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Inorganica Chimica Acta 334 (2002) 113–121

Inorganica Chimica Acta

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Supported organometallic complexes Part 31: diaminediphosphineruthenium(II) precursor complexes for parallel synthesis in interphases☆

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Received 12 September 2001; accepted 10 December 2001

Dedicated to Professor Andrew Wojcicki

Abstract

The hemilabile, triethoxysilyl functionalized ether–phosphine ligand **4**(**T**^{o}) was obtained by reaction of $PhP(H)CH_2CH_2OCH_3$ (**2**) with 4-fluorobenzylamine in 1,1′-dimethoxyethane in the presence of potassium and subsequent treatment of the resulting coupling product **3** with $(EtO)_3Si(CH_2)_3NCO$ in dichloromethane. The modified ligand **4**(**T**^{o}) was used in the synthesis of a matrix of T-silyl functionalized ruthenium(II) complexes $Cl_2Ru(P\sim O)_2$(diamine) [**6a**(**T**^{o})–**6g**(**T**^{o})] by addition of a series of aliphatic and aromatic diamines **a**–**g** to the bis(chelated) precursor complex $Cl_2Ru(P\sim O)_2$ [**5**(**T**^{o})]. The corresponding monocationic ruthenium(II) complexes [$ClRu(P\cap O)(P\sim O)$(diamine)][BF_4] [**7a**(**T**^{o})–**7g**(**T**^{o})] were available by chloride abstraction from **6a**(**T**^{o}) to **6g**(**T**^{o}) with $AgBF_4$ or $TlPF_6$ in dichloromethane. Only in the case of **6a**(**T**^{o}) it was possible to partially abstract both chlorides to give the dicationic complex [$Ru(P\cap O)_2$(diamine)] [PF_6]$_2$ [**8a**(**T**^{o})] in low yields. Complexes **6a**(**T**^{o})–**6g**(**T**^{o}) and **7a**(**T**^{o})–**7g**(**T**^{o}) can be regarded as valuable precursors for sol–gel processing to carry out parallel synthesis in interphases in the field of catalysis.

Keywords: Ruthenium complexes; Diamine ligands; Hemilabile ligands; Interphase chemistry

1. Introduction

An intermediate step between combinatorial chemistry and traditional synthesis is parallel synthesis with commonly one compound per well [2,3], coupled to automated screens. Recently this technique was transferred to heterogeneous [4–7] and homogeneous [8,9] catalysis. In a recent paper [10], we reported on a synthetic route to a set of neutral and cationic diamine-bis(ether-phosphine)ruthenium(II) complexes and their complete structural characterization. Compounds of this type are potential candidates for the application of parallel methods. Diaminediphosphineruthenium(II) complexes with classical phosphine ligands were already successfully employed in the catalytic hydrogenation of unsaturated ketones with high diastereo- and enantioselectivity (Scheme 1) [11–15]. Subsequent investigations concentrate on the combination of interphase chemistry and parallel synthesis. Interphase catalysts demonstrate a great importance since they are able to combine the advantages of homogeneous and heterogeneous catalysis with a marked reduction of notorious drawbacks like leaching and reduced catalytic activity of the reactive centers [16].

Here we wish to present the preparation and characterization of a variety of diamine-bis(ether-phosphine)ruthenium(II) complexes which function as suitable precursors for parallel synthesis in interphases. An imperative prerequisite to meet these conditions is the generation of a novel phosphine which is provided with an adequate spacer carrying a triethoxysilyl group (T-silyl) at the periphery of the ligand system and the utilization of a series of different and easily accessible diamines as co-ligands to establish an array of ruthe-

☆ For Part 30, see Ref. [1].

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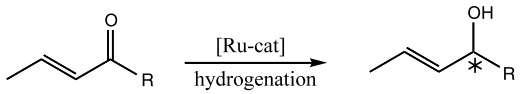
0020-1693/02/$ - see front matter
PII: S0020-1693(02)00749-1



Scheme 1.

nium(II) complexes for the mentioned purpose. To increase the catalytic activity by producing empty coordination sites also cationic forms of the complexes are prepared. The ether moieties incorporated into the phosphine ligands play a significant role, because they protect empty coordination sites at the metal center and hence the stability of these complexes is increased [17,18]. Such systems with T-silyl functions are suited to be subjected in a further step to a sol–gel process [16] in the presence of appropriate co-condensation agents to achieve highly mobile stationary phases.

2. Experimental

2.1. General comments

All experiments were carried out under an atmosphere of dry argon by use of standard Schlenk techniques. Solvents were dried with appropriate reagents, distilled, degassed, and stored under argon.

