

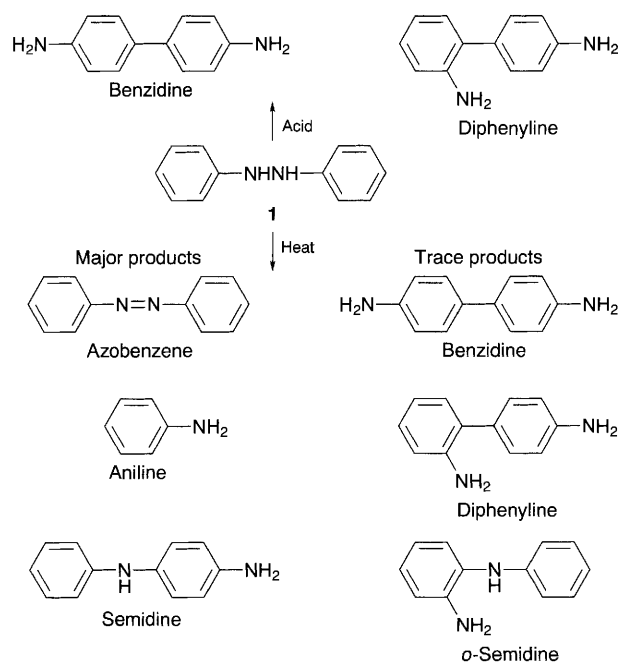
Rhodium Catalysed Rearrangement of 1,2-Diphenylhydrazine to *o*-Semidine

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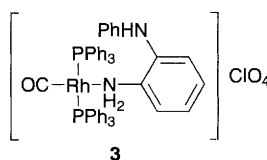
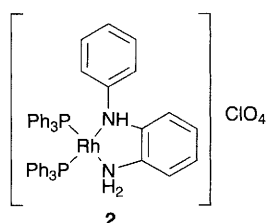
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Rearrangement of 1,2-diphenylhydrazine occurs exclusively to *o*-semidine in the presence of a rhodium catalyst with *o*-semidine bonding to rhodium(II) as a bidentate ligand.

1,2-Diphenylhydrazine **1** is a versatile reagent. It undergoes a variety of rearrangements, which have been extensively studied:¹ acid catalysis gives benzidine and diphenylene (in the approximate ratio 3:1) and thermal rearrangement gives a mixture of products² (see Scheme 1). Compound **1** can also behave as a reducing agent as exemplified by the recent conversion of $[V_4O_6F(PhPO_3)_4]^-$ to $[V_4O_6F(PhPO_3)_4]^{2-}$, although the fate of **1** in this and related reactions has generally not been further investigated.³ The complexation behaviour of **1** to metals has not been widely studied⁴ although reactions of **1** with Sm or W complexes have resulted in either the formation



Scheme 1 Rearrangement products of 1,2-diphenylhydrazine



of η^2 -hydrazido complexes or cleavage of the N–N bond;^{5–7} in these studies, no other rearrangement of **1** was observed.

We now report that **1** rearranges exclusively to *o*-semidine in the presence of square planar rhodium(II) complexes and this reaction is catalytic when there are two *cis*-sites in the square plane which are occupied by labile ligands.

Previous work has shown that displacement of norbornadiene from $[Rh(PPh_3)_2(nbd)]ClO_4$ (*nbd* = norbornadiene = bicyclo[2.2.1]hepta-2,5-diene) occurs on reaction with H_2 in coordinating solvents, *S*, to give $[RhH_2(PPh_3)_2S_2]ClO_4$.⁸ We now find that treatment of a dichloromethane solution of $[Rh(PPh_3)_2(nbd)]ClO_4$ containing an equimolar amount of **1** with H_2 gas gives a deep-red solution of **2** which contains a bidentate *o*-semidine ligand bonded to rhodium(II).

Although it has not been possible to obtain crystals of **2** which are suitable for X-ray structural determination, the spectroscopic data of **2** are in complete accord with this formulation and **2** was also obtained on carrying out the reaction of $[Rh(PPh_3)_2(nbd)]ClO_4$ with H_2 in the presence of *o*-semidine instead of **1**. The proton-decoupled ^{31}P NMR spectrum of **2** consists of two doublets of doublets due to two nonequivalent PPh_3 groups; $\delta_P(CH_2Cl_2-CD_2Cl_2)$ 50.6 and 47.7; $^1J(RhP)$ 183.2 and 181.9 Hz, respectively; $^2J(PP)$ 53.1 Hz; the $^{15}N\{^1H\}$ spectrum, obtained at natural abundance using the INEPTD pulse sequence⁹ as described earlier,¹⁰ shows two equally intense doublets of doublets, as $^2J(P_{cis}-N)$ is too small to be observed;¹¹ $\delta_N(CD_2Cl_2)$ -318.8 and -353.6 , $^1J(RhN)$ 10.0 and 10.4 Hz, respectively; $^2J(P_{trans}-N)$ 25.9 and 28.3 Hz, respectively; and the proton-coupled spectrum is entirely consistent with the resonance at $\delta -318.8$ being due to the NH group and that at $\delta -353.6$ being due to the NH_2 group. Furthermore, a solution of **2** under an atmosphere of either N_2 or H_2 produced identical NMR spectra with no evidence for high-field resonances in the 1H NMR spectra. The above rearrangement is shown to be catalytic since complete conversion of **1** to *o*-semidine occurs on stirring a CH_2Cl_2 solution of $[Rh(PPh_3)_2(nbd)]ClO_4$ and **1** (ratio 1 : 1000) under H_2 for 5 min. This rapid rearrangement should be contrasted with the more sluggish[‡] but analogous rearrangement of **1** which occurs on reaction of *trans*- $[Rh(PPh_3)_2(CO)(OCIO_3)]$ to give **3**.

We have previously shown that 1-substituted and 1,1-disubstituted hydrazines readily displace the perchlorato group in *trans*- $[Rh(PPh_3)_2(CO)(OCIO_3)]$ and coordination of NH_2NR_2 ($R = Me$ or Ph) occurs without any rearrangement,¹² but the spectroscopic data on **3** are entirely in accord with the above formulation. Thus, the ^{31}P NMR spectrum consists of one doublet [$\delta_P(CH_2Cl_2-CD_2Cl_2)$ 32.2; $^1J(RhP)$ 133.5 Hz] and the $^{15}N\{^1H\}$ INEPTD spectrum consists of a singlet and a doublet [$\delta_N -299.5$ and -355.8 , respectively; $^1J(RhN) = 12.1$ Hz] and the ^{15}N proton-coupled spectrum is entirely consistent with the resonance at $\delta -299.5$ being due to the NH group and the resonance at $\delta -355.8$ being due to the NH_2 group.

We propose that the rearrangement involves the initial coordination of **1** as a bidentate ligand to rhodium(II) and then steric constraints place the phenyl rings of coordinated **1** into the perfect position to allow the exclusive formation of *o*-semidine via a similar mechanism to the acid-catalysed benzidine rearrangement.¹³

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Footnotes

† The perchlorate salts have always been used in solution. We have no evidence about their explosive hazards as a solid but advise caution.

‡ After two days at 25 °C, the reaction of equimolar amounts of *trans*-[Rh(PPh₃)₂(CO)(OCIO₃)] and **1** shows that only approximately 15% of **1** has rearranged to *o*-semidine.

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