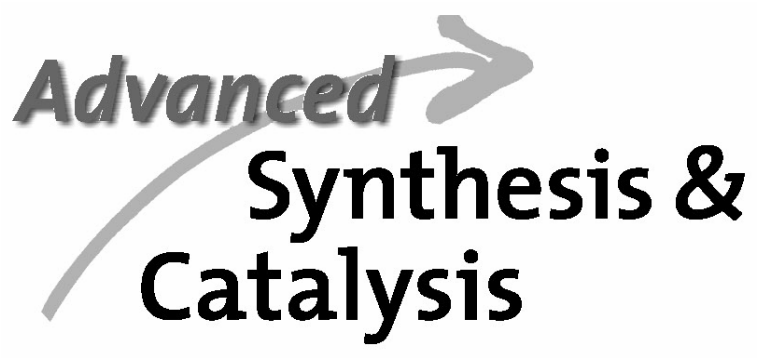

Supporting Information

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S U P P L E M E N T A R Y M A T E R I A L
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Synthesis and characterization of *N*-heterocyclic carbene substituted phosphine and phosphite rhodium complexes and their catalytic properties in hydrogenation reactions

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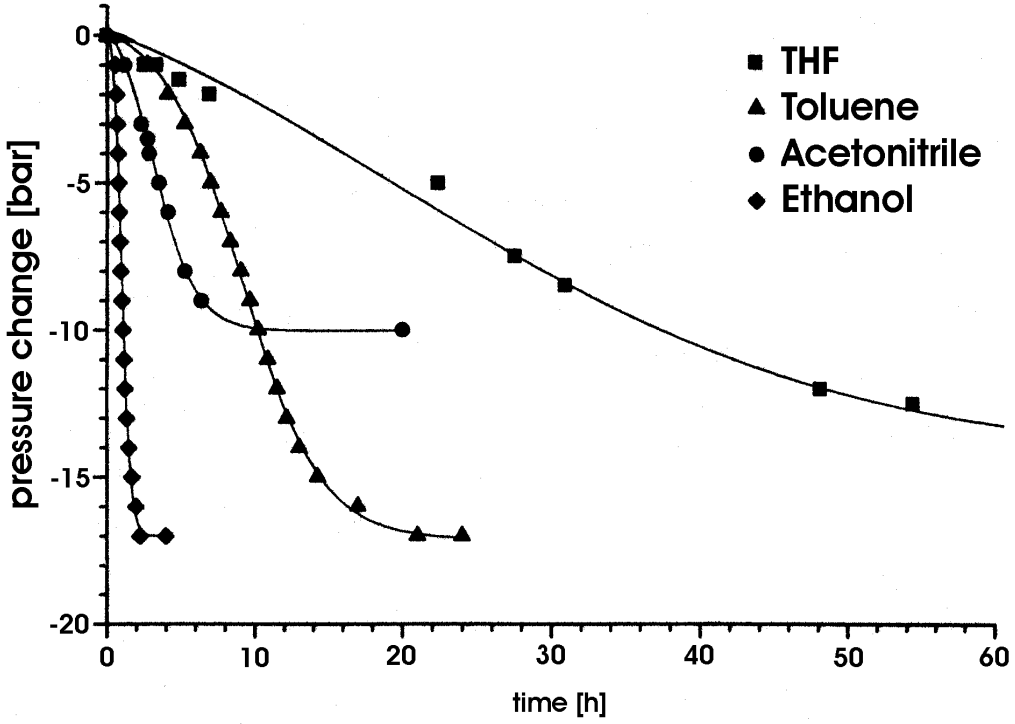
Summary of crystallographic data for compounds **5, 6·(CH_2Cl_2)** and **8**

