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Short Communication

Coordination of a Ru(II)-complex to a tetrafunctional P-ligand: a model for Ru–P carbosilane dendrimers

Herlinde I. Beerens [a],*, Peter Wijkens [b], Johann T.B.H. Jastrzebski [b], Francis Verpoort [a], Ludo Verdonck [a], Gerard van Koten [b]

[a] *Department of Inorganic and Physical Chemistry, Organometallics and Catalysis Division, University of Ghent, Krijgslaan 281 (S-3), B-9000 Gent, Belgium*
[b] *Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Abstract

Organophosphine-functionalised carbosilane (CS) dendrimers (**5**, **6**) can be synthesised in high yield. Furthermore, new kinds of metallodendrimers (**7**, **8**) are obtained by coordination of a Ru(II) complex, containing the tridentate triamine ligand: 2,6-bis[(dimethylamino)methyl]pyridine, to these P-functionalised CS-dendrimers. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbosilane dendrimers; Phosphines; Ruthenium(II)-complexes; Metalations

1. Introduction

Recently, new dendritic structures with a precise number and location of chemical functionalities on the surface have been reported [1]. Dendritic compounds with phosphine or amine ligands have been used for the synthesis of supported metal catalysts by coordinating a suitable metal salt to the surface supported ligand [2]. However, an obvious problem of these supported metal catalysts is metal leaching as a result of reversibility of the metal–ligand (surface) coordination. Even in the case of bi- or tridentate ligand–metal binding, metal leaching can occur.

In a previous study we found that mononuclear Ru(II) complexes, [Ru($NN'N$)(PPh$_3$)Cl$_2$] (**1**, $NN'N$ = 2,6-bis[(dimethylamino)methyl]pyridine), are interesting catalysts for the cycloalkylation of aromatic amines with alcohols to give piperazines and piperidines [3].

We observed that during the catalysis the PPh$_3$–Ru bond is inert. Furthermore, the synthesis of **1** is easy
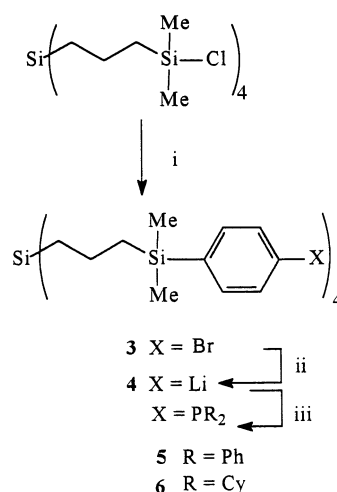
Scheme 1. Synthesis of phosphine-functionalised CS-dendrimers. Reagents and conditions: (i) 4.4 eq. 1,4-Br$_2$C$_6$H$_4$, 4.2 eq. *n*-BuLi, Et$_2$O, RT; (ii) 4.2 eq. *n*-BuLi, Et$_2$O, RT; (iii) 4.4 eq. ClPR$_2$ (**5**, R = Ph; **6**, R = Cy), Et$_2$O, RT.

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* Corresponding author. Tel.: +32-92-644440; fax: +32-92-644983.
  E-mail address: herlinde.beerens@rug.ac.be (H.I. Beerens)
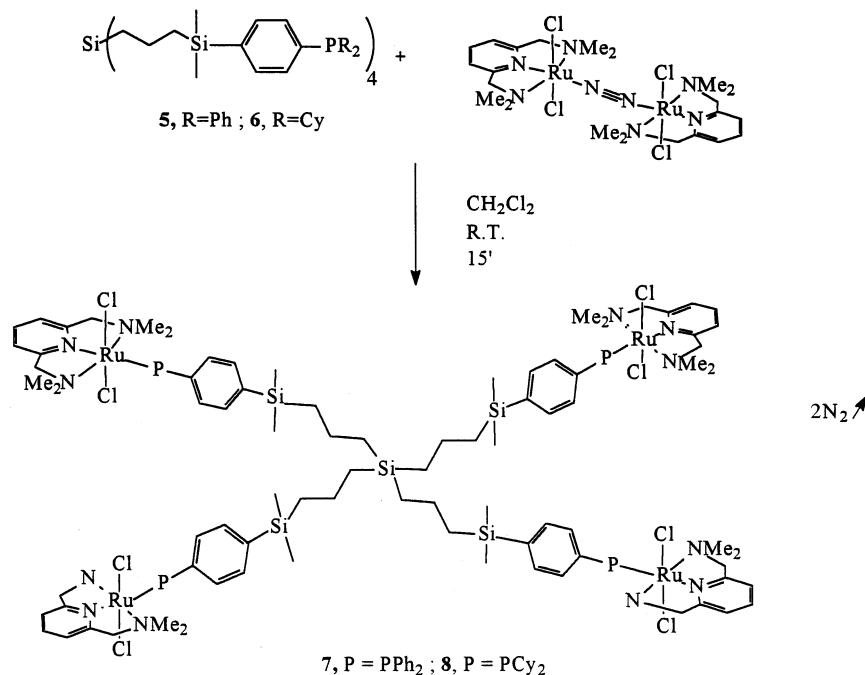
Scheme 2. Coordination of the Ru-complexes on the phosphine-functionalised CS-periphery.