$RuCl_3 \cdot 3H_2O$ was purchased from ChemPur, 1,8-diaminonaphthaline, $ClCH_2CH_2OCH_3$, *n*-BuLi, *p*-fluorobenzylamine, and $AgBF_4$ were available from Fluka. 3-(Triethoxysilyl)propyl isocyanate was obtained from Aldrich. 1,2-Diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-phenylenediamine, 2,2′-bipyridine, 1,10-phenanthroline were purchased from Merck, and $TlPF_6$ was bought from Strem. The precursor complex $RuCl_2(PPh_3)_3$ was prepared according to the literature [19]. Elemental analyses were performed with an Elementar Vario EL analyzer. Mass spectra were acquired on a Finnigan MAT 711A modified by AMD (8 kV, 303 K) and reported as mass/charge (*m*/*z*). ESI FTICR MS measurements were carried out with a passively shielded 4.7 T APEX^{TM}II ESI MALDI FTICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany). High resolution $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies and standards are as follows: $^{31}P\{^1H\}$ NMR 101.25 MHz, $^{13}C\{^1H\}$ 62.90 MHz. ^{13}C chemical shifts were measured relative to deuterated solvent peaks, which are reported relative to TMS. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 ($\delta = 0$). The assignment of the ^{13}C NMR data is based on the 135 DEPT experiment and the comparison of the appropriate starting compound. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer.

2.2. Preparation of compound **1**

Phenylphosphinic acid (180.0 g, 1.32 mol) was heated in a simple distillation apparatus equipped with an air-cooling condenser. By controlling the internal temperature, the acid melts at about 82 °C and by gradual heating it started to decompose at 220 °C. The temperature should not exceed 260 °C. The crude product was dried with Na_2SO_4 to eliminate water which was formed together with benzene as a by-product. The phosphine **1** was distilled to yield 50 g (38%) of a colorless air sensitive oil. B.p. 433 K. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) −120.0 (s). ^1H NMR ($CDCl_3$): δ (ppm) 4.22 (d, $^1J_{PH} = 201$ Hz, PH_2), 7.40–7.75 (5H, C_6H_5).

2.3. Preparation of compound **2** [20]

A solution of *n*-BuLi in *n*-hexane (60.28 ml of a 1.6 M solution) was added dropwise to a solution of phenylphosphine (10.0 g, 90.8 mmol) in THF (100 ml). The yellow solution consisting of C_6H_5PHLi was stirred 30 min at ambient temperature. Then a solution of $ClCH_2CH_2OCH_3$ (8.7 g, 91.85 mmol) in THF (50 ml) was added dropwise within 10 min. Subsequently the solution was stirred for another 30 min under reflux to complete the reaction and then it was cooled to 20 °C. To the colorless mixture a degassed aqueous solution saturated with NH_4Cl (250 ml) was added and the organic layer was separated. The solution was dried with Na_2SO_4 and separated from the solid residue. After evaporation of the volatile materials under vacuum the crude product was distilled to yield 10.82 g (70%) of **2** as a colorless air sensitive oil. B.p. 333 K (5 mbar). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) −61.6 (s). ^1H NMR ($CDCl_3$): δ (ppm) 1.89 (m, 2H, PCH_2), 3.09 (s, 3H, OCH_3), 3.27 (m, 2H, PCH_2CH_2), 4.03 (d, $^1J_{PH} = 205$ Hz, PH), 7.04–7.38 (5H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 23.1 (d, $^1J_{PC} = 14.2$ Hz, PCH_2), 57.7 (s, OCH_3), 70.5 (d, $^2J_{PC} = 7.1$ Hz, PCH_2CH_2).