	5	**6·(CH_2Cl_2)**	**8**
Formula	$C_{51}H_{54}ClN_2O_6P_2Rh$	$C_{49}H_{65}Cl_3N_4PRh$	$C_{31}H_{52}ClN_2Rh$
M_w	991.26	950.28	591.11
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
Crystal size [mm^3]	$0.24 \times 0.36 \times 0.41$	$0.24 \times 0.28 \times 0.38$	$0.25 \times 0.38 \times 0.38$
a [Å]	16.2012(7)	11.4774(6)	15.2329(7)
b [Å]	16.7537(8)	12.3284(6)	15.3016(8)
c [Å]	34.904(2)	17.9341(10)	13.0458(5)
a [°]	90	81.389(6)	90
ß [°]	90	72.756(6)	90
? [°]	90	78.869(6)	90
V [$Å^3$]	9474.0(8)	2366.4(2)	3040.8(2)
Z	8	2	4
D_{calc} [g cm^{-3}]	1.390	1.334	1.291
µ [mm^{-1}]	0.536	0.601	0.670
Θ-range [°]	1.84/24.70	2.28/25.64	2.05/25.66
Reflections collected	70336	16230	42110
Reflections independent [I_o>2s (I_o)/all data/R_{int}]	12001/16018/0.047	7237/8291/0.030	5373/5743/0.040
Data / restraints / parameters	16018/0/1136	8291/0/783	5743/0/524
R1 [I_o>2s (I_o)/all data]	0.0255/0.0420	0.0240/0.0294	0.0164/0.0188
wR2 [I_o>2s (I_o)/all data]	0.0442/0.0462	0.0594/0.0608	0.0330/0.0334
GOF	0.828	1.027	0.962
? $?_{max/min}$ [e·$Å^{-3}$]	0.49/-0.26	0.62/-0.63	0.21/-0.25

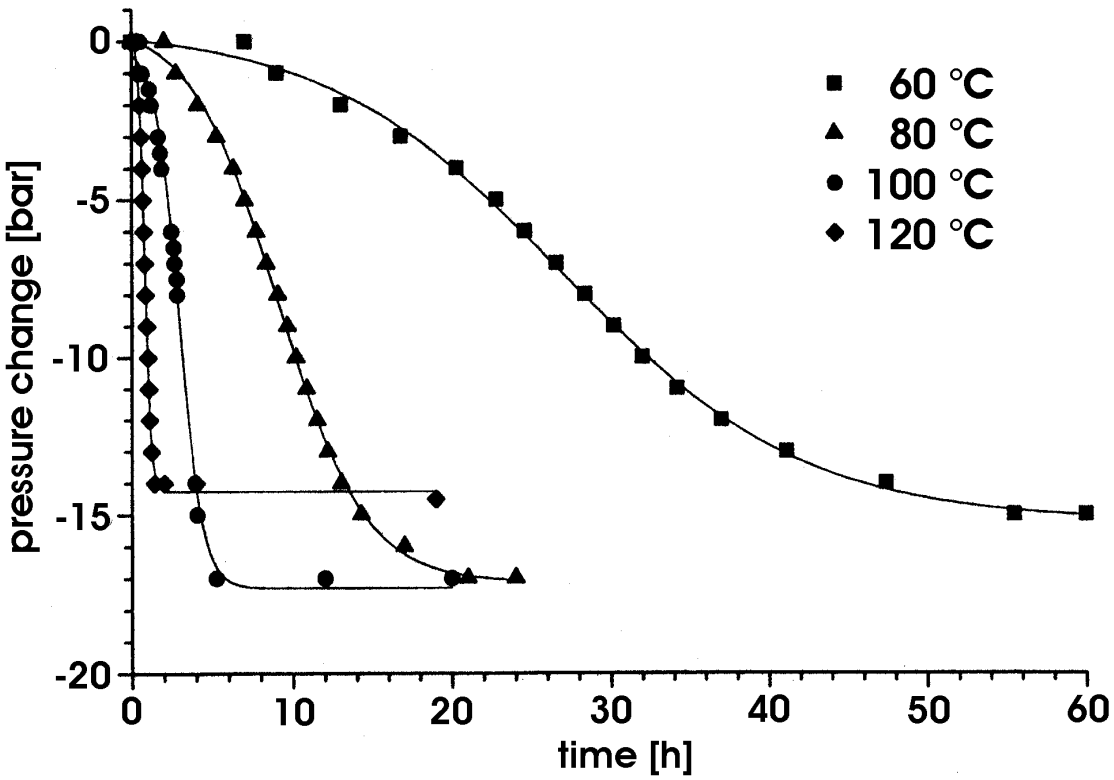
Tables and graphs for the hydrogenation experiments:

Fig. 5. Hydrogenation of cyclohexene in different solvents (80 °C, 20 bar H_2, 4 eq. PPh_3).



solvent	induction period	reaction time [h]	conversion [%]
THF	90	90	64
toluene	60	22	98
acetonitrile	60	10	58
ethanol	30	2.5	100

Fig. 6. Hydrogenation of cyclohexene in toluene at different temperatures (20 bar H_2, 4 eq. PPh_3).