and comprises a 2:1 reaction of the free phosphine ligand with the N_2-bridged binuclear complex $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)]$ (**2**) [4].

The inert PPh_3–Ru binding in **1** as well as its straightforward synthesis, prompted the present study which is directed to the synthesis of carbosilane (CS) dendrimers which carry a well-defined number of tri-arylphosphine or dicyclohexylphosphine ligands, and also the study of the binding of a $RuCl_2(NN'N)$-unit to these phosphine ligands.

2. Results and discussion

The organophosphine-functionalised CS dendrimers, which were prepared via the route shown in Scheme 1, starts from the reaction of the CS dendrimer with the p-lithiated bromobenzene in Et_2O. The organophosphine dendrimers, **5** and **6** were obtained in 97 and 93% yield, respectively.

The structures of the dendritic phosphine ligands were confirmed by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$-NMR spectroscopy and mass spectrometric analysis (MALDI-TOF) (see Section 4). In the ^{31}P-NMR, the resonance signal shifted from -4.7 ppm for the free PPh_3 to -4.9 ppm for compound **5**. This may be caused by a small effect of the p-Si attachment of Ph_3P on the chemical shift in ^{31}P-NMR. A similar effect of a p-Si aryl substituent on the chemical shift in ^{31}P-NMR was found by the combination of a p-Si-fluorotail to PPh_3 [5].

For the coordination of the Ru-complexes to the triphenylphosphine CS-dendrimers, the organophosphine dendrimer, **5**, is stirred with an equimolar quantity of the RuN_2Ru-complex [6] for 4 h in CH_2Cl_2 at r.t.

The two sharp $^{31}P\{^1H\}$-NMR resonances at -4.9 and 38.2 ppm, for the uncoordinated phosphine and the coordinated phosphine, respectively, indicated that an incomplete metal loading had occurred; only 70% of the surface phosphine ligands were occupied. In further experiments the reaction mixture was stirred for longer periods, but even after 25 h only 80% of the $RuCl_2(NN'N)$-units were linked to the CS dendrimers.

Upon reacting **5** with an excess of the Ru-complex, within 15 min full metallation was obtained (Scheme 2). The excess of the Ru-complex could be removed completely by washing crude **7** with a mixture of Et_2O–pentane (1:5 mol ratio).

In spite of the better donating properties of the PCy_2-ligands, the 1:2 molar reaction of the CS–PCy_2 ligand with the RuN_2Ru-complex lead likewise to incomplete metal loading. This is evident by the observation of two $^{31}P\{^1H\}$-NMR resonances at 2.2 ppm (free phosphine) and 12.5 ppm (coordinated phosphine). Again using an excess of the Ru-complex afforded the fully metalled CS–PCy_2–Ru complex **8**. However attempts to remove the excess of the Ru-complex by washing with a mixture of Et_2O–pentane (1:5 mol ratio) failed; still unreacted Ru-complex was present in the solids obtained.

Both $^{31}P\{^1H\}$-NMR spectra of **7** and **8** show only one sharp signal at 38.2 ppm (CS–PPh_2Ru, **7**) and 12.5 ppm (CS–PCy_2Ru, **8**). No peaks for any residual un-

bounded dendritic phosphine groups were observed, suggesting high efficiency of metal loading on these organophosphine dendrimers. The spectrum of **7** resembled that of the corresponding PPh_3 complex [Ru($NN'N$)PPh$_3$Cl$_2$], which showed a signal at 37 ppm [4]. The coordination chemical shifts of **7** and **8** are 43.1 and 10.3 ppm, respectively. Both are positive as expected since on coordination the phosphorus atom is deshielded.

