Supplementary Material (ESI) for Catalysis Science & Technology

Supporting information for:

On the rate-determining step and the ligand electronic effects in rhodium catalysed hydrogenation of enamines and the hydroaminomethylation of alkenes.

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Supporting information:

Computational Details

Geometries were fully optimized at the RI-BP86/ECP0 level, i.e. employing the exchange and correlation functionals of Becke[1] and Perdew,[2] respectively, in conjunction with the small-core Stuttgart–Dresden (SDD) relativistic effective core potential (ECP) and its valence basis set on Rh,[3] 6-31G(d,p) basis for the two H atoms being transferred, 3-21G basis on the Ph groups and 6-31G(d) elsewhere, together with suitable auxiliary basis sets for the fitting of the Coulomb potential[4] and a fine integration grid (75 radial shells with 302 angular points per shell). Stationary points were characterised through harmonic vibrational frequencies at that level, and the nature of transition states was checked by visual inspection of the single imaginary mode. Structures were then reoptimised at RI-BP86/ECP1, i.e. with SDD on Rh, 6-31G(d,p) on the two H atoms being transferred, and 6-31G(d) elsewhere. These calculations were performed with the Gaussian03 program.[5a] No extensive conformational searches were performed. For the reactant olefin complexes **1a** and **2a**, a *trans* orientation of the two PPh_3 moieties in propeller conformations was adopted, similar to the $Rh(PPh_3)_2I(H)$ fragment in an alkyl complex,[6] and the same relative conformation of the PPh_3 moieties was maintained throughout.

Refined energies were obtained from single points calculations on the RI-BP86/ECP1 geometries at the RI-B97-D level[7,8] with a larger basis set (denoted ECP2), consisting of the same SDD ECP and valence basis on Rh,[3] and 6-311+G(d,p) basis elsewhere. The B97-D functional is based on the re-parameterization of Becke's ansatz from 1997,[7] in which Grimme's empirical dispersion term[8] was taken in account during the parameterization of the functional, and has been shown to perform well for binding energies of bulky phosphines[9] and the description of complex catalytic cycles.[10] Selected test calculations for basis set superposition error (BSSE) between the Rh complex fragment and the organic ligand using the counterpoise method[11] afforded BSSE corrections between 14 kJ/mol and 19 kJ/mol, i.e. rather small and systematic, so that the overall qualitative conclusions would not be affected by such corrections. The same is true for thermodynamic corrections evaluated from the RI-BP86/ECP0 harmonic frequencies (see Table S1). These computations were performed using the Gaussian 09 program.[5b]

Table S1: Thermodynamic corrections to the B97-D/ECP2 energies from BP86/ECP0 harmonic frequencies (relative to **1a** or **2a**, at 298 K and 1 atm).

Level	E_{rel} [kJ/mol] (rel. to **1b**)			E_{rel} [kJ/mol] (rel. to **2b**)		
	1a	**TS1a**	**TS1b**	**2a**	**TS2a**	**TS2b**
DE	91.2	143.3	111.3	34.1	108.8	55.9
DH	79.2	134.7	103.6	28.6	94.5	51.8
DG	70.6	120.8	100.3	37.3	99.0	49.6

Useful references for computation part

(1) Becke, A. D., *Phys. Rev. A* **1988**, *38*, 3098.

(2) (a) Perdew, J. P., *Phys. Rev. B* **1986**, *33*, 8822; (b) Perdew, J. P., *Phys. Rev. B* **1986**, *34*, 7406.

(3) Andrae, D., Häußermann, U., Dolg, M., Stoll, H., Preuß, H., *Theor. Chim. Acta* **1990**, *77*, 123.

(4) Generated automatically according to the procedure implemented in Gaussian 03.

(5) (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Pittsburgh PA, 2003; (b) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

(6) Albinati, A.; Arz, C.; Pregosin, P. S. *J. Organomet. Chem.* **1987**, *335*, 379. (CSD-Refcode VABJIR).

(7) Becke, A. D., *J. Chem. Phys.* **1997**, *107*, 8554.

(8) (a) Grimme, S., *J. Comput. Chem.* **2004**, *25*, 1463; (b) Grimme, S., *J. Comput. Chem.* **2006**, *27*, 1787.

(9) Along with other explicitly or implicitly dispersion-corrected functionals, see e.g.: (a) Sieffert, N.; Bühl, M. *Inorg. Chem.* **2009**, *48*, 4622; (b) Minenkov, Y.; Occhipinti, G.; Jensen, V. R. *J. Phys. Chem. A* **2009**, *113*, 11833.

