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Homogeneous Hydrogenations of Nitriles Catalyzed by Rhenium Complexes

Kunjanpillai Rajesh,[a] Balz Dudle,[a] Olivier Blacque,[a] and Heinz Berke[a,*]

[a] Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
Fax: (+41)-1-635-6802; e-mail: hberke@aci.uzh.ch

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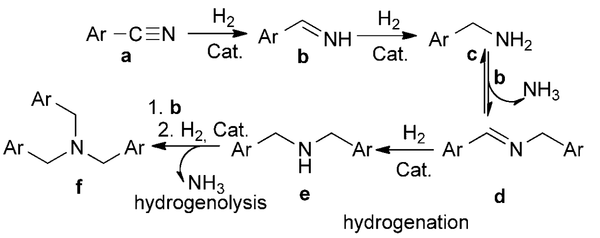
Abstract: Rhenium(I) nitrosyl complexes bearing large bite angle diphosphines efficiently catalyze the hydrogenation of nitriles to the corresponding symmetrical secondary amines.

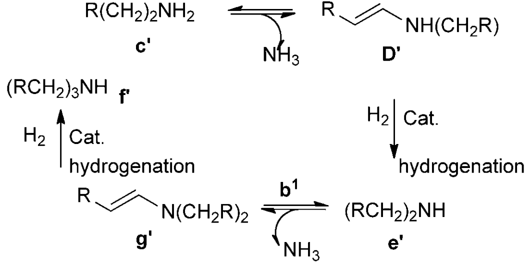
Keywords: homogeneous hydrogenation; nitrile reduction; rhenium catalysts; secondary amines; triethylsilane

Nitriles are difficult to hydrogenate[1] and if they can be hydrogenated, a crucial selectivity problem arises concomitant with the reduction processes: the formation of mixtures of primary, secondary and tertiary amine, as well as intermediate imines.[2] Although many proposals on the mechanism of the formation of secondary amines and tertiary amines have been put forward (Scheme 1, Scheme 2), it is still unclear whether the reductions to amines occur through the hydrogenation of imines, enamines or the hydrogenolysis of *gem*-diamines.[2a] But what is mechanistically well established, is the reaction between the formed primary amine and the intermediate imine accompanied by the expulsion of ammonia, which can give rise to a symmetrical secondary amine and repetition of this type of reaction sequence with the formed secondary amine. This can lead to a symmetrical tertiary amine.[2] The composition of the reduction products depends mainly on the nature of the reducing agent, catalyst, reaction temperature and hydrogen pressure, and on the structure of the nitrile.[3] Due to a facile access to nitriles and their frequent avalability as commodity chemicals, the reaction has great potential in synthetic organic chemistry and in the production of pharmaceuticals, agrochemicals, textile and rubber chemicals.[2a,b] Apart from this aspect, syntheses of secondary amines are particularly significant in view of their role as biologically active molecules[3,4] and versatile ligands.[3,5]

Catalytic reduction of nitriles using molecular hydrogen is of great interest as it is more efficient, economic and environmental friendly in processes as they have been applied in both academia and industry.[2b,6] The formation of amines is often achieved by heterogeneously[7] or homogeneously catalyzed processes that involve the hydrogenation of nitriles, in which the latter is accomplished using Ni,[8] Ru,[2c,9] Rh,[1b] Pd,[10] Ir[11] and Pt[12] complexes. Alkylamines can also be produced by amination of alcohols over acidic catalysts, however this tends to form also undesired alkenes.[13] Hydroaminomethylation of al-



Scheme 1. Formation of different types of imines/amines in the hydrogenation of aromatic nitriles.

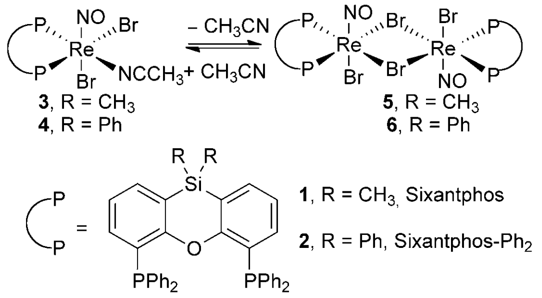


Scheme 2. Formation of different types of imines/amines/enamines in the hydrogenation of aliphatic nitriles