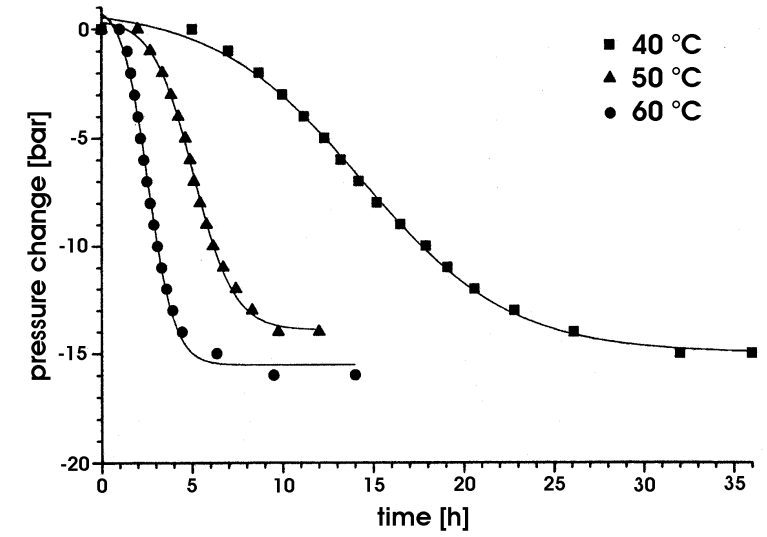
Temp. [°C]	induction period	reaction time [h]	conversion [%]
60	420	56	100
80	60	22	98
100	30	5	83
120	20	2	65

Table 2

Hydrogenation of cyclohexene at various temperatures in ethanol (20 bar H_2, 2 or 4 eq. PPh_3).

Temp. [°C]	induction period [min]	reaction time [h]	conversion [%]
40	330	32	100[a]
50	135	10	100[a]
60	70	10	100[a]
60	75	10	100[b]
80	30	2.5	100[b]
100	15	1.5	54[b]

[a] 2 eq. of PPh_3; [b] 4 eq. of PPh_3 were added relative to the metal precursor.