(10) Sieffert, N.; Bühl, M. *J. Am. Chem. Soc.* **2010**, *132*, 8056.

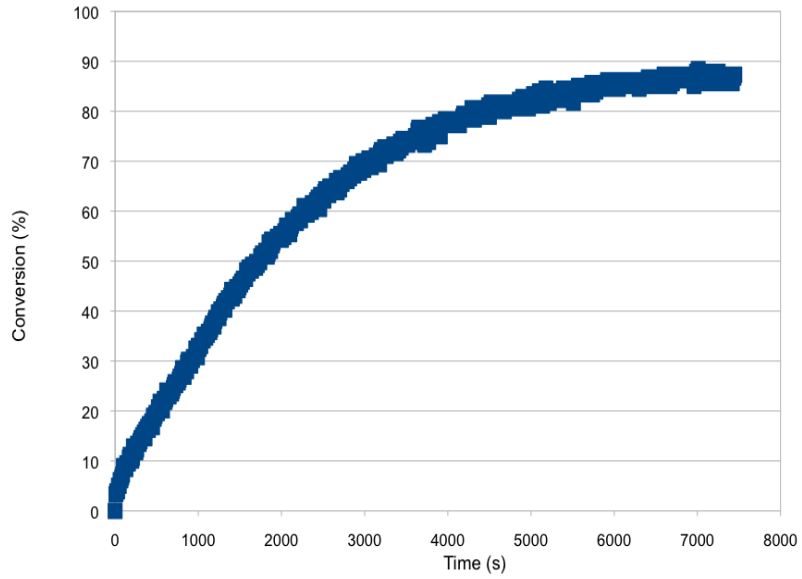
(11) Boys, S. F., Bernardi, F., *Mol. Phys.* **1970**, *19*, 553.

Further experiments on the hydrogenation of 4-((*E*)-2-phenylprop-1-enyl)morpholine.

All hydrogenation mechanisms tend to require hydrogen in the rate-determining step or in the reactions leading up to the rate-determining step. Experiments ran at 10 bar, 40 bar and 50 bar show there is a positive order in hydrogen in these reactions as expected. Conversions after 2 hours at 70 ^{o}C in reactions set up under (to all extensive purposes) identical conditions were; (i) 10 bar: not determined-low (54 % after 5 hours at 10 bar, 70 ^{o}C); (ii) 40 bar: 76% in 2h; (iii) 50 bar 84% in 2h.

Gas-uptake monitoring of a reaction at 70 Centrigrade and 20 bar pressure (S/C = 500) was carried out and a full set of data was obtained for the hydrogenation using L1 (After 23 hours the reaction mixture was also analysed by ^{1}H NMR and found to give 99% conversion in agreement with the kinetics data). A reaction carried out under similar conditions using L2 was too slow to obtain meaningful gas-uptake data despite several attempts. In this case, 18% conversion was realised in 23 hours-The average initial turnover for L2 is therefore calculated at 18% conversion as being 4 mol prod./mol.catalysts/h. Since the very early part of the kinetics measuring (first few minutes) is subject to stabilisation of the autoclave temperature after the reagent is added, rather than measuring an average at 18% conversion, we measure average initial T. O. F. for L1 at 50% conversion since this should be a truer reflection of average initial rate. For L1, an average initial rate of 514 mol prod./mol.catalysts/h is calculated. As a result of the temperature stabilisation occurring in the first minutes of reaction, this part of the data should be interpreted with some caution, although the full data-set is used in graphs 1 and 2 overleaf. Despite our caution regarding the initial minutes of the reaction, there is a suggestion that an even higher initial rate may initially be observed that then falls to the slower rate and first order behaviour encountered for the bulk of the reaction. If this is not purely an artefact of the data collection method, it could be rationalised by non-competitive inhibition by the product. In any event, (i) this has no bearing on the key findings presented here, and (ii) experiments in which product is added at the start confirm that this effect does not have a strong bearing on the productivity of the reaction (Table S2). We also note here that these catalysts show a positive order dependence in phosphine concentration (Table S3) in contrast to the hydrogenation of simple alkenes (see ref 7a in main paper). This is consistent with either non-competitive product inhibition, or the lower electron donating character of L1 preventing phosphine inhibition by being more labile, and/or the enamine being a strong binding substrate relative to simple alkenes. All our comparative studies in the main paper were carried out at relatively low phosphine/Rh ratio's that are close to ideal for the more electron-donating phosphines; thus, without recourse to the theoretical studies, the relative rates seen at low L/Rh ratios can not be explained by increased lability alone. Thus, while this is interesting, it does not seem to alter or modify our main conclusions.