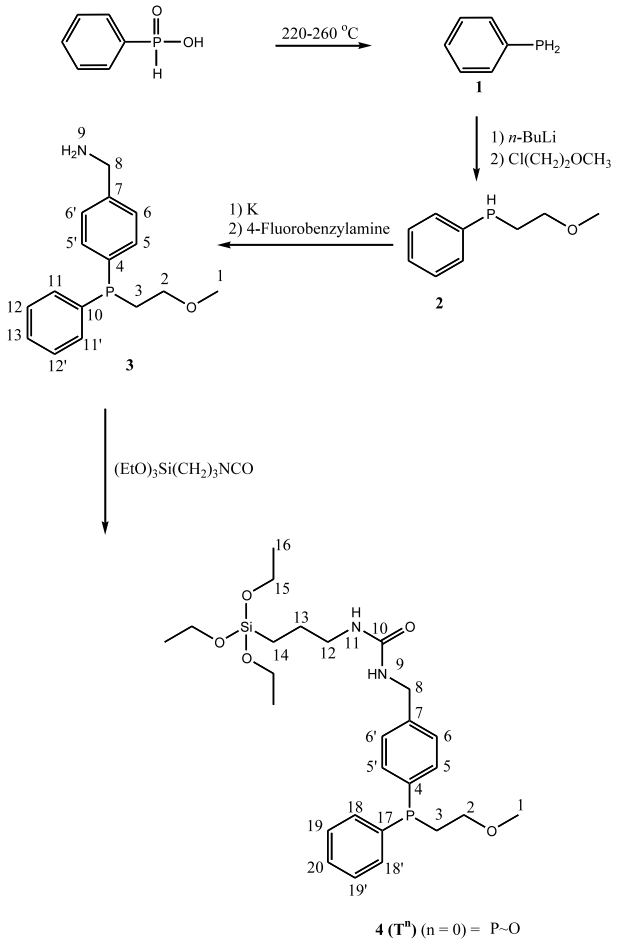
2.4. Preparation of compound **3**

Small pieces of metallic potassium (1.16 g, 29.8 mmol) were added to a solution of $PhP(H)CH_2CH_2OCH_3$ (**2**) (5 g, 29.8 mmol) in 1,1′-dimethoxyethane (DME) (50 ml). The reaction started immediately evolving molecular hydrogen and the corresponding potassium phosphide was formed. After the potassium had been consumed the red solution of $C_6H_5PK(CH_2CH_2OCH_3)$ was added dropwise within 3 h to a solution of *p*-fluorobenzylamine (3.9 g, 31.24 mmol) in DME (150 ml). The color of the solution changed gradually to deep green. The reaction mixture was stirred for 6 h at ambient temperature, then another 6 h at 50 °C followed by reflux for 24 h. The solvent was evaporated under

reduced pressure and the yellowish residue was washed with water (100 ml). The crude product was dried and isolated by distillation under vacuum to produce 5.3 g (65%) of **2**. B.p. 471 K (10^{-3} mbar). MS (EI): *m/z* 273.2 [M^+]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) −22.2 (s). ^1H NMR ($CDCl_3$): δ (ppm) 1.27 (s, $2H^9$), 2.26 (t, $^2J_{HH}$ = 7.5 Hz, $2H^3$), 3.17 (s, $3H^1$), 3.42 (m, $2H^2$), 3.71 (s, $2H^8$), 7.10–7.23 (m, H^5, H^6), 7.25–7.65 (m, H^{11}, H^{12}, H^{13}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 29.2 (d, $^1J_{PC}$ = 12.8 Hz, C^3), 46.6 (s, C^8), 58.9 (s, C^1), 70.2 (d, $^2J_{PC}$ = 23.6 Hz, C^2), 127.6 (d, $^4J_{PC}$ = 7.4 Hz C^6), 128.8 (m, C^{12}, C^{13}), 136.6 (d, $^1J_{PC}$ = 12.3 Hz, C^4), 138.9 (d, $^1J_{PC}$ = 12.8 Hz, C^{10}), 132.7 (C^5, C^{11}), 146.9 (s, C^7). IR (KBr, cm^{-1}): $\nu(NH_2)$ 3378, $\nu_{as}(C_2O)$ 1109.

2.5. Preparation of ligand 4(T°) (see Scheme 2)

To a solution of compound **3** (5.0 g, 18.29 mmol) in dichloromethane (250 ml) a solution of 3-(triethoxysilyl)propyl isocyanate (4.5 g, 18.29 mmol) in CH_2Cl_2 (20 ml) was added dropwise. The reaction mixture was stirred at room temperature (r.t.) for 24 h. The solvent



T = T type of silicon atom (three oxygen neighbors)
n = 0 - 3 (number of Si-O-Si bonds)

Scheme 2.

