Sol–gel entrapped lipophilic and hydrophilic ruthenium–, rhodium–, and iridium–phosphine complexes as recyclable isomerization catalysts

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Abstract

The phosphinated complexes $RuCl_2(PPh_3)_3$, **1**, $RhCl(PPh_3)_3$, **2**, $IrCl(CO)(PPh_3)_2$, **3**, their water soluble sulfonated analogs $RuCl_2[Ph_2P(3-C_6H_4SO_3Na)]_2 \cdot 4H_2O$, **4**, $RhCl[Ph_2P(3-C_6H_4SO_3Na)]_3 \cdot 4H_2O$, **5**, $IrCl(CO)[Ph_2P(3-C_6H_4SO_3Na)]_2$, **6**, as well as the dirhodium compounds $trans$-$[Rh(CO)(PPh_3)(\mu$-pz$)]_2$, **7**, and $trans$-$[Rh(CO)(PPh_3)(\mu$-Cl$)]_2$, **9** were entrapped physically in SiO_2 sol–gel matrices. Replacement of the PPh_3 ligands in the two latter complexes by $Ph_2P(CH_2)_2Si(OEt)_3$ groups enabled to bind of the dirhodium complexes chemically to the matrix backbone via the silyloxy functions. The activity of the immobilized complexes as allylbenzene isomerization catalysts was studied and compared. Entrapped complex **4** was found to be the most efficient catalyst.

1. Introduction

Stabilizing of organic compounds by their entrapment in sol–gel matrices has become an important technique for a wide spectrum of applications in the field of optics [1], chemical sensing [2], photochemistry [3] and biochemistry [4]. The technique has also become applicable to heterogenizing of soluble transition metal catalysts, using modified sol–gel backbones with specific functional groups [5]. Re-

cently [6,7] we reported the entrapment of ion pairs of platinoid metal halides and quaternary ammonium salts into plain SiO_2 sol–gel matrices without specific metal-binding functions. These *physically* encapsulated catalysts proved highly stable, leach-proof, and in many cases, more efficient and selective than the corresponding non-immobilized ion pair catalysts [8]. We have now found that this physical entrapment of molecules is applicable to the classical transition metal–phosphine complexes, $RuCl_2(PPh_3)_3$, **1**, $RhCl(PPh_3)_3$, **2**, $IrCl(CO)(PPh_3)_2$, **3**, their sulfonated analogs

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$RuCl_2[Ph_2P(3-C_6H_4SO_3Na)]_2 \cdot 4H_2O$, **4**, $RhCl[Ph_2P(3-C_6H_4SO_3Na)]_3 \cdot 4H_2O$, **5**, $IrCl(CO)[Ph_2P(3-C_6H_4SO_3Na)]_2$, **6**, and to several chlorine- and pyrazolato-bridged dirhodium complexes. In most cases the encapsulation process furnished recyclable catalysts with superior properties to those of the soluble non-entrapped complexes.

As the model reaction, we selected for the comparative evaluation of these immobilized catalysts, the well-studied isomerization of allylbenzene to the *cis*- and *trans*-1-propenylbenzenes (Eq. (1)).

$PhCH_2CH=CH_2 \rightleftharpoons$ *cis*- and

trans-$PhCH=CHMe$ (1)
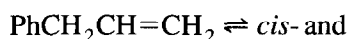
2. Experimental

2.1. General

Dichlorobis[3-(diphenylphosphino)benzenesulfonato-*P*]ruthenate(2 −) disodium salt tetrahydrate, **4** [9], chlorotris[3-(diphenylphosphino)benzenesulfonato-*P*]rhodate(3 −) trisodium salt tetrahydrate, **5** [10], *trans*-dicarbonylbis(μ-(1*H*-pyrazolato-N^1:N^2)bis-(triphenylphosphinedirhodium, **7**, and *trans*-dicarbonyldi-μ-chlorobis(triphenylphosphine) dirhodium **9** [12] were prepared as described in the literature.