Graph 1: Gas uptake measurements for the hydrogenation of 4-(-2-phenylprop-1-enyl)morpholine using $[Rh(COD)Cl]_2$ (0.2%) and phosphine L1 (0.8%) at 70°C and 20 bar pressure in toluene.



Graph 2: Natural log plot shows a reasonable fit to first order kinetics.

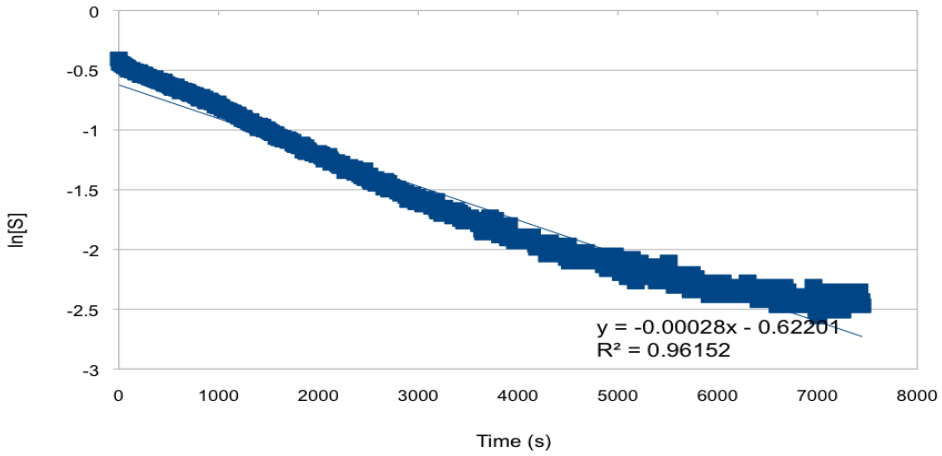


Table S2: Effect of addition of product to the hydrogenation of 4-(-2-phenylprop-1-enyl)morpholine using $[Rh(COD)Cl]_2$ (0.2%) and phosphine L1 at 70°C and 40 bar pressure in (0.5 mmol enamine in 2 ml of dry toluene).

Entry	T (ºC)	P (bar)	$[Rh(COD)Cl]_2$ %	Ligand %	Amine %	t h	Conversion[a] %
1	35	40	0.2	**1**, 0.8	0	16	53
2	35	40	0.2	**1**, 0.8	1.5	16	50
3	35	40	0.2	**1**, 0.8	10	16	51
4	35	40	0.2	**1**, 0.8	50	16	39
5	70	40	0.2	**1**, 0.8	50	3	68[b]
6	70	40	0.2	**1**, 0.8	0	3	63[b]

a: Conversion determined by ^{1}H-NMR integration using methyl naphthalene as I.S. b: average of two runs.

Table S3: Phosphine inhibition effects in the hydrogenation of 4-(-2-phenylprop-1-enyl)morpholine using $[Rh(COD)Cl]_2$ (0.2%) and phosphine L1 at 70°C and 40 bar pressure in (0.5 mmol enamine in 2 ml of dry toluene).

Entry	T (ºC)	P (bar)	$[Rh(COD)Cl]_2$ %	L Ligand/Rh	Ligand %	time (min.)	Conversion.[a] %
1	70	40	0.2	-	0	70	0
2	70	40	0.2	**1**, 2:1	0.8	70	27
3	70	40	0.2	**1**, 6:1	2.4	70	26
4	70	40	0.2	**1**, 8:1	3.2	70	26
5	70	40	0.2	**1**, 12:1	4.8	70	30
6	70	40	0.2	**1**, 18:1	7.2	70	48
7	70	40	0.2	**1**, 24:1	9.6	70	49
8	70	40	0.2	**1**, 48:1	19.2	70	42

a: Conversion determined by ^{1}H-NMR integration using methyl naphthalene as I.S.

Experimental

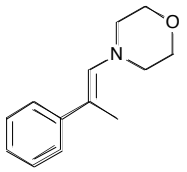
General Experimental procedures and instrumentation.