was evaporated to dryness to give 9.5 g (100%) of **3**. M.p. 117 °C. MS (EI): *m/z* 520 [M^+]. *Anal*. Calc. for $C_{26}H_{41}N_2O_5PSi$ (520.67): C, 59.98; H, 7.94; N, 5.38. Found: C, 59.76; H, 7.65; N, 5.36%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) −22.1 (s). ^1H NMR ($CDCl_3$): δ (ppm) 0.64 (m, $2H^{14}$), 1.22 (t, $^3J_{HH}$ = 7.0 Hz, $9H^{16}$), 1.61 (m, $2H^{13}$), 2.37 (t, $^3J_{HH}$ = 7.6 Hz, $2H^3$), 3.17 (m, $2H^{12}$), 3.21 (s, $3H^1$), 3.50 (q, $^3J_{HH}$ = 7.6 Hz, $2H^2$), 3.86 (q, $^3J_{HH}$ = 7.0 Hz, $6H^{15}$), 4.34 (d, $^3J_{HH}$ = 5.9 Hz, $2H^8$), 4.94 (t, $^3J_{HH}$ = 6.1 Hz, $1H^{11}$), 5.14 (t, $^3J_{HH}$ = 5.9 Hz, $1H^9$), 7.20–7.50 (m, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 7.7 (s, C^{14}), 18.4 (s, C^{16}), 23.8 (s, C^{13}), 28.9 (d, $^1J_{PC}$ = 12.8 Hz, C^3), 43.0 (s, C^{12}), 44.1 (s, C^8), 53.8 (s, C^{15}), 58.8 (s, C^1), 69.9 (d, $^2J_{PC}$ = 23.6 Hz, C^2), 127.6 (d, $^3J_{PC}$ = 6.7 Hz, C^6), 128.7 (d, $^3J_{PC}$ = 6.7 Hz, C^{19}), 128.8 (s, C^{20}), 132.7 (d, $^2J_{PC}$ = 16.8 Hz, C^5), 133.0 (d, $^2J_{PC}$ = 17.5 Hz, C^{18}), 137.0 (d, $^1J_{PC}$ = 12.1 Hz, C^4), 138.4 (d, $^1J_{PC}$ = 12.1 Hz, C^{17}), 140.5 (s, C^7), 158.5 (s, C^{10}). IR (KBr, cm^{-1}): ν(NH) 3329, ν(C=O) 1597, $\nu_{as}(C_2O)$ 1111, ν(SiO) 1077.

2.6. Preparation of 5(T°)

A solution of **4**(T°) (3.3 g, 6.29 mmol) in dichloromethane (15 ml) was added to a solution of $RuCl_2(PPh_3)_3$ (3.0 g, 3.15 mmol) in the same solvent (15 ml). The reaction mixture was stirred for 3 h, then the product was precipitated from the solvent by adding dropwise diethyl ether (100 ml). This procedure was repeated two times and the solvent was removed by decanting. The pink-colored precipitate was collected by filtration (P3) and washed three times with diethyl ether (50 ml). Then the product was dried under vacuum to yield 3.6 g (95%) of **5**(T°). MS (FAB, NBA, 50 °C): *m/z* 1213 [M^+]. *Anal*. Calc. for $C_{26}H_{41}N_2O_5PSi$ (1213.32): C, 51.48; H, 6.81; N, 4.62. Found: C, 51.49; H, 6.74; N, 4.48%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) −68.6 (s). ^1H NMR ($CDCl_3$): δ (ppm) 0.56 (m, $4H^{14}$), 1.3 (t, $^3J_{HH}$ = 6.9 Hz, $18H^{16}$), 1.53 (m, $4H^{13}$), 2.82 (m, $4H^3$), 3.09 (m, $4H^{12}$), 3.65–3.85 (m, $6H^1+12H^{15}$), 3.9–4.44 (m, $4H^2+4H^8$), 5.51 (m, $2H^{11}$), 5.61 (t, $^3J_{HH}$ = 5.8 Hz, $2H^9$), 6.78–7.30 (m, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 7.8 (s, C^{14}), 18.5 (s, C^{16}), 23.9 (s, C^{13}), 31.4 (m, C^3), 43.1 (s, C^{12}), 43.5 (s, C^8), 58.6 (s, C^{15}), 62.4 (s, C^1), 72.6 (s, C^2), 133.0 (m, C^{18}), 142.1 (s, C^7), 159.2 (s, C^{10}), 125–160 (C_6H_5, C_6H_4). IR (KBr, cm^{-1}): ν(NH) 3352, ν(C=O) 1558.

2.7. General procedure for the preparation of the neutral complexes 6a(T°)–6g(T°)

To a stirred solution of **2** in 25 ml of dichloromethane was added dropwise the corresponding diamine **a**–**g** (5% excess) dissolved in 25 ml of dichloromethane. The solution was stirred for 45 min at r.t. and concentrated to about 5 ml under reduced pressure. Addition of 80 ml

of diethyl ether caused a precipitation of a solid which was filtered off (P3), washed three times with 25 ml of diethyl ether and dried under vacuum.