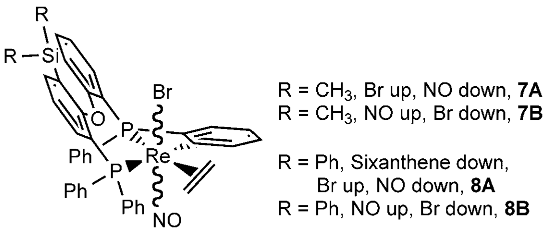
kenes,[14] reductive amination of carbonyl compounds, treatment of primary amines with alkyl halides or dialkyl sulfates or sulfonates, addition of nucleophiles or radicals to *N*-substituted imines etc., have been widely reported for the synthesis of secondary amines.[4] However, the traditional methods for secondary amine formation are often problematic, because of harsh reaction conditions, generally poor yields and/or low chemoselectivities.[4]

Herein we communicate the first example of the homogeneous reduction of nitriles to amines using rhenium catalysts bearing large bite angle bisphosphines. Bite angles were shown to be crucial ligand parameters and their tuning allowed us to boost the performance of catalysts.[15] A large bite angle of the ligands induces distortion from octahedral geometry that can lead to activation of the metal center and the bound atoms involved in the catalyses.[15] A series of novel rhenium(I) catalysts was prepared with the large bite angle sixantphos (**1**)[16] and the related, but previously unknown sixantphos-Ph$_2$ (**2**) ligands of the xanthphos family. Sixantphos-Ph$_2$ (**2**) was prepared by an analogous procedure adopted for the synthesis of sixantphos (**1**).[17] The complexes $[Re(\mathbf{1})(CH_3CN)Br_2(NO)]$ (**3**) and $[Re(\mathbf{2})(CH_3CN)Br_2(NO)]$ (**4**) were prepared by reacting $[ReBr_5(NO)]\,[NEt_4]_2$[18] with **1** and **2** in acetonitrile in 56% and 52% yields, respectively. Complex **3** was found to be in equilibrium with its bromo-bridged dimer $[Re(\mathbf{1})Br_2(NO)]_2$ (**5**) expelling acetonitrile, a process which was much less prominent for **4** to give $[Re(\mathbf{2})Br_2(NO)]_2$ (**6**) (Scheme 3).

Complexes **3** and **4** were treated with excess of triethylsilane and ethylene in dichloromethane to produce the *ortho* metallated complexes $[Re(oC_{PPh}\text{-}\mathbf{1})(\eta^2\text{-ethylene})Br(NO)]$ (**7**) and $[Re(oC_{PPh}\text{-}\mathbf{2})(\eta^2\text{-ethylene})Br(NO)]$ (**8**) in 70% and 74% yield, respectively. Both these products **7** and **8** were obtained as a mixture of diastereomers **A** and **B** in a ratio of 1:0.4 and 1:0.3, respectively, which could be separated by column chromatography. Although *ortho* metallations of aromatic compounds are common with transition metals and sufficient reports on rhenium-catalyzed reactions on these lines are available,[19] much more interesting seemed the fact of the activation of the C–H bond *ortho* to the phosphorus substituent giving rise to the unusually stable four-membered rhenacycles (Scheme 4). From X-ray diffraction studies (Figure 1) it was derived that both **7A** and **7B** differ by the axial arrangement of Br and NO, as a consequence by which in **7A** the sixanthene moiety gets close to Br, whereas in **7B**, it is close to NO. Although **8B** is analogous to **7B**, surprisingly, **8A** and **7A** differ by the spatial arrangenent of the sixanthene moiety.[16]



Scheme 3. Complexes **3** and **4** and their splitting equlibria with **5** and **6** respectively, in acetonitrile.



Scheme 4. Structure of the diastereomers **A** and **B** of **7** and **8**.