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Dry degassed diethyl ether, petroleum ether, THF and toluene were obtained from an Innovative Technologies Puresolve 400 solvent still. Other solvents were bought and used as received without further purification other than degassing by either purging with nitrogen or repeated freeze/thaw cycles under vacuum. Other reagents were purchased commercially and used as received. Solvents were removed by rotary evaporation on a Heidolph labrota 4000. Flash column chromatography was performed on Davisil silica gel Fluorochem 60 Å, particle size 35-70 mm. Thin layer chromatography was performed using 0.20mm layers of silica gel supported on plastic sheets (Macherey-Nagel, Polygram Sil G/UV_{254}) or using 0.20mm layers of aluminium oxide supported on plastic sheets (Merck Aluminium oxide F_{254}). NMR spectra were recorded on Bruker Avance 300 and 400 instruments. Chemical shifts are expressed in parts per million. Proton chemical shifts are referenced to internal residual solvent protons. Proton signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of the above. When appropriate, coupling constants (*J*) are quoted in Hz and are reported to the nearest 0.1 Hz. All spectra were recorded at room temperature and the solvent for a particular spectrum is given in parentheses. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Chemical ionisation mass spectroscopy and electron ionisation mass spectroscopy were performed on a Micromass GCT spectrometer. Electrospray mass spectroscopy was performed on a Micromass LCT spectrometer. Only major peaks are reported, and intensities are quoted as percentages of the base peaks.

General procedure for the reaction of styrene, syngas and morpholine (Table 1)

$[Rh(COD)Cl]_2$ (3.8 mg, 0.0077 mmol, 0.2 mol%) and the corresponding phosphine PR_3 were added into a Biotage 5 ml microwave vial. A stirring bar was added and the vial was sealed with a crimp cap and put under inert atmosphere. Toluene (2 ml) followed by styrene (443 μl, 3.88 mmol) and morpholine (373 μl, 4.27 mmol) were added using a syringe. Two needles were pierced into the vial and this was introduced into the autoclave, which had been previously purged with three vacuum/argon cycles. The autoclave was then purged three times with syngas (1:1 H_2/CO), pressurised to 60 bar and immersed into an oil bath preheated at the required temperature. After the desired reaction time, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken and analysed by ^{1}H NMR to calculate the conversion. In some cases, the hydroaminomethylation products were isolated as follows: The reaction mixture was concentrated and partitioned between 1M HCl and diethyl ether. The HCl layer was made basic with 1M NaOH and extracted three times into ether. The combined organic phases were dried with $MgSO_4$ and the final solution concentrated under vacuum to give the corresponding mix of branched and linear amines.

Synthesis of 4-((*E*)-2-phenylprop-1-enyl)morpholine



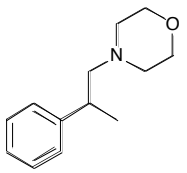
A mixture of 2-phenylpropionaldehyde (2.67 ml, 20.0 mmol) and morpholine (1.83 ml, 21.0 mmol) and $MgSO_4$ (1 g) in toluene (10 ml) was stirred at 100 °C for four hours. The mixture was concentrated and taken up in acetonitrile and repeatedly extracted into hexane. The combined hexane extracts were concentrated to give (2.3 g, 11.3 mmol, 57%) of a light yellow waxy solid. ^{1}H NMR showed a little residual aldehyde and a 3.4:1 *E/Z* ratio. *E-enamine*: δ_H(300 MHz, $CDCl_3$) 2.01 (3H, d *J* = 1.3 Hz, CH_3), 2.74-2.76 (4H, m, $(CH_2)_2N$), 3.68-3.71 (4H, m, $(CH_2)_2O$), 5.96 (1H, q *J*= 1.3 Hz, CH), 7.0-7.50 (5H, m, ArH); *Z-enamine*: δ_H(300MHz, $CDCl_3$) 1.88 (3H, d *J* = 1.3 Hz, CH_3), 2.59-2.61 (4H, m, $(CH_2)_2N$), 3.49-3.52 (4H, m, $(CH_2)_2O$), 5.68 (1H, q *J*= 1.3 Hz, CH), 7.0-7.50 (5H, m, ArH).

L. Duhamel, P. Duhamel, S. Combrisson, P. Siret, *Tetrahedron Lett.*, 1972, **13**, 3603.

General procedure for the hydrogenation of 4-((*E*)-2-phenylprop-1-enyl)morpholine

$[Rh(COD)Cl]_2$ (9.9 mg, 0.02 mmol, 0.2 mol%) and the corresponding phosphine PR_3 (0.08 mmol, 0.8 mol%) were added to a Schlenk tube and put under inert atmosphere. Toluene (2 ml) was added and the solution stirred for 15 min. A Parr autoclave was previously filled with a solution of enamine (2.033 g, 10 mmol) and 1-methylnaphthalene (0.2 ml as internal standard) in toluene (13 ml). The autoclave was then purged three times with H_2 and heated to 70 °C. The catalyst solution was then taken with a syringe and injected in the autoclave. The system was pressurised at the required pressure and maintained under isobaric conditions using an automatic gas-measuring apparatus. After the desired reaction time, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken and analysed by ^{1}H NMR to calculate the conversion.