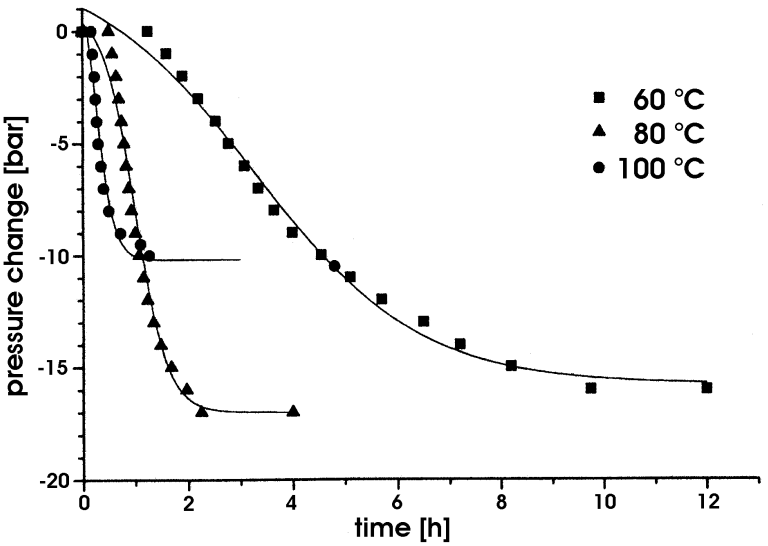
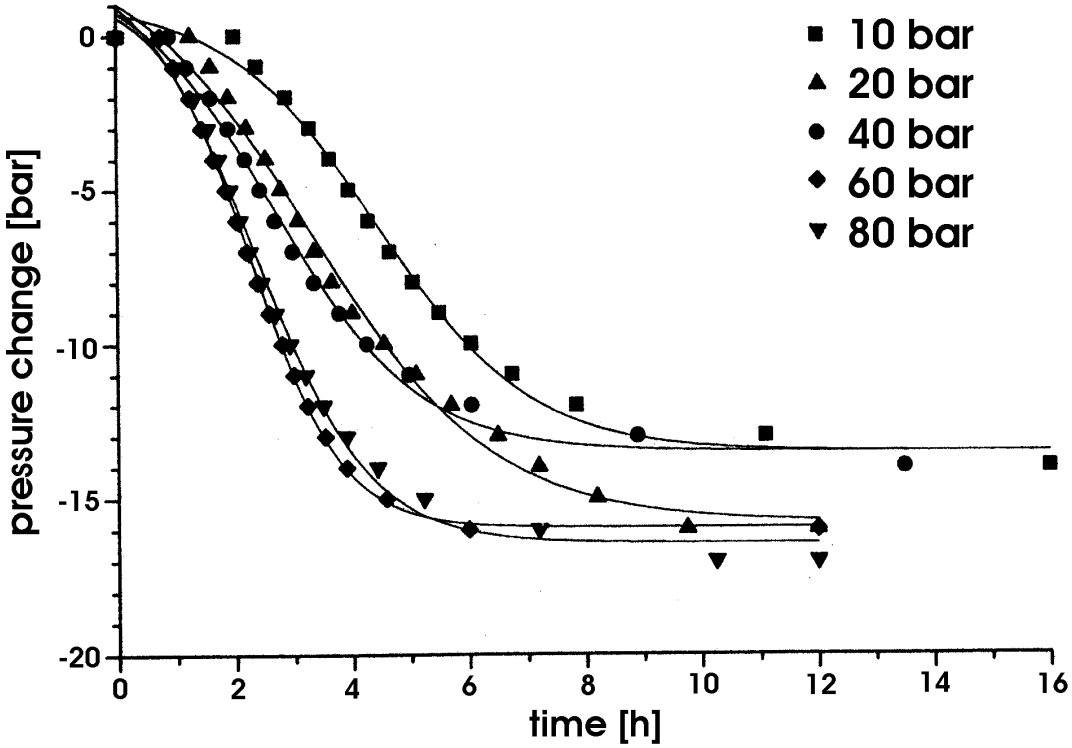
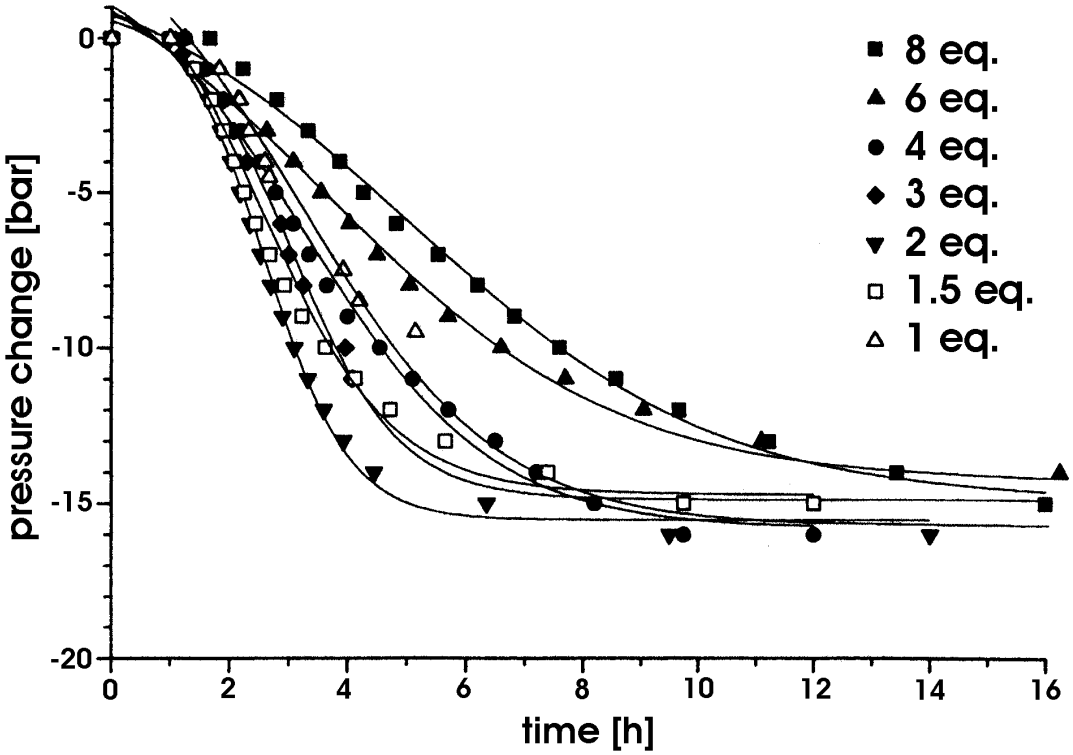