All the four complexes **3**, **4**, **7** and **8** turned out to be catalysts and could hydrogenate nitriles to the corresponding symmetrical secondary amines. Although the formation of dibenzylimine **d** was observed in the hydrogenation of benzonitrile, no benzylimine **b** or benzylamine **c** was detected during the course of the reaction. However, tribenzylamine **f** was observed as a side product. The formation of a considerable amount of dibenzylimine during the course of the reaction and its decrease at the end of the reaction indicated that dibenzylamine was formed by the hydrogenation of dibenzylimine rather than by hydrogenolysis of the *gem*-diamine; whereas the formation of additional tribenzylamine is attributed as a consequence of the hydrogenolysis of the *gem*-diamine. But when the aliphatic nitrile, phenylacetonitrile was subjected to hydrogenation, diphenethyl-2-phenylethenamine **g′** was detected which revealed that the tertiary amine **f′** was formed by hydrogenation of the enamine **g′** rather than the hydrogenolysis of *gem*-diamine. Hydrogenation of benzonitrile using 0.1 mol% of **7** was carried out under different conditions (Table 1). An initial TOF of 90 h^{-1} was observed at 50 bar of hydrogen pressure and 140 °C in THF as solvent (Table 1, entry 1). When 25 equivalents of triethylsilane with respect to the amount of the catalyst were added, the TOF was raised to 205 h^{-1} (Table 1, entry 3) however, addition of 5 equivalents of triethylsilane was found to be inferior (Table 1, entry 5) and addition of 50 equivalents was found to have an effect comparable to the reaction with 25 equivalents of triethylsilane (Table 1, entry 6). A TOF of 156 h^{-1} was obtained, when dichloromethane was used as the solvent, but gave 31% of tribenzylamine (Table 1,

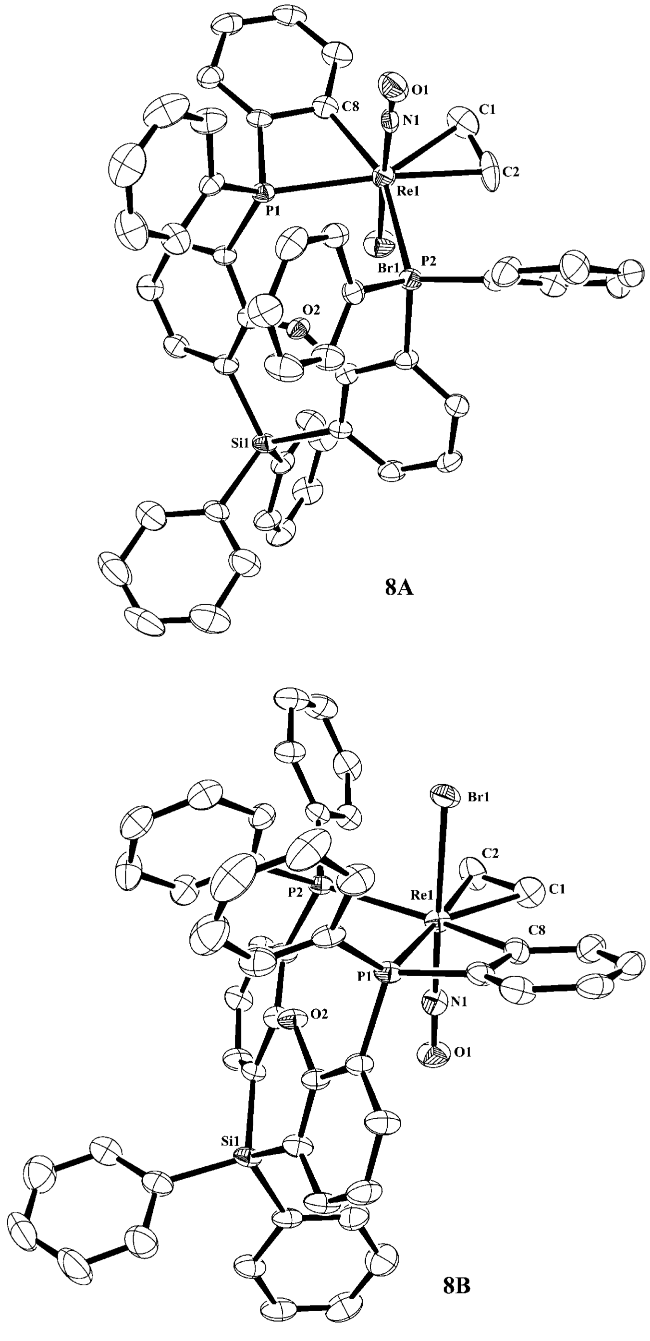


Figure 1. Molecular structure of **8A** and **8B**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