2.2. Carbonylchlorobis[3-diphenylphosphino)benzenesulphonato-*P*]iridate(3 −) disodium salt, 6

To a solution of 390 mg (0.5 mmol) of carbonylchlorobis(triphenylphosphine) iridium, **3**, in 25 ml of boiling THF (freshly degassed by passing a stream of Ar for 10 min) was added a solution of 400 mg (1.1 mmol) of sodium 3-diphenylphosphinobenzene sulfonate dihydrate, $Ph_2P(3-C_6H_4SO_3Na) \cdot 2H_2O$ [13] in 2 ml of cold THF. The mixture was further refluxed for 30 min under Ar. After cooling, the bright

yellow crystals of $IrCl(CO)[Ph_2P(3-C_6H_4SO_3Na)]_2$ were filtered under exclusion of air, dissolved in a minimum amount of EtOH and reprecipitated by addition of peroxide-free Et_2O. Drying for 3 days over P_2O_5 under reduced pressure (0.1 mm) at 50°C afforded 320 mg (65%) of **6**; softens at > 220°C; IR (Nujol) 1966 cm^{-1} (CO); ^{31}P NMR (162 MHz, CDCl$_3$, 85% H$_3$PO$_4$): 26.65 (in the ^{31}P NMR of the crude complex appeared two small additional peaks at 29.29 and 38.10 ppm). Analysis: Found: C, 44.98; H, 2.80; Cl, 3.32%. $C_{37}H_{28}ClIrNa_2O_7P_2S_2$ requires: C, 45.15; H, 2.87; Cl, 3.60%.

2.3. trans-Dicarbonylbis(μ-1H-pyrazolato-N^1:N^2)bis[diphenyl[2-triethoxysilyl)ethyl]phosphine]dirhodium, 8

To a solution of 110 mg (0.24 mmol) of tetracarbonylbis(μ-1*H*-pyrazolato-N^1:N^2)dirhodium [11] in 15 ml of degassed ether was added dropwise under Ar within 2 min at room temperature 183 mg (0.49 mmol) of diphenyl[2-triethoxysilyl)ethyl]phosphine. After stirring overnight the ether was removed under reduced pressure and the residue was extracted (×2) with hexane. Concentration of the hexane solution and cooling to 6°C afforded 173.7 mg (63%) of **8** as yellow needles; decomposes above 120°C; IR (KBr): 1959, 2072 (RhC≡O); ^{1}H NMR (200 MHz, CDCl$_3$): 0.78 (m, 4H, SiCH_2), 1.08 (m, 18H, CH_3), 2.19 (m, 4H, PCH_2), 3.63 (m, 12H; OCH_2), 7.15–7.75 (m, 24H, C_6H_5, pz-3,5H); ^{13}C NMR (50 MHz, CDCl$_3$): 5.48 (SiCH_2), 18.70 (CH_3), 23.35 (d, $J = 29$ Hz, PCH_2), 58.91 (s, OCH_2), 128.75, 128.83, 130.33, 130.65; 133.72 (d, $J = 12$ Hz, PCH_2), 134.01, 134.13, 140.16, (C_6H_5, pz), 178.60 (CO). Analysis: Found: C, 50.22, H, 5.81; N, 4.71%. $C_{48}H_{64}N_4O_8P_2Rh_2Si_2$ requires: C, 50.18; H, 5.61; N, 4.88%.

A suitable crystal of **8** for X-ray analysis was obtained by recrystallization from hexane. The crystallographic data are listed in Table 1. Data collection was carried out with an Enraf–Non-