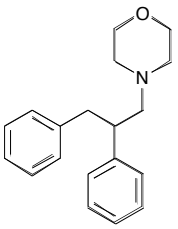
4-(2-phenylpropyl)morpholine



δ_H(300 MHz, $CDCl_3$) 1.31 (3H, d *J* = 6.9 Hz, CH_3), 2.37-2.54 (6H, m, $(CH_2)_2N$, C*H*$_2$-CH), 2.92-3.04 (1H, m, CH), 3.65-3.76 (4H, m, $(CH_2)_2O$), 7.19-7.36 (5H, m, ArH).

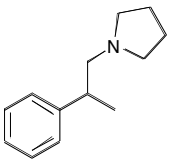
R. Thorsten, P. Elibracht, *Synthesis*, 1997, 1331.

_N_-(2,3-diphenylpropyl)morpholine



$[Rh(COD)Cl]_2$ (1.0 mg, 0.002 mmol, 0.2 mol%) and tris-(3,4,5-trifluoro phenyl)phosphine (3.4 mg, 0.008 mmol, 0.8 mol%) were added into a Biotage 5 ml microwave vial. A stirring bar was added and the vial was sealed with a crimp cap and put under inert atmosphere. Toluene (1.5 ml) followed by cis-stilbene (179 μl, 1.0 mmol), morpholine (96 μl, 1.1 mmol) and 1-methylnaphthalene (20 μl) as internal standard were added using a syringe. Two needles were pierced into the vial and this was introduced into the autoclave, which had been previously purged with three vacuum/argon cycles. The autoclave was then purged three times with syngas (1:1 H_2/CO), pressurised to 60 bar and immersed into an oil bath preheated at 80°C. After 20 h, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken and analysed by ^{1}H NMR to calculate the conversion. The reaction mixture was concentrated under vacuum and purified by chromatography on silica gel using hexane/ethyl acetate (2:1) as eluent to give the corresponding hydroaminomethylation product as a colourless oil (109 mg, 0.38 mmol, 38%). δ_H(300 MHz, $CDCl_3$) 2.25-2.48 (5H, m, $(CH_2)_2N$, CH_2N), 2.56 (1H, dd J_1= 7.9, J_2= 12.4 Hz, CH_2N), 2.75 (1H, dd J_1= 8.0, J_2= 12.7 Hz, CH_2Ph), 2.95-3.11 (2H, m, CH_2Ph, CH), 3.52-3.63 (4H, m, $(CH_2)_2O$), 6.87-6.90 (2H, m ArCH), 6.98-7.19 (8H, m, ArCH); δ_C(75 MHz, $CDCl_3$) 41.2 (CH_2Ph), 45.5 (CH), 54.4 (2 x NCH_2), 64.6 (CH_2), 67.5 (2 x OCH_2), 126.2 (ArCH), 126.7 (ArCH), 128.3 (2 x ArCH), 128.4 (2 x ArCH), 128.6 (2 x ArCH), 129.6 (2 x ArCH), 140.9 (ArC), 144.1 (ArC); *m/z* (CI) 282.2 (MH^+, 100%), 100.1 (30); Found (TOF CI) 282.1864 (MH^+); $C_{19}H_{24}NO$ requires 282.1858.

_N_-(2-phenylpropyl)pyrrolidine

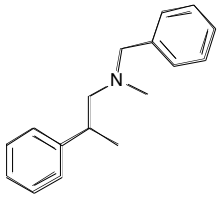


$[Rh(COD)Cl]_2$ (1.9 mg, 0.004 mmol, 0.2 mol%) and tris-(3,4,5-trifluoro phenyl)phosphine (6.8 mg, 0.016 mmol, 0.8 mol%) were added into a Biotage 5 ml microwave vial. A stirring bar was added and the vial was sealed with a crimp cap and put under inert atmosphere. Toluene (3 ml) followed by styrene (228 μl, 2.0 mmol), pyrrolidine (184 μl, 2.2 mmol) and 1-methylnaphthalene (40 μl) as internal standard were added using a syringe. Two needles were pierced into the vial and this was introduced into the autoclave, which had been previously purged with three vacuum/argon cycles. The autoclave was then purged three times with syngas (1:1 H_2/CO), pressurised to 60 bar and immersed into an oil bath preheated at 70°C. After 20 h, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken and analysed by ^{1}H NMR to calculate the