Fig. 7. Hydrogenation of cyclohexene in ethanol using different hydrogen pressures (60 °C, 4 eq. PPh_3).



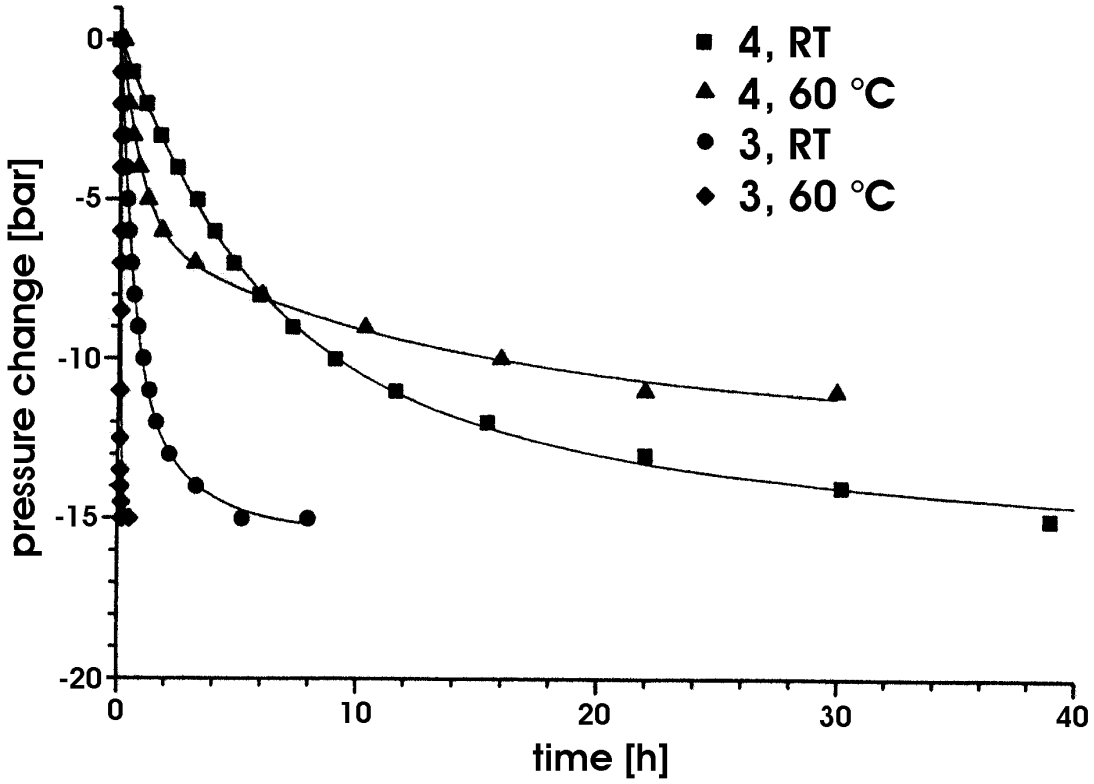
pressure [bar H_2]	induction period [min]	reaction time [h]	conversion [%]
10	120	16	100
20	75	10	100
40	50	13	100
60	45	6	100
80	45	11	100

Fig. 8. Hydrogenation of cyclohexene in ethanol using different amounts of triphenylphosphine (60 °C, 20 bar H_2).