Table 1

Crystal data for and details of structure determination for **8**

|	
Formula	$C_{18}H_{64}N_4O_8P_2Rh_2Si_2$
Molecular weight	1148.97
Crystal dimension (mm × mm × mm)	0.15×0.35×0.1
Space group	$P\bar{1}$
a, Å	15.282(4)
b, Å	19.628(3)
c, Å	9.156(3)
α (°)	99.65
β, (°)	99.43
γ (°)	81.30
V, Å^3	2649.2 (11)
Z	2
ρ_{calcd}, g cm^{-3}	1.440
Linear absorption coefficient (cm^{-1})	0.781
F(000)	1184
Radiation	MoK_α ($\lambda = 0.71069$ Å)
Temperature (K)	160
Range (°)	$1 \geq 2\theta \geq 46$
hkl boundaries	$-16 \to 16$, $-21 \to 21$, $0 \to 10$
Scan technique	$\omega - 2\theta$
Scan time variable (s)	max. 50
Scan angle (°)	$1.15 + 0.35 \cdot \tan\theta$
Aperture (mm)	3
No. of reflections measured	7850
No. of unique reflections	6364 ($R_{int} = 0.0384$)
No. of observed reflections with $F_o \leq 2\sigma(F_o)$	6302
Residual electron density (eÅ^3)	max. 0.590; min. -0.471
Absorption (DIFABS)	max. 1.070; min. 0.935
No. of refined parameters	585
Goodness-of-fit on F^2	1.032
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	$R^1 = 0.0581$, $wR^2 = 0.1233$
R for all data	$R^1 = 0.0885$, $wR^2 = 0.1414$

ius CAD-4 automatic diffractometer, controlled by a micro-Vax II computer fitted with a low-temperature attachment. The cell parameters were obtained from the angles of 25 reflections in the range of $10.2° < 2\theta < 21.0°$. Reflections were scanned with variable scan time (ca. 50 s), depending on the intensities. Two third of the time was used for scanning the peak, a sixth for measuring the left-hand background and a sixth for measuring the right-hand background. The crystal orientation was checked every 200 intensity measurements by scanning 3 reflections. A new orientation matrix was automatically calcu-

lated from a list of 25 recentered reflections when the angular change was $> 0.1\%$. The intensities of 3 reflections were checked every 2 h. No significant loss in intensity was observed during the 116 h of measurements. The crude data were corrected for Lorentz and polarization effects [14]. Refinements in space group $P\bar{1}$ were successful. The position of two rhodium atoms was determined from a three dimensional Patterson synthesis (SHELXS 86) [15]. The calculated difference Fourier map (SHELXL 93) [16] revealed all missing silicon, phosphorus, oxygen, nitrogen and carbon atoms. All solvent molecules attached to the silicon atoms Si(1) and Si(2) were found to be disordered and a satisfactory model with each of 50% occupancy was found. Disordered carbons were refined isotropically, all other non-hydrogen atoms anisotropically. The hydrogen atoms were calculated in idealized positions (C–H 0.96 Å, $U_{iso} = 0.08$ Å^2). After all atoms were added to the model of the structure an empirical absorption correction was applied (DIFABS [17]; min. and max. correction factors: 0.935, 1.070). Several least-squares cycles converged at $R = 5.81\%$. Data reduction was performed using the SDP software package [14]. Atomic scattering factors were taken from Refs. [18], [19] and [20]. The discrepancy indices and other pertinent crystallographic data are shown in Table 1 [1]. An ORTEP drawing [21] of **8** is shown in Fig. 1.

2.4. trans-Dicarbonyldi-μ-chlorobis[diphenyl[2-(triethoxysilyl)ethyl]phosphine]dirhodium, 10

To a solution of 300 mg (0.77 mmol) of tetracarbonyldi-μ-chlorodirhodium in 10 ml of degassed benzene, was added under Ar atmo-
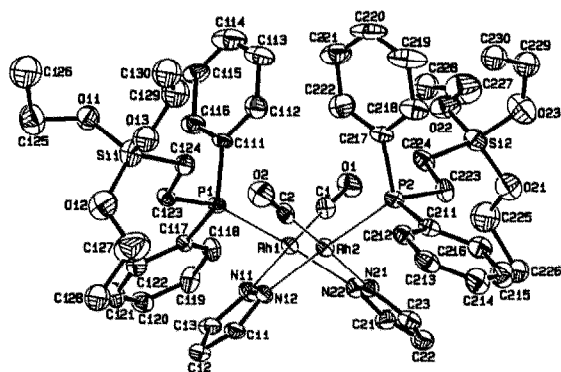
Fig. 1. ORTEP drawing [21] of 8.