entry 9). When the reaction was carried out at a pressure of 30 bar hydrogen and a temperature of 140 °C, a TOF of 135 h^{-1} was accomplished with the formation of 11% of tribenzylamine (Table 1, entry 7), whereas the reaction at 50 bar hydrogen and 120 °C gave a TOF of 79 h^{-1} with the formation of 5% of tribenzylamine (Table 1, entry 8). However, still longer reaction times using catalyst **7** with 50 bar of hydrogen pressure at 140 °C and the addition of 25 equivalents of triethylsilane in THF gave 30% of tribenzylamine and 4% of dibenzylimine in 18 h (Table 1, entry 4), whereas without the addition of silane 13% of tribenzylamine and 7% of dibenzylimine were obtained within 16 h (Table 1, entry 2) with 90% conversions in both the cases. Although the initial TOF was comparatively higher, the longer reaction time would be accompanied by the formation of higher amounts of tertiary amine with much prominence in the former case. Under the former conditions, reaction with catalysts **3**, **4** and **8** gave initial TOFs of 250 h^{-1}, 229 h^{-1} and 161 h^{-1}, respectively (Table 1, entries 10, 12 and 13).

The hydrogenation of the aliphatic phenylacetonitrile using catalyst **7** under these conditions gave a TOF of 248 h^{-1}, with a conversion of 50%, but showed selectivity towards triphenethylamine **f′** (Table 2, entry 1) and continuing this reaction gave a conversion of 97% with 53% of triphenethylamine **f′**, 38% of diphenethylamine **e′** and 9% of diphenethyl-2-phenylethenamine **g′** in 18 h (Table 2, entry 2). The selectivity toward the tertiary amine in this case can be due to higher reactivity towards nucleophilic attack on the non-conjugated aliphatic imine functionality. Hydrogenation of the aliphatic cyclohexanecarbonitrile gave a TOF of 150 h^{-1} with a conversion of 30%, but interestingly it showed selectivity towards the secondary amine rather than the tertiary amine (Table 2, entry 3), which can be attributed as a consequence of the bulkiness, as well as electron richness, which is expected to retard the nucleophilic attack on this system. Further runs of this reaction gave a conversion of 99% in 18 h with 94% of bis(cyclohexylmethyl)amine **e′** along with 5% of tris(cyclohexylmethyl)amine **f′** and 1% of cyclohexylidene(cyclohexylmethyl)methanamine **D′** (Table 2, entry 4).

Keeping the other parameters unchanged, the selectivity of the hydrogenation of benzonitrile was reversed (in comparision to Table 3, entry 2 and 4) with respect to silane with a catalyst loading of 0.5 mol% at a pressure of 75 bar (optimized conditions) gave a TOF of 396 h^{-1} with a conversion of 99% forming 90% of dibenzylamine, 4% of tribenzylamine and 6% of the dibenzylimine (Table 3, entry 2) in 0.5 h. However, only very little improvement of the conversion was observed even after 3 h, but an increased portion of tertiary amine (6%) and a reduced amount of dibenzylimine (4%) was noticed.

Under these conditions, reaction in the absence of silane gave a TOF of 180 h^{-1} with 90% conversion forming 66% of dibenzylamine, 24% of tribenzylamine and 10% of dibenzylimine in the first 1 h (Table 2, entry 1). The generality of the reaction was tested by applying all the other catalysts in the benzonitrile reduction and reductions of a few other nitriles under the given optimized condition (Table 3).

Table 1. Optimization table for the hydrogenation of benzonitrile.[a]

Entry	Et_3SiH[b] [equiv]	Pressure [bar]/Catalyst	Yield [%][c] after 2 h **d**	 **e**	 **f**	Initial TOF [h^{-1}]	Initial Conv.[c] [%/2 h]
1	–	50/**7**	28	72	–	90	18
2	–	50/**7**	7	80	13	–	90/16 h
3	25	50/**7**	17	79	4	205	41
4	25	50/7	8	86	6	–	90/18 h
5	5	50/**7**	8	86	6	161	32
6	50	50/**7**	11	85	4	208	42
7	25	30/**7**	7	82	11	135	27
8	25	50/**7**	33	62	5	79	16[d]
9	25	50/**7**	7	62	31	156	31[e]
10	25	50/**3**	16	81	3	250	50
11	25	50/**3**	8	73	19	–	91/18 h
12	25	50/**8**	17	81	2	229	46
13	25	50/**8**	19	76	5	161	32

[a] 0.1 mol% of catalyst was used, reaction at 140 °C in THF, TOFs were calculated as an average of the first 2 h.
[b] With respect to catalyst.
[c] By GC/MS.
[d] Reaction at 120 °C.
[e] Solvent: dichloromethane.