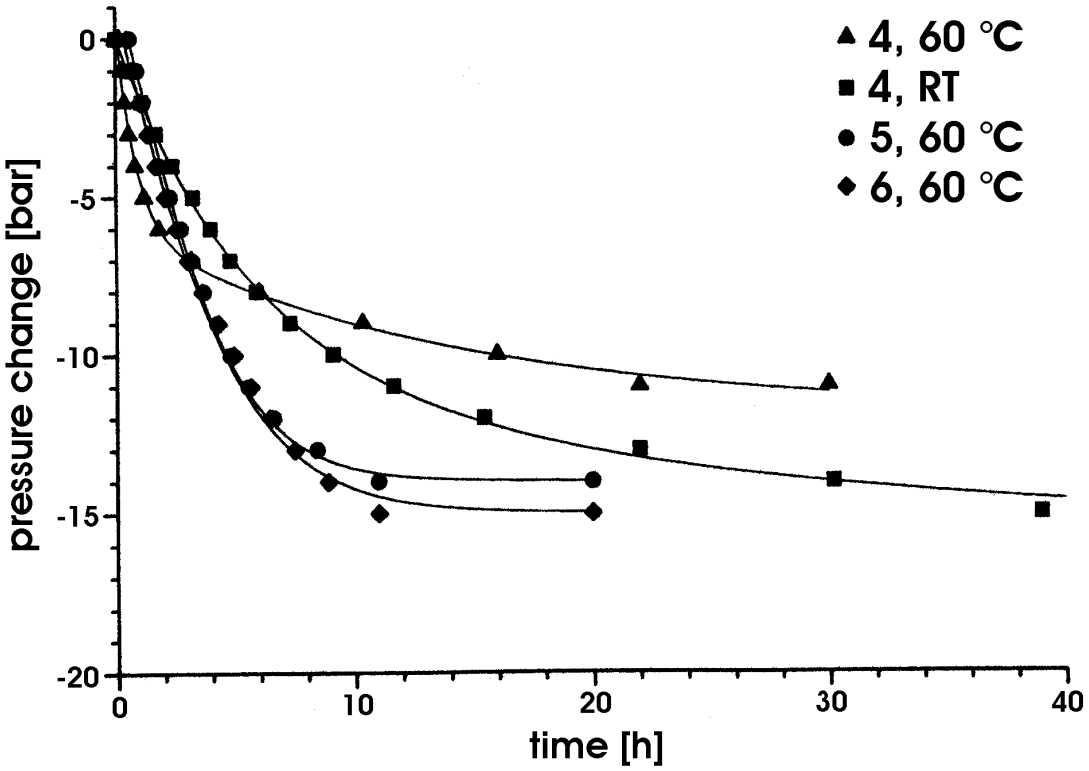
PPh_3 [eq.]	induction period [min]	reaction time [h]	conversion [%]
8	100	17	86
6	90	24	90
4	75	10	100
3	70	9	100
2	70	10	100
1.5	70	10	100
1	70	9	100

Fig. 9. Hydrogenation of cyclohexene in ethanol using catalyst **3** and **4**.



Catalyst	Temp. [°C]	reaction time [h]	TOF [h^{-1}]	conversion [%]
4	25	38	267	100
3	25	3	1333	100
4	60	22	667	68
3	60	0.25	8000	100

Fig. 10. Hydrogenation of cyclohexene in ethanol using catalyst **4 - 6**.



Catalyst	Temp. [°C]	reaction time [h]	TOF [h^{-1}]	conversion [%]
4	25	38	267	100
4	60	22	667	68
5	60	11	400	100
6	60	11	429	100

Table 3

Hydrogenation of cyclohexene in ethanol using catalyst **7** (60 °C, 20 bar H_2, 2 eq. phosphine).

Phosphine	induction period [min]	reaction time [h]	TOF [h^{-1}]	conversion [%]
PPh_3	70	10	750	100
PCy_3	180	190	20	59
PPy_3	660	95	38	100
$P(OPh)_3$ [4 eq.]	no reaction	20	no reaction	3
dppe, $NaBPh_4$ [1 eq.]	35	1.25	3000	100

Fig. 11. Hydrogenation of cyclohexene in ethanol using different phosphines.