Comparison of the ^1H- and $^{13}C\{^1H\}$-NMR spectra of **2** and **7** was also instructive. In particular the resonances of the CH$_2$-groups and the NMe$_2$ groups of **2** at 4.20 and 2.80 ppm, respectively, were shifted to higher field in **7** (3.98 ppm and 2.06 ppm), which was a clear indication of the coordination of the Ru-complex to the periphery of the dendrimer. The same chemical shift was found for the CS–PCy$_2$–Ru complex, **8**. Additionally, the peak broadening for these resonances evidenced the ligation of the Ru-complexes to the phosphines.

An unambigous assignment of all the ^1H-NMR signals of compound **8** was not possible.

The pattern of the CH$_2$-protons of the dendrimer is completely mixed with the signals of the cyclohexylprotons.

The MALDI-TOF spectrum of **7** doesn't provide additional information about the triphenylphosphine CS-dendrimer with Ru-complexes on the periphery. The mass spectrum showed characteristic fragmentation of which only a few peaks could be determinated.

3. Conclusions

In conclusion we have demonstrated in this paper the synthesis of organo-phosphine-functionalised CS dendrimers. New kinds of metallodendrimers are synthesized by specific complexation of the phosphine groups on the outer surface of the carbosilane dendrimers with the bridged RuN$_2$Ru-complex. The dendrimer surface can be easily and effectively occupied with the metal centers. This is to the best of our knowledge the first example of a Ru-complex linked to phosphine-functionalised carbosilane dendrimers. The aim of further investigations is the application of these Ru phosphine-functionalised CS dendrimers as catalyst precursors.

4. Experimental

All manipulations were performed under a dry and deoxygenated N$_2$ atmosphere using standard Schlenck techniques. All solvents were carefully dried and distilled prior to use. The bridged Ru-complex, **2** and the dendritic silicon chloride G0–SiMe$_2$Cl [8] were synthesized according to literature [6,7]. ^1H (300 MHz), ^{13}C (75 MHz) and ^{31}P (81 and 121 MHz)-NMR were recorded on a Varian inova 200–300 MHz spectrometer. For ^1H and ^{13}C-NMR, TMS was used as external standard and C$_6$D$_6$ or CD$_2$Cl$_2$ were used as solvents. For ^{31}P-NMR, 85% H$_3$PO$_4$ was used as standard and C$_6$D$_6$ or CD$_2$Cl$_2$ were used as solvents. MALDI-TOF: The MALDI-TOF mass spectra were obtained using a Voyager-DE BioSpectrometry Workstation (PerSeptive Biosystems Inc., Framingham, MA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The instrument was operated in the linear mode at an accelerating voltage in the range of 23 000–25 000 V. Detection was done by means of a linear detector and a digitizing oscilloscope operating at 500 MHz. Sample solutions with an approximate concentration of 30 mg ml^{-1} in CH$_2$Cl$_2$ were prepared. The matrix was 9-nitroantracene. In the case of the unloaded dendrimer the silver salt of trifluoroacetic acid was added to the matrix to improve the ionization. The elemental analysis was performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

4.1. Synthesis of G0–SiMe$_2$C$_6$H$_4$Br (3)

To a solution of 1,4-dibromobenzene (10.5 ml, 44.40 mmol) in Et$_2$O (50 ml) was added nBuLi (26.40 ml, 1.6 M solution in hexane) at −78°C. The resulting reaction mixture was stirred for 2 h at r.t. Then a solution of G0–SiMe$_2$Cl (5.7 g, 10.0 mmol) in Et$_2$O (10 ml) was added dropwise to the lithiation reaction mixture at 0°C. The reaction mixture was allowed to warm up to r.t. and stirred overnight. Water was slowly added and the organic layer was washed three times with water, dried over MgSO$_4$, filtered and concentrated in vacuo. The residue was purified by Kugelrohr distillation (1.5 h at 120°C, 0.1 mmHg) and column chromatography (silica/hexane; hexane:ether = 3:1). Yield: 7.9 g (75%) of an off-white syrup.