sphere during 7 min at 60°C 575 mg (1.53 mmol) of diphenyl[2-(triethoxysilyl)ethyl]phosphine. The mixture was heated for 2 h at 80°, stirred for 24 h at room temperature, and the solvent was removed under reduced pressure. The residue was extracted several times with hexane. Removal of the solvent afforded 627 mg (75%) of **10** as a pale yellow powder; mp 87–88°C; ^{1}H NMR (200 MHz, CDCl$_3$): 0.77 (t (br), 4H, SiCH_2), 1.08 (t, 18H, $J_1 = 7$ Hz, CH_3), 2.35 (s (br), 4H, PCH_2), 3.65 (q, 12H, $J = 7$ Hz, OCH_2), 7.18–7.70 (m, 20H, C$_6$H$_5$); ^{13}C NMR (50 MHz, CDCl$_3$), 5.51 (SiCH_2), 18.68 (CH_3), 24.00 (d, $J = 30$ Hz, PCH_2), 58.95 (OCH_2), 128.74, 130,87, 133.78 (d, $J = 26$ Hz, PCH), 134.10 (C$_6$H$_5$), 184.13 (CO); ^{31}P NMR (81 MHz, CDCl$_3$): 48.97. Analysis: Found: C, 45.96; H, 5.50%. C$_{42}$H$_{58}$Cl$_2$O$_8$P$_2$Rh$_2$Si$_2$ requires: C, 46.46; H, 5.38%.

2.5. General procedure for entrapment of the soluble catalysts

2.5.1. Method A

A 50 ml flask equipped with a magnetic bar and a rubber septum with gas inlet and outlet was charged, under Ar atmosphere, with 0.05 mmol of the appropriate metal complex. Into the flask were injected successively 8 ml (102 mmol) of freshly purified peroxide-free THF, 1 ml (51 mmol) of degassed water (pH = 5.5) and

2.5 ml (17 mmol) of tetramethoxysilane (TMOS). The mixture was stirred until a clear solution was obtained, and then allowed to stand at 25°C until gelation was complete (2–3 days). The gel was dried at 25°C at 0.1 mm. The xerogel obtained, was treated for 1 h with boiling CH$_2$Cl$_2$, sonicated, retreated with CH$_2$Cl$_2$ and dried at 0.1 mm until constant weight was achieved. The washings were concentrated and the metal content in the residue was determined by atomic absorption analysis. In most cases the amount of metal that leached during the entrapment of the soluble catalyst was negligible (< 1 ppm).

2.5.2. Method B

Into the reaction flask with 0.05 mmol of the metal complex, was injected under Ar atmosphere, 2.5 ml (138 mmol) of degassed water and 3.5 ml (86 mmol) of degassed MeOH. After complete dissolution of the complex, 2.5 ml (17 mmol) of TMOS was added. Gelation, drying and workup was processed as in Method A.

2.6. Isomerization of allylbenzene

A reaction flask equipped with a reflux condenser, a magnetic bar and a rubber sealed side arm was charged under nitrogen atmosphere with 2 ml of freshly distilled allylbenzene. The vessel was placed in an oil bath thermostated at 120 ± 0.5°C. After temperature equilibration, the immobilized catalyst containing 0.05 mmol of the metal complex was added. At intervals of 1–5 min 2 μl samples were withdrawn and frozen to await GC analysis on a 2 m long column packed with Carbowax 20 M on Chromosorb W. When the reaction was completed, the equilibrium mixture consisted of 1.1% of the starting material, 8.9% of cis- and 90% of trans-1-propenylbenzene.

Upon completion of the reaction, or when the desired reaction period had passed, the liquid was decanted and analyzed by atomic absorption for leached metal. The used catalyst was

washed with 20 ml of boiling CH_2Cl_2, soni-
cated for 1 h, washed again and dried at 0.1 mm
for 3 h. The dried catalyst was then used in a
second run. The results obtained with 10 differ-
ent sol–gel-entrapped catalysts are summarized
in Table 2.