Table 2. Hydrogenation of phenylacetonitrile and cyclohexanecarbonitrile[a]

Entry	Et_3SiH[b] [equiv.]	Pressure [bar]/Catalyst	Yield [%][c] after 2 h **D′**	 **e′**	 **f′**	Initial TOF [h^{-1}]	Initial Conv.[c] [%/2 h]
1	25	50/**7**	–	31	37	248	50[d]
2	25	50/**7**	–	38	53	–	97[e,f]
3	25	50/**7**	17	83	–	150	30
4	25	50/**7**	1	94	5	–	99[e]

[a] 0.1 mol% of catalyst was used, reaction at 140 °C in THF, TOFs were calculated as an average of the first 2 h.
[b] With respect to catalyst.
[c] By GC/MS.
[d] 32% of **g**' was formed.
[e] Conversion in 18 h.
[f] 9% of **g**′ was formed.

To exclude any heterogeneous reaction course in the hydrogenation catalyses, filtration and mercury poisoning experiments were carried out.[20] The hydrogenation of benzonitrile was carried out using catalyst **7** under the conditions of Table 3. The reaction was stopped at 20 min and the obtained clear pale yellow solution, which showed a conversion of 71%, was filtered through a plug of celite into a new vessel with a new stirring bar, and the reaction was continued for another 40 min under the same conditions showed identical results to Table 3, entry 2. A mercury poisoning experiment was carried out on the hydrogenation of benzonitrile using catalyst **7** under the conditions of Table 3. In the presence of 60 equivalents of Hg (per Re atom) the reaction again showed identical results to Table 3, entry 2. The filtration and mercury poisoning tests were thus all negative which rules out any colloid or amalgam formation. This is consistent with the fact that rhenium metal has a very high atom binding energy (second largest in the periodic table of elements) with low propensity for colloid or amalgam formation.[20c]

In summary, we have developed an efficient, air-stable, homogeneous rhenium-catalyzed hydrogenation of nitriles with good selectivities for symmetrical secondary amines or tertiary amines. Addition of triethylsilane could increase the TOFs and suppress over-alkylation of the amines at higher pressures with a relatively high loading of the catalyst. Secondary amines are anticipated to be formed by the hydrogenation of the imine (for aryl nitriles) or enamine (for alkyl nitriles) intermediates generated by the elimination of ammonia from the *gem*-diamine species whereas the tertiary amines were formed by the hydrogenolysis of the *gem*-diamines (for aryl nitriles) or hydrogenation of the enamines (for alkyl nitriles).

Table 3. Hydrogenation of nitriles under optimized conditions.[a]

Entry	Nitrile	Cat.	Yield [%]			TOF [h^{-1}]	Conv.[c]
			d	**e**	**f**		
1	Ph	**7**[d]	10	66	24	180	90
2	Ph	**7**	6	90	4	198	99
3	Ph	**3**	5	85	10	198	99
4	Ph	**4**	8	86	6	198	99
5	Ph	**8**	7	82	11	196	99
6	3-tolyl	**3**	2	89	9	198	99
7	3-tolyl	**4**	4	87	9	198	99
8	2-thienyl	**7**	5	83	12	162	99
9	2-thienyl	**8**	5	85	10	160	99
10	3-tolyl	**7**	2	81	17	170	99
11	3-tolyl	**8**	21	80	18	169	99
12	PhCH$_2$	**3**	–	10	85	176	99[e]
13	*cyclo*-hexyl	**3**	2	95	3	198	99

[a] 0.5 mol% of catalyst with 25 equiv. of triethylsilane with respect to catalyst at 75 bar H$_2$, 140 °C in THF, run for 1 h except for entries 1 and 8–12 for which reaction was run for 1 h and 4 h respectively.

