
space group, Z	P1 (No. 2), 2
Ĵ, ℃	-100
a, Å	12.6815(6)
b, Å	14.5655(7)
<i>c</i> , Å	17.7277(9)
α, deg	98.350(1)
β , deg	104.198(1)
γ , deg	90.932(1)
V, Å ³	3136.3(3)
d_{calcd} , g/cm ³	1.879
λ, Å	0.7093 (Mo)
μ , mm ⁻¹	7.259
no. of data collected	30851
no. of unique data (> $2\sigma(I)$)	13 559 (10 902)
R(int)	0.0365
GOF	0.996
$R1$, ^{<i>a</i>} w $R2^{b}$ (obsd)	0.0328, 0.0671

^a R1 = $(\sum ||F_0| - |F_c|) / \sum |F_0|$. ^b wR2 = $[(\sum w (F_0^2 - F_c^2)^2) / \sum w (F_c^2)^2]^{1/2}$ with weight = $1/[\sigma^2(F_0^2) + (0.0328P)^2 + 0.8021P]; P = (F_0^2 + 2F_c^2)/(0.0328P)^2 + 0.8021P]$

trum of the product mixture consists of two singlets at 28.9 and 28.6 ppm. The ¹H NMR spectrum consists of two singlets at 5.66 and 6.29 ppm for the NH groups, as well as multiplets for the phenyl protons. Pale yellow crystals of 1 are obtained from recrystallization of the mixture from CH₂Cl₂/Et₂O and were subjected to singlecrystal X-ray analysis. Details are given in Tables 1 and 2, in the Experimental Section, and in the Supporting Information. A drawing of the cationic portion of 1 is shown in Figure 2. The average Au-N1 distance is 2.071 Å, comparable to those of similar gold imido complexes.⁵ The average Au-Au distance of 3.079 Å

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Figure 2. ORTEP drawing of the cationic portion of $[(Ph_3-PAu)_3(\mu-N-1,4-C_6H_4-NHPh)]BF_4$ (1). All atoms, except phenyl carbons of the phosphines, are represented by 50% probability thermal ellipsoids.

Table 2. Selected Distances (Å) and Angles (deg) for $[(Ph_3PAu)_3(\mu-N-1,4-C_6H_4-NHPh)]BF_4\cdot1.5CH_2Cl_2$ $(1\cdot1.5CH_2Cl_2)$

Au3-N1	2.071(4)	Au3-P3	2.2521(14)
Au3-Au2	3.1093(3)	Au3-Au1	3.1484(3)
Au2-N1	2.069(4)	Au2–P2	2.2518(13)
Au2-Au1	2.9802(3)	Au1-N1	2.074(4)
Au1-P1	2.2454(14)	N1-C1	1.414(6)
N2-C7	1.411(7)	N2-C4	1.433(6)
C1-C2	1.391(7)	C1-C6	1.407(7)
C2-C3	1.379(7)	C3-C4	1.400(8)
C4-C5	1.385(7)	C5-C6	1.385(7)
C7-C8	1.377(8)	C7-C12	1.399(7)
C8-C9	1.397(9)	C9-C10	1.377(9)
C10-C11	1.375(9)	C11-C12	1.381(8)
N1-Au1-P1	172.83(12)	N1-Au1-Au2	43.93(11)
P1-Au1-Au2	133.47(4)	N1-Au1-Au3	40.53(12)
P1-Au1-Au3	132.93(4)	Au2-Au1-Au3	60.900(7)
N1-Au2-P2	171.24(12)	N1-Au2-Au1	44.06(12)
P2-Au2-Au1	130.57(4)	N1-Au2-Au3	41.33(12)
P2-Au2-Au3	132.01(4)	Au1-Au2-Au3	62.222(7)
N1-Au3-P3	177.00(11)	N1-Au3-Au2	41.29(11)
P3-Au3-Au2	140.60(4)	N1-Au3-Au1	40.60(12)
P3-Au3-Au1	141.52(4)	Au2-Au3-Au1	56.878(7)
C1-N1-Au2	123.2(3)	C1-N1-Au3	120.6(3)
Au2-N1-Au3	97.4(2)	C1-N1-Au1	118.7(3)
Au2-N1-Au1	92.0(2)	Au3-N1-Au1	98.9(2)
C7-N2-C4	123.1(4)	C2-C1-C6	116.2(4)
C2-C1-N1	122.2(5)	C6-C1-N1	121.6(4)
C3-C2-C1	122.9(5)	C2-C3-C4	119.9(5)
C5-C4-C3	118.5(5)	C5-C4-N2	120.1(5)
C3-C4-N2	121.4(5)	C4-C5-C6	120.9(5)
C5-C6-C1	121.5(5)	C8-C7-C12	118.1(5)
C8-C7-N2	123.6(5)	C12-C7-N2	118.2(5)
С7-С8-С9	121.0(6)	C10-C9-C8	120.3(6)
C11-C10-C9	118.9(6)	C10-C11-C12	121.2(6)
C11-C12-C7	120.4(6)	C10-C11-C12	