conversion. The reaction mixture was concentrated and partitioned between 1M HCl and diethyl ether. The HCl layer was made basic with 1M NaOH and extracted three times into ether. The combined organic phases were dried with $MgSO_4$ and the final solution concentrated under vacuum to give the corresponding hydroaminomethylation products as a 7:1 branched to linear mix (221 mg, 1.05 mmol, 53%). An analytically pure sample of the branched amine could be obtained by chromatography on silica gel using hexane/ethyl acetate (1:1) and then EtOAc as eluents. *Branched amine*: Colourless oil; δ_H(300 MHz, $CDCl_3$) 1.22 (3H, d J_1= 6.9, CH_3), 1.60-1.73 (4H, m, CH_2-CH_2), 2.32-2.48 (5H, m, $(CH_2)_2N$, CH_2CH), 2.64 (1H, dd J_1= 8.6, J_2= 11.9 Hz, CH_2CH), 2.80-2.91 (1H, m, CH), 7.08-7.25 (5H, m, ArCH); δ_C(75 MHz, $CDCl_3$) 20.3 (CH_3), 23.5 (2 x CH_2), 39.5 (CH), 54.5 (2 x NCH_2), 64.5 (*C*H_2CH), 126.1 (ArCH), 127.1 (2 x ArCH), 128.4 (2 x ArCH), 146.5 (ArC); *m/z* (ES) 190.0 (MH^+, 100%), Found (TOF ES) 190.1593 (MH^+); $C_{13}H_{20}N$ requires 190.1596.

N. Kaway, T. Shioiri, *Chem. Pharm. Bull.*, 1983, **31**, 2564

***N*-benzyl-*N*-methyl-2-phenylpropan-1-amine**



$[Rh(COD)Cl]_2$ (1.9 mg, 0.004 mmol, 0.2 mol%) and tris-(3,4,5-trifluoro phenyl)phosphine (6.8 mg, 0.016 mmol, 0.8 mol%) were added into a Biotage 5 ml microwave vial. A stirring bar was added and the vial was sealed with a crimp cap and put under inert atmosphere. Toluene (3 ml) followed by styrene (228 μl, 2.0 mmol), *N*-methyl(phenyl)methanamine (284 μl, 2.2 mmol) and 1-methylnaphthalene (40 μl) as internal standard were added using a syringe. Two needles were pierced into the vial and this was introduced into the autoclave, which had been previously purged with three vacuum/argon cycles. The autoclave was then purged three times with syngas (1:1 H_2/CO), pressurised to 60 bar and immersed into an oil bath preheated at 70°C. After 20 h, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken and analysed by ^{1}H NMR to calculate the conversion. The reaction mixture was concentrated and partitioned between 1M HCl and diethyl ether. The HCl layer was made basic with 1M NaOH and extracted three times into ether. The combined organic phases were dried with $MgSO_4$ and the final solution concentrated under vacuum to give the corresponding hydroaminomethylation products as a 9:1 branched to linear mix (233 mg, 0.97 mmol, 49%). *Branched amine*: Colourless oil; δ_H(300 MHz, $CDCl_3$) 1.34 (3H, d J = 6.9 Hz, CH_3), 2.27 (3H, s, NCH_3), 2.49-2.62 (2H, m, *C*H_2CH), 2.98-3.10 (1H, m, CH), 3.52 (1H, d J = 13.3, CH_2Ph), 3.60 (1H, d J = 13.3, CH_2Ph), 7.21-7.44 (10H, m, ArH); δ_C(75 MHz, $CDCl_3$) 20.0 (CH_3), 38.1 (CH), 42.7 (NCH_3), 62.7 (CH_2Ph), 65.1 (CH_2), 126.1 (ArCH), 126.8 (ArCH), 127.3 (2 x ArCH), 128.1 (2 x ArCH), 128.3 (2 x ArCH), 128.9 (2 x ArCH), 139.5 (ArC), 146.2 (ArC); Found (ES) 240.1754 (MH^+); $C_{17}H_{22}N$ requires 240.1752.

J. A. Seijas, M. P. Vázquez-Tato, C. Entenza, M. M. Martínez, M. G. Ònega, S. Veiga, *Tetrahedron Lett.*, 1998, **39**, 5073 .