[b] Ar = R for entries 12 and 13 which corresponds to Scheme 2, wherein **d** = **D′**, **e** = **e′**, **f** = **f’** and for entry 13, RCH$_2$ = cyclohexyl.

[c] By GC/MS.

[d] No silane was added.

[e] 5% of **g′** was formed.

Rhenium as a neighbouring element to precious metals can represent a ligand sphere tuned to adopt similar catalytic properties providing an appropriate alternative to precious metal catalyses.

Experimental Section[22]

Crystallographic Details for 8A and 8B

Intensity data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, ruby CCD detector, and a single wavelength enhance X-ray source with MoKα radiation, $\lambda = 0.71073$ Å).[21a] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption corrections[21b] were performed with the Oxford program suite *CrysAlisPro*.[21c] The crystal structures were solved with SHELXS-97[21d] using direct methods. The structure refinements were performed by full-matrix least-squares on F^2 with SHELXL-97.[21d] All programs used during the crystal structure determination process are included in the WINGX software.[21e] The program PLATON[21f] was used to check the result of the X-ray analyses.

Crystal data for 8A: $C_{50}H_{39}BrNO_2P_2ReSi\cdot CHCl_3$, $M_r = 1161.33$, triclinic space group P-1, $a = 11.478(2)$, $b = 14.542(3)$, $c = 16.4780(14)$ Å, $\alpha = 67.281(15)$, $\beta = 78.654(11)$, $\gamma = 66.87(3)°$, $V = 2329.8(9)$ Å^3, $T = 183(2)$ K, $Z = 2$, 37199 reflections measured ($R_{int} = 0.061$), $\rho = 1.655$ Mg m^{-3}, $\mu = 3.774$ mm^{-1}, R_1 [I > 2σ(I)] = 0.048, wR2 (all data) = 0.135 for 568 refined parameters, 11556 independent reflections ($\theta_{max} = 28.28$), GOF = 1.080, maximum and minimum residual electron density 2.760 and −1.526 e Å^{-3}.

Crystal data for 8B: $C_{50}H_{39}BrNO_2P_2ReSi\cdot CHCl_3$, $M_r = 1161.33$, triclinic space group P-1, $a = 11.2646(5)$, $b = 14.3396(7)$, $c = 16.6916(6)$ Å, $\alpha = 67.050(4)$, $\beta = 79.232(4)$, $\gamma = 68.365(4)°$, $V = 2304.95(19)$ Å^3, $T = 183(2)$ K, $Z = 2$, 25807 reflections measured ($R_{int} = 0.036$), $\rho = 1.673$ Mg m^{-3}, $\mu = 3.814$ mm^{-1}, R_1 [I > 2σ(I)] = 0.047, wR2 (all data) = 0.114 for 563 refined parameters, 11394 independent reflections ($\theta_{max} = 28.28$), GOF = 0.984, maximum and minimum residual electron density 3.811 and −2.107 e Å^{-3}.

CCDC 787796 and 787797 contain the supplementary crystallographic data for compounds **8A** and **8B**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif and are contained in the Supporting Information.

General Procedure for the Catalytic Hydrogenation of Benzonitrile

Catalyst **7** (0.002 g, 2.18×10^{-3} mmol) was taken in a stainless steel autoclave and benzonitrile (0.045 g, 0.44 mmol) was added followed by THF (0.2 mL) and triethylsilane (9 μL, 5.63×10^{-2}). Naphthalene (0.028 g, 0.22 mmol) was added as internal standard. It was pressurized with 75 bar of hydrogen and kept in an oil bath maintained at 140 °C. After an appropriate reaction time, the vessel was immediately cooled to room temperature and the hydrogen was released slowly in a fume hood. The reaction mixture was filtered through a short plug of silica gel and the yield was measured by GC/MS (CP-3800 Saturn 2000MS/MS spectrometer, benzonitrile: 2.90 min ($m/z = 103.1$), dibenzylamine: 7.87 min ($m/z = 197.1$), dibenzylimine: 8.15 min ($m/z = 195.0$), tribenzylamine: 10.65 min ($m/z = 287.1$). For the GC/MS data of other compounds, see Supporting Information.

Acknowledgements

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[22] For syntheses and characterization of all the rhenium nitrosyl diphosphine complexes, see Supporting Information.