^1H-NMR (300 MHz, acetone-d_6): $\delta = 7.53$ (d, 8H, $J = 8.2$ Hz, ArH), 7.45(d, 8H, $J = 8.2$ Hz, ArH), 1.35–1.39 (m, 8H, –C–CH$_2$–C–), 0.82 (t, 8H, $J = 8.1$ Hz, –CH$_2$–Si–Ar), 0.58 (t, 8H, $J = 8.1$Hz, –CH$_2$–Si–CH$_2$–), 0.28 (s, 24H, Si–Me).$^{13}C\{^1H\}$-NMR (75 MHz, acetone-d_6): $\delta = 138.8$, 135.7, 131.1, 123.5 (4 × Ar–C), 20.5 (CH$_2$SiAr), 18.7 (–C–CH$_2$–C), 17.4 (CH$_2$–Si–CH$_2$), −3.1 (Si–Me). B MS (MALDI-TOF): $m/z = 1159.74$ [M + Ag]$^+$ (calc. 1160.95). Anal. Calc. for C$_{44}$H$_{64}$Br$_4$Si$_5$ ($M_w = 1053.08$): C, 50.18; H, 6.13; Br, 30.35; Si, 13.34. Found: C, 50.32; H, 6.25; Br, 30.45; Si, 13.31.

4.2. Synthesis of G0–SiMe$_2$C$_6$H$_4$P(C$_6$H$_5$)$_2$ (5)

To a solution of G0–SiMe$_2$C$_6$H$_4$Br (1.64 g, 1.56 mmol) in Et$_2$O (25 ml) was added nBuLi (4.2 ml, 1.6 M solution in hexane) at room −78°C. The resultant reaction mixture was allowed to warm up to r.t. and

whirl-mixed for 1 h, during which a sticky material was formed along the glass walls. After addition of chlorodiphenylphosphine (1.2 ml, 6.9 mmol), the mixture was whirl-mixed until the sticky material was dissolved and the product, which was precipitated as a white solid, was formed. The reaction mixture was stirred overnight and the precipitate was collected by centrifugation. After evaporation of the solvents, the last volatiles were removed by Kugelrohr distillation (2 h at 130°C, 0.05 mmHg) to afford **5** (2.23 g, 97%) as an off-white sticky material.

^{1}H-NMR (300 MHz, C_6D_6): $\delta = 7.48–7.15$ (m, 24H, C_6H_5 and C_6H_4, H_o vs. P), 7.10–6.85 (m, 32H, Ar$H_{m,p}$) 1.47–1.43 (m, 8H, –C–CH_2–C), 0.80 (t, 8H, $J = 8.1$ Hz, CH_2SiAr), 0.62 (t, 8H, $J = 8.1$ Hz, –CH_2–Si–CH_2–), 0.21 (s, 24H, SiMe).^{13}C{^{1}H}-NMR (75 MHz, C_6D_6): $\delta = 140.2$ (s, ArC–Si), 138.8 (d, $J = 12.1$ Hz, C_{ipso}–P of –C_6H_4–), 137.9 (d, $J = 12.1$ Hz, C_{ipso} of C_6H_5), 134.2 (d, $J = 19.4$ Hz, C_6H_5–C *ortho* vs. C_{ipso}–P), 134. (d, $J = 6.7$ Hz, C_6H_4–C, *meta* vs. C_{ipso}–P), 133.5 (d, $J = 18.8$ Hz, C_6H_4–C, *ortho* vs. C_{ipso}–P), 128.9 (s, C_6H_5–C *para* vs. C_{ipso}–P), 128.8 (d, $J = 6.7$ Hz, C_6H_5–C *meta* vs. C_{ipso}–P), 20.7 (CH$_2$SiAr), 19.1 (–CH$_2$–CH$_2$–CH$_2$), 17.8 (CH$_2$–Si–CH$_2$), -2.8 (SiMe). ^{31}P{^{1}H}-NMR (81 MHz, C_6D_6) $\delta = -4.9$ (s). MS (MALDI-TOF): $m/z = 1583.69$ [5 + Ag]$^+$ (calc. 1582.06).

4.3. Synthesis of G0–SiMe$_2$C$_6$H$_4$P(C$_6$H$_{11}$)$_2$ [9](6)

The biscyclohexyl compound was synthesized as described for **5**: To a solution of G0–SiMe$_2$C$_6$H$_4$Br (1.64 g, 1.56 mmol) in Et$_2$O (25 ml) was added *n*BuLi (4.2 ml, 1.6 M solution in hexane) at -78°C. The reaction mixture was allowed to warm up to r.t., during which time a sticky material was formed along the glass walls. The resulting reaction mixture was whirl-mixed during 1 h. After addition of chlorodicyclohexylphosphine

(1.64 ml, 6.9 mmol), the mixture was whirl-mixed until the sticky material was dissolved and a white precipitate was formed. The reaction mixture was stirred overnight, whereupon the precipitate was collected by centrifugation. After evaporation of the solvents the last volatiles were removed by Kugelrohr distillation (1.5 h at 110°C, 0.05 mmHg). Yield: 2.21 g (93%).