3. Results and Discussion

The so called Stephenson, Wilkinson and
Vaska complexes (**1**, **2** and **3**, respectively) were
found already in the 1960's to catalyze double
bond migration in allylbenzene (Eq. (1)) [22].
At 160°C the three catalysts showed different
durability, as well as different catalytic activity
[22]. In order to increase the stability of the
complexes, and to convert them into recyclable
catalysts, they were anchored onto phosphinated
crosslinked polystyrene supports [23]. Some of
these immobilized catalysts were found to be
recyclable, but to react slower than the soluble
complexes, and often leached in advanced cy-

cles [23]. In the present study the homogeneous
catalysts have been entrapped within sol–gel
matrices rather than anchored to the surface of
the support. Admixing of either **1**, **2** or **3** with
TMOS in an aqueous organic solvent under the
conditions described in the Experimental section
resulted in simple encapsulation of the metal
complexes. It is possible that during the entrap-
ment process the latter became linked to the
sol–gel backbone to the in-cage silanols by
hydrogen bonds, but probably not through strong
coordinative linkages as in those cases where
the complexes were admixed with phosphinated
sol–gel precursors [24,25]. Nevertheless, we
found that **1**, **2** and **3** leached neither during
encapsulation nor during their application as
isomerization catalysts. The immobilized com-
plexes could be recycled in several runs, how-
ever, their activity usually dropped in advanced
runs for different reasons. As sol–gel encapsu-
lated **1** proved to be perfectly stable, the de-
crease in its activity is attributed to partial
blockage of the pores during the catalytic pro-

Table 2
Isomerization of allylbenzene in the presence of several sol–gel entrapped catalysts [a]

Entrapped catalyst	Method of entrapment [b]	10^3 (initial rate) mmol l^{-1} min^{-1}	Conversion after 1 h (%), run: 1	2	3	Turnover no. [c] mol (prods) mol^{-1} (catal) h^{-1}
1	A	4.27	93	86	74	1691
2 [d]	A	1.55	32	10	6	596
3 [e]	A	0.45	18	9	8	291
4	B	3.86	97	97	95	1150
5 [d]	B	0.68	47	38	20	265
6	B	1.58	31	10	8	612
7 [d,f]	A	3.44	98	81	34	1079
8	A	0.55	28			187
9 [g]	A	0.33	43			276
10 [h]	A	0.71	32			734

[a] Reaction conditions as described in the Experimental section. The results are the average of at least three experiments that did not differ by > 5%.

[b] See Experimental section.

[c] During the first 10 min.

[d] Slow darkening on the catalyst's surface.

[e] Owing to low solubility of **3** only 0.025 mmol could be encapsulated.

[f] At 100°C the catalyst is stable and recyclable. At 100°C, there is 24% conversion after 1 h in all three runs.

[g] Only 30 meq of **9** could be entrapped. Life-times of 10 and 30 min at 120 and 100°C, respectively. Stable at 80°C. At 80°C, there is 15% conversion after 1 h.

[h] Only 0.17 meq of **10** has been encapsulated. At 120°C the catalyst slowly darkens. At 80°C it is inactive.

cess. This shortcoming could be overcome to some extent by successive treatment of the recovered catalyst with water and with an organic solvent followed by sonication (cf. [6]). The deactivation of the encapsulated rhodium complex 2 is rationalized by slow reduction of the metal during the hydrogen transfer process. The deterioration of the catalyst could be diminished by lowering the temperature, albeit on account of the reaction rate. Encapsulated 3 lost part of its activity in the first cycle but in further runs its performance remained practically constant.

Although the encapsulation of the phosphine complexes in sol–gel matrices is straightforward, the selection of solvents in which the entrapment can be carried out is limited. Because of the lipophilicity of 1, 2 and 3 we had to exchange the standard aqueous MeOH medium [26] by a 8:1 mixture of THF and H_2O (method A in the Experimental section). However, even in this medium the complexes did not dissolve with ease, and a maximum of only 0.025 mmol of the iridium complex 3 could be incorporated in a 2.5 g sol–gel matrix.