within the triangular Au cluster is typical for "aurophilic" interactions. 6

Both **1** and **2** can be prepared independently by reaction of the gold oxo complex $[(PPh_3Au)_3(\mu-O)]BF_4$ with *p*-semidine or *o*-semidine, respectively. Reaction of **1** with hydrazine gives the gold dinitrogen complex $[(PPh_3Au)_6(\mu-N_2)](BF_4)_2$, first prepared by this lab recently,⁷ along with *p*-semidine (eq 2). Similarly, reaction

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of **2** and hydrazine gives the same gold dinitrogen complex, along with *o*-semidine.



Extensive studies suggest that the rearrangement of 1,2-diphenylhydrazine is an intramolecular process, as the cleavage into two independent pieces, either radical or cation, has been ruled out by many types of crossover experiments.⁸ Several mechanisms, such as a "polar-transition-state mechanism" and a " π -complex mechanism" have been postulated for the rearrangement.⁹ Recently, Heaton and co-workers reported a Rh-catalyzed rearrangement of 1,2-diphenylhydrazine exclusively to *o*-semidine. The rearrangement was suggested as an intramolecular 1,3-sigmatropic shift after coordination of 1,2-diphenylhydrazine to Rh.¹⁰

A crossover study was carried out to determine the molecularity of the Au(I)-induced rearrangement. The gold oxo complex was treated with a 1:1 mixture of 1,2-diphenylhydrazine and 1,2-diphenylhydrazine- d_{10} . The reaction products were then treated with hydrazine to release semidines. GC-MS analysis of the semidines found only semidines with deuterated or nondeuterated phenyl groups, neither semidine- d_4 nor semidine- d_5 , containing both deuterated and nondeuterated phenyl groups, was found. This indicates an intramolecular process, consistent with the rearrangement of 1,2-diphenylhydrazine under acidic or thermal conditions.

In conclusion, we report the facile rearrangement of 1,2-diphenylhydrazine induced by reaction with the gold oxo complex $[(Ph_3PAu)_3(\mu-O)]BF_4$. $[Ph_3PAu]^+$ has been classified as isolobal with H⁺.¹¹ The reaction of the gold oxo complex $[(Ph_3PAu)_3(\mu-O)]BF_4$ facilitates the cleavage of the N–N bond of 1,2-diphenylhydrazine in a role

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apparently similar to that of H⁺. However, for reasons that are not understood at this time, the formation of benzidine, the favored product with H⁺, is not observed with [Ph₃PAu]⁺. Additionally, the gold semidine products are both rather stable (no change in THF at 70 °C over 24 h) and do not react further with 1,2-diphenyl-hydrazine; therefore, the [Ph₃PAu]⁺- induced rearrangement is stoichiometric rather than catalytic. Our work on elucidating the details of [LAu]⁺- induced rearrangements of hydrazines will be published in a future paper.

Experimental Section

General Procedures. Experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres Corp. drybox. Solvents were dried by standard techniques and stored under nitrogen over 4 Å molecular sieves. NMR spectra were recorded on a Bruker AMX-250 spectrometer. The semidines and 1,2-diphenylhydrazine were used as received (Aldrich). [(Ph₃PAu)₃(μ -O)]BF₄ and 1,2-diphenylhydrazine- d_{10} were prepared by literature procedures.^{12,13}

Reaction of 1,2-diphenylhydrazine with [(Ph₃PAu)₃-(μ -**O)]BF**₄. 1,2-Diphenylhydrazine (0.009 g, 0.05 mmol) was dissolved in CH₂Cl₂ (2 mL), followed by addition of a solution of [(PPh₃Au)₃(μ -O)]BF₄ (0.030 g, 0.020 mmol) in CH₂Cl₂ (2 mL). After the solution was stirred at ambient temperature for 4 h, Et₂O (20 mL) was added. The precipitate was collected through filtration and washed twice with Et₂O (3 mL) to obtain a light yellow solid (0.030 g, 91.0%). The ³¹P NMR spectrum of the product mixture consists of two singlets at 28.9 and 28.6 ppm at a ratio of 82:18.