^{1}H-NMR (300 MHz, C_6D_6): $\delta = 7.62–7.51$ (m, 16H, ArH), 2.10–1.80, 1.80–1.40 (all m, 56H, Cy), 1.25–1 (m, 40H, SiCH$_2$CH_2 + Cy), 0.85 (t, 8H, $J = 8.1$ Hz, CH_2SiAr), 0.59 (t, 8H, $J = 8.1$ Hz CH_2–Si–CH_2), 0.24 (s, 24H, SiMe). ^{13}C{^{1}H}-NMR (75 MHz, C_6D_6) $\delta = 140.6$ (s, C_{ipso}–Si, C_5), 136.5 (d, $J = 20.6$ Hz, C_{ipso}–P, C_8), 134.6 (d, $J = 18.8$ Hz, ArC_o vs. P, C_7), 133.4 (d, $J = 6.7$ Hz, ArC_m vs P, C_6), 33 and 30.5 (d, $J = 13.4$ Hz and $J = 17$ Hz, CyC, C_{10}), 29.3 and 27.4 (d, $J = 7.9$ Hz and $J = 7.3$ Hz, CyC, C_{11}), 27.6 (d, $J = 12$ Hz, CyC, C_9), 26.8 (s, CyC, C_{12}), 20.9 (CH$_2$SiAr, C_3), 19.1 (–C–CH$_2$–C, C_2), 17.8 (CH$_2$–Si–CH$_2$, C_1), $-2,7$ (SiMe, C_4). ^{31}P{^{1}H}-NMR (81 MHz, C_6D_6) δ 2.2. MS (MALDI-TOF): $m/z = 1630.60$ [6 + Ag]$^+$ (calc. 1630.44).

4.4. Synthesis of G0–SiMe$_2$–PPh$_2$–[Ru] [9] (7)

To a solution of the bridged Ru-complex, **2** (0.08 g, 0.17 mmol) in CH$_2$Cl$_2$ (8 ml) was added a solution of **5** (0.062 g, 0.042 mmol) in CH$_2$Cl$_2$ (15 ml). The resulting reaction mixture was stirred for 15 min at r.t. Then Et$_2$O–pentane (1:5) was added to precipitate the crude product. After washing with the mixture of Et$_2$O–pentane (1:5) a brown viscous slurry of CS–PPh$_2$–[Ru] was obtained in 86% (0.12 g). (based on starting 1,4-dibromobenzene).

^{1}H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 8.06–8.14$ (m, 24H, C_6H_5 and C_6H_4, H_o vs. P, H_6 and H_7), 7.73 (t, 4H, $J = 7.5$ Hz, ArH$_p$, pyr, H_{13}), 7.43 (dd, 8H, $J_{P-H} = 1.8$ Hz, $J_{H-H} = 6.3$ Hz, C_6H_4, H_m vs. P, H_5), 7.37 (d, 8H,
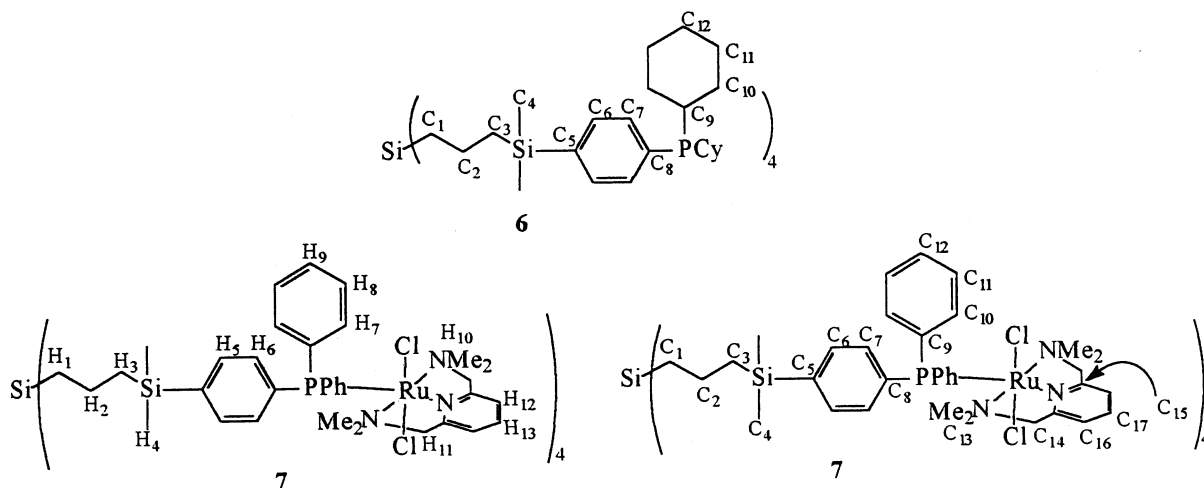
Scheme 3.