In order to overcome this difficulty we exchanged the original lipophilic phosphine complexes by their hydrophilic sulfonated analogs 4, 5 and 6. While the preparation and the utilization of the sulfonated ruthenium and rhodium complexes had been studied extensively in the past [27], no detailed procedure for the formation of the sulfonated Vaska compound has been reported. The encapsulation of these catalysts could be carried out in aqueous MeOH using any desired MeOH: H_2O ratio. Under conditions of method B (see Experimental section) sol–gel glasses with an average N_2-Langmuir surface area of 760 m^2 g^{-1} were formed, as compared with 600 m^2 g^{-1} for those obtained by method A.

Under exclusion of air, encapsulation of 4 gave an extremely efficient isomerization catalyst that retained its activity at 120°C in numerous successive runs. Sol–gel entrapped 5 proved more active than immobilized 2, but its surface darkened after several runs and consequently

lost some of its catalytic power. The sulfonated iridium complex could be encapsulated in large amounts and its (low) activity hardly changed after the second run.

In contrast to the short activity period of the Wilkinson complex as isomerization catalysts [22] several dirhodium complexes proved to catalyze reaction (1) to its completion under exclusion of oxygen [28]. The air sensitivity of these complexes could be reduced substantially by their anchoring to silica, alumina or polystyrene resins [29,30]. We have now encapsulated (by method A) the pyrazolato-bridged dirhodium complex $trans$-[(CO)Rh(PPh$_3$)(μ-pz)]$_2$, 7 in a sol–gel matrix, and investigated its catalytic properties. The immobilized complex was found to be air stable, and a much better isomerization catalyst than the entrapped monorhodium complexes. However, like the latter catalysts it was slowly reduced at 120°C and lost activity in advanced runs. At 100°C, however, neither its color nor its performances changed during the three first runs. With the intention to further stabilize 7 we have replaced the two PPh$_3$ by Ph$_2$P[CH$_2$CH$_2$Si(OEt)$_3$] groups that enable copolymerization of the complex with TMOS. Complex 8, which has been prepared according to Eq. (2), and was fully characterized by X-ray diffraction analysis, was interacted with TMOS to give a sol–gel entrapped catalyst with chemical bonds to the

$$[(COD)Rh(\mu\text{-Cl})]_2$$

$$\xrightarrow[-2Cl^-]{2pz} [(COD)Rh(\mu\text{-pz})]_2$$

$$\xrightarrow[-2COD]{4CO} [(CO)_2Rh(\mu\text{-pz})]_2$$

$$\xrightarrow[-2CO]{2Ph_2PCH_2CH_2Si(OEt)_3}$$

$$[[Ph_2PCH_2CH_2Si(OEt)_3]Rh(CO)(\mu\text{-pz})]_2$$
$$\textbf{8}$$

$$(2)$$

matrix backbone. It did not darken at 120°C under the conditions of Table 2 but reacted much slower than the physically encapsulated complex **7**.

Since soluble chloro-bridged dirhodium complexes are easily cleaved to monorhodium compounds (see e.g. [31]) we tried to stabilize the dinuclear structure by their entrapment in sol–gel matrices. We chose the known $[Rh(CO)(PPh_3)(\mu\text{-Cl})]_2$, **9**, as a representative chloro-bridged complex. Infrared measurement indicated that the chloro-bridge is retained during the encapsulation process, however it proved more sensitive to reduction than the other entrapped rhodium complexes. At 120°C, in the presence of allylbenzene the catalyst deteriorated within 10 min. At 100°C, it decomposed during 30 min, and only at 80°C it did not deteriorate. At this temperature, under the conditions of Table 2 allylbenzene isomerized within 1 h to an extent of 15%.

Substitution of the PPh_3 ligands in **9** by $Ph_2PCH_2CH_2Si(OEt)_3$ groups as in **10** did not improve the sensitivity of the immobilized complex to reduction.

In conclusion, we have shown that direct entrapment of transition metal–phosphine complexes in sol–gel matrices is a convenient route for heterogenizing of representative homogeneous catalysts.

Acknowledgements

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