Preparation of [(Ph₃PAu)₃(\mu-N-1,4-C₆H₄-NHPh)]BF₄ (1). *p***-Semidine (0.009 g, 0.050 mmol) was dissolved in CH₂-Cl₂ (2 mL), followed by addition of a solution of [(Ph₃PAu)₃(\mu-O)]BF₄ (0.030 g, 0.020 mmol) in CH₂Cl₂ (2 mL). After the solution was stirred at ambient temperature for 4 h, Et₂O (20 mL) was added. The precipitate was collected through filtration and washed twice with Et₂O (3 mL) to obtain a light yellow solid (0.030 g, 91.0%). Anal. Calcd (found): C, 48.09 (48.09); H, 3.34 (2.94); N, 1.70 (1.94). Mp: 170–172 °C. ¹H NMR (CD₂-Cl₂, 250 MHz, 25 °C, ppm): 5.66 (NH). ¹³C{¹H} NMR (CD₂-Cl₂, 63 MHz, 25 °C, ppm): 153.7 (C_{ipso} of C₆H₄), 145.3 (C_{ipso} of**

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Ph), 137.2 (C_{para} of C_6H_4), 134.2 (d, ${}^2J_{CP} = 13.5$ Hz, C_{ortho} of PPh₃), 132.3 (br s, C_{para} of PPh₃), 129.6 (d, ${}^3J_{CP} = 11.7$ Hz, C_{meta} of PPh₃), 129.5 (d, ${}^1J_{CP} = 60.0$ Hz, C_{ipso} of PPh₃), 125.7 (C_{ortho} of C_6H_4), 120.3 (C_{meta} of Ph), 119.8 (C_{para} of Ph), 116.0 (C_{ortho} of Ph). Assignments are tentative. ${}^{31}P{}^{1}H{}$ NMR (CH₂Cl₂, 101 MHz, 25 °C, ppm): 28.9. UV-vis (CH₂Cl₂, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 300 (16 574). IR (KBr, cm⁻¹): 3370 (s, NH).

Preparation of [(Ph₃PAu)₃(µ-N-1,2-C₆H₄-NHPh)]BF₄ (2). o-Semidine (0.009 g, 0.050 mmol) was dissolved in CH₂-Cl₂ (2 mL), followed by addition of a solution of [(Ph₃PAu)₃(µ-O)]BF4 (0.030 g, 0.020 mmol) in CH2Cl2 (2 mL). After the solution was stirred at ambient temperature for 4 h, Et₂O (20 mL) was added. The precipitate was collected through filtration and washed twice with Et₂O (3 mL) to obtain a light yellow solid (0.030 g, 91.0%). Mp: 153-156 °C. ¹H NMR (CD₂Cl₂, 250 MHz, 25 °C, ppm): 6.29 (NH). ¹³C{¹H} NMR (CD₂Cl₂, 63 MHz, 25 °C, ppm): 151.7 (C1 of C₆H₄), 144.6 (C_{ipso} of Ph), 136.0 (C2 of C₆H₄), 134.2 (d, ${}^{2}J_{CP} = 13.4$ Hz, C_{ortho} of PPh₃), 132.3 (br s, C_{para} of PPh₃), 129.9 (C6 of C₆H₄), 129.6 (d, ${}^{3}J_{CP} = 11.7$ Hz, C_{meta} of PPh₃), 129.2 (d, ${}^{1}J_{CP} = 60.4$ Hz, C_{ipso} of PPh₃), 127.9 (C3 of C₆H₄), 122.6, 122.5 (C4/C5 of C₆H₄), 121.4 (C_{para} of Ph), 120.7 (Cortho of Ph), 117.6 (Cmeta of Ph). Assignments are tentative. ³¹P{¹H} NMR (CH₂Cl₂, 101 MHz, 25 °C, ppm): 28.6. UV-vis (CH₂Cl₂, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 300 (14 745). IR (KBr, cm⁻¹): 3327 (s, NH).

X-ray Crystallography. Yellow prismatic crystals of 1 were grown from CH₂Cl₂/Et₂O at −30 °C. A crystal of dimensions 0.5 \times 0.2 \times 0.1 mm was selected and mounted with grease on the end of a glass fiber. The crystal was placed in the cold nitrogen stream of the diffractometer for data collection. This followed routine procedures with a Siemens SMART CCD system as outlined in Table 1. Data were corrected for absorption with the SADABS program. The structure was solved using direct methods, completed by subsequent Fourier difference syntheses, and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized "riding" positions. Software for data collection and processing were contained in the Siemens SMART software package. SHELXTL version 5 (Sheldrick, 1994), RES2INS (Len Barbour, 1996), and ORTEP III were used for solution, refinement, and structure drawing.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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