$J = 7.8$ Hz, ArH$_m$, pyr, H$_{12}$), 7.26–7.35 (m, 24H, C$_6$H$_5$, H$_{m,p}$ vs. P, H$_8$ and H$_9$), 3.98 (s, 16H, CH_2NMe$_2$, H$_{11}$), 2.06 (s, 48H, N(CH_3)$_2$, H$_{10}$), 1.40–1.26 (m, 8H, C–CH_2–C, H$_2$), 0.76 (t, 8H, $J = 8.1$ Hz, CH_2–Si–Ar, H$_3$), 0.52 (t, 8H, $J = 8.1$ Hz, CH_2–Si–CH_2, H$_1$), 0.19 (s, 24H, SiMe, H$_4$). ^{13}C{^{1}H}-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 162.1$ (C$_o$ to N py, C$_{15}$), 140.4 (d, $J = 1.2$ Hz, Ar–C–Si, C$_5$), 140.2 (d, $J = 30.9$ Hz, C$_{ipso}$–P of C$_6$H$_4$, C$_8$), 139.3 (d, $J = 31.6$ Hz, C$_{ipso}$–P of C$_6$H$_5$, C$_9$), 135.4 (C$_p$, py, C$_{17}$), 134.7 (d, $J = 9.2$ Hz, C$_6$H$_5$–C *ortho* vs. C$_{ipso}$–P, C$_{10}$), 133.7 (d, $J = 9.1$ Hz, C$_6$H$_4$–C *ortho* vs. C$_{ipso}$–P, C$_7$), 132.9 (d, $J = 7.9$ Hz,C$_6$H$_4$–C *meta* vs. C$_{ipso}$–P, C$_6$), 128.5 (ArC$_p$, PPh$_2$, C$_{12}$), 127.7 (d, $J = 8.5$ Hz, C$_6$H$_5$–C *meta* vs. C$_{ipso}$–P, C$_{11}$), 119.7 (C$_m$, py, C$_{16}$), 74 (CH_2N(CH$_3$)$_2$, C$_{14}$), 55.7 (N(CH_3)$_2$, C$_{13}$), 20.8 (C–CH_2–C, C$_2$), 19 (CH_2–Si–Ar, C$_3$), 17.7 (CH_2–Si–CH_2, C$_1$), -2.8 (SiMe, C$_4$). ^{31}P{^{1}H}-NMR (121 MHz, CD$_2$Cl$_2$): $\delta = 38.2$. MS (MALDI-TOF): $m/z = 331.14$ [Ru($NN'N$)Cl]$^+$ (calc. 330.4), 363.00 [Ru($NN'N$)Cl$_2$] (calc. 365.3), 1490.00 [CS–PPh$_2$-ox1] (calc. 1490.19), 1511.44 [CS–PPh$_2$-ox2] (calc. 1506.19), 398.83 [Ru($NN'N$)Cl$_3$]$^-$ (calc. 401.8).

4.5. Synthesis of G0–SiMe$_2$–PCy$_2$–[Ru] (**8**)

To a solution of the bridged Ru-complex, **2** (0.08 g, 0.17 mmol), in CH$_2$Cl$_2$ (8 ml) was added a solution of **6** (0.064 g, 0.042 mmol) in CH$_2$Cl$_2$ (15 ml). The resulting reaction mixture was stirred for 15 min at r.t., whereupon the mixture was concentrated to a third. Then Et$_2$O–pentane (1:5) was added to precipitate the crude product. After washing with the mixture of Et$_2$O–pentane (1:5) a brown viscous slurry of CS–PCy$_2$–[Ru] was obtained.

^{1}H-NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 6.76$–6.63 (m, 16H, ArH), 6.98 (t, 4H, $J = 7.5$ Hz, ArH$_p$, pyr), 6.36 (d, 8H, $J = 7.8$ Hz, ArH$_m$, pyr), 3.72 (s, 16H, CH_2NMe$_2$), 2.27 (s, 48H, N(CH_3)$_2$), 0.34 (s, 24H, SiMe).

^{31}P{^{1}H}-NMR (121 MHz, CD$_2$Cl$_2$): $\delta = 12.5$

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References

[1] (a) J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, Nature 372 (1994) 659. (b) M.A. Hearshaw, J.R. Moss, J. Chem. Soc. Chem. Commun. 1 (1999) 1. (c) C. Gorman, Adv. Mater. 10 (1998) 295. (d) E. Constable, P. Harverson, Inorg. Chim. Acta 252 (1996) 9. (e) C. Galliot, D. Prévoté, A.M. Caminade, J.P. Majoral, J. Am. Chem. Soc. 117 (1995) 5470. (f) G. L'abbé, B. Forier, W. Dehaen, J. Chem. Soc. Chem. Commun. 18 (1996) 2143. (g) J.W. Leon, M. Kawa, M.J. Fréchet, J. Am. Chem. Soc. 118 (1996) 8847. (h) M. Slany, A.M. Caminade, J.P. Majoral, Tetrahedron Lett. 37 (1996) 50 9053. (i) H. Frey, K. Lorenz, R. Mülhaupt, Macromol. Symp. 102 (1996) 19. (j) M. Jayaraman, M.J. Fréchet, J. Am. Chem. Soc. 120 (1998) 12996. (k) N.J.Hovestad, E.B. Eggeling, J.H. Heidbüchel, J.T.B.H. Jastrzebski, U. Kragl, W. Keim, D. Vögt, G. van Koten, Angew. Chem. Int. Ed. 30 (1999) 1655. (l) M. Petrucci-Samija, V. Guillemette, M. Dasgupta, A.K. Kakkar, J. Am. Chem. Soc. 121 (1999) 1968.

[2] (a) A. Miedaner, C.J. Curtis, R.M. Barkley, D.L. Dubois, Inorg. Chem. 33 (1994) 5482. (b) M. Bardaji, M. Kustos, A. Caminade, J.P. Majoral, Organometallics 16 (1997) 403. (c) M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem. Int. Ed. 36 (1997) 1526. (d) M. Slany, M. Bardaji, A.M. Caminade, B. Chaudret, J.P. Majoral, Inorg. Chem. 36 (1997) 1939. (e) M. Bardaji, A.M. Caminade, B. Chaudret, J.P. Majoral, Organometallics 16 (1997) 3489. (f) C. Köllner, B. Pugin, A. Togni, J. Am. Chem. Soc. 120 (1998) 10274. (g) C. Valério, E. Alonso, J. Ruiz, J.C.D. Blais-Astruc, Angew. Chem. Int. Ed. Engl. 38 (1999) 1747. (h) J. Issberner, M. Böhme, S. Grimme, M. Nieger, W. Paulus, F. Vögtle, Tetrahedron: Asymm. 7 (1996) 2223.

[3] R.A.T.M. Abbenhuis, J. Boersma, G. van Koten, J. Org. Chem. 63 (1998) 4282.

[4] I. del Río, R.A. Gossage, M. Lutz, A.L. Spek, G. van Koten, J. Organomet. Chem. 583 (1999) 69.

[5] B. Richter, E. De Wolf, G. van Koten, B.J. Deelman, J. Mol. Cat. 145 (1999) 317.

[6] R.A.T.M. Abbenhuis, I. del Río, M.M. Bergshoef, J. Boersma, N. Veldman, A.L. Spek, G. van Koten, Inorg. Chem. 37 (1998) 1750.

[7] A.W. van de Made, P.W.N.M. van Leeuwen, J. Chem. Soc. Chem. Commun. 19 (1992) 1400.

[8] G0 = tetraallylsilane; G0–SiMe$_2$Cl = tetraallylsilane, silated with HSiMe$_2$Cl.

[9] The different hydrogen and carbon atoms are labelled in Scheme 3.