*2.7.1. Preparation of **6a**(**T**^{o})*

5(**T**^{o}) (300 mg, 0.247 mmol) was reacted with the diamine **a** (17.4 μl, 0.289 mmol) to give 290 mg (92%) of **6a**(**T**^{o}) as a yellow powder. FT ICR MS: *m*/*z* 1237.5 [M^+–Cl]. *Anal.* Calc. for $C_{54}H_{90}Cl_2N_6O_{10}P_2RuSi_2$ (1273.42): C, 50.93; H, 7.12; N, 6.60. Found: C, 50.91; H, 7.12; N, 6.50%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 38.7 (s). ^1H NMR ($CDCl_3$): δ (ppm) 0.58 (m, 4H^{14}), 1.3 (t, $^3J_{HH} = 6.9$ Hz, 18H^{16}), 1.56 (m, 4H^{13}), 2.3 (m, 4H^3), 2.6–2.9 (br, 8H, CH_2NH_2), 3.00 (s, 6H^1), 3.0–3.2 (m, 4H^{12}+4H^2), 3.73 (q, $^3J_{HH} = 6.9$ Hz, 12H^{15}), 4.1–4.4 (br, 4H^8), 5.5 (br, 2H^{11}), 5.83 (br, 2H^9), 6.9–7.6 (m, 18H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 7.8 (s, C^{14}), 18.4 (s, C^{16}), 23.9 (s, C^{13}), 25.9 (m, C^3), 43.0 (s, C^{12}), 43.5 and 43.5 (2s, C^8, CH_2NH_2), 58.5 (s, C^{15}), 58.2 (s, C^1), 69.2 (s, C^2), 133.0 (m, C^{18}), 141.1 (s, C^7), 159.0 (s, C^{10}), 125–160 (C_6H_5, C_6H_4). IR (KBr, cm^{-1}): ν(NH) 3339, ν(C=O) 1558.

*2.7.2. Preparation of **6b**(**T**^{o})*

5(**T**^{o}) (300 mg, 0.247 mmol) was reacted with the diamine **b** (21.7 μl, 0.292 mmol) to give 172 mg (54%) of **6b**(**T**^{o}) as a yellow powder. FT ICR MS: *m*/*z* 1251.5 [M^+–Cl]. *Anal.* Calc. for $C_{55}H_{92}Cl_2N_6O_{10}P_2RuSi_2$ (1287.45): C, 51.31; H, 7.20; N, 6.53. Found: C, 51.08; H, 6.91; N, 6.13%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 40.0 (s). ^1H NMR ($CDCl_3$): δ (ppm) 0.58 (m, 4H^{14}), (t, $^3J_{HH} = 7.0$ Hz, 18H^{16}), 1.56 (m, 4H^{13}), 2.4 (m, 4H^3), 2.75–2.97 (br m, 10H, $CH_2CH_2CH_2(NH_2)_2$), 3.05 (s, 6H^1), 3.06–3.32 (m, 4H^{12}+4H^2), 3.8 (q, $^3J_{HH} = 7.0$ Hz, 12H^{15}), 4.1–4.6 (br, 4H^8), 5.3 (br, 2H^9), 5.9 (br, 2H^{11}), 6.9–7.6 (m, 18H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 8.1 (s, C^{14}), 18.7 (s, C^{16}), 24.4 (s, C^{13}), 26.5 (m, C^3), 29.9 (s, $NH_2CH_2\mathit{C}H_2$), 39.7 (s, $NH_2\mathit{C}H_2CH_2$), 43.4 (s, C^{12}), 43.6 (s, C^8), 58.2 (s, C^1), 58.5 (s, C^{15}), 69.6 (s, C^2), 133.0 (m, C^{18}), 141.7 (s, C^7), 159.6 (s, C^{10}), 125–160 (C_6H_5, C_6H_4). IR (KBr, cm^{-1}): ν(NH) 3320, ν(C=O) 1569.

*2.7.3. Preparation of **6c**(**T**^{o})*

5(**T**^{o}) (300 mg, 0.247 mmol) was reacted with the diamine **c** (22.2 μl, 0.292 mmol) to give 127 mg (40%) of **6c**(**T**^{o}) as a yellow powder. FT ICR MS: *m*/*z* 1251.5 [M^+–Cl]. *Anal.* Calc. for $C_{55}H_{92}Cl_2N_6O_{10}P_2RuSi_2$ (1287.45): C, 51.31; H, 7.20; N, 6.53. Found: C, 51.06; H, 7.06; N, 6.77%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 39.8 (s). ^1H NMR ($CDCl_3$): δ (ppm) 0.60 (m, 4H^{14}), 1.0 (m, 3H, $CHC\mathit{H}_3$), 1.17 (t, $^3J_{HH} = 6.9$ Hz, 18H^{16}), 1.58 (m, 4H^{13}), 2.8 (s, 1H, $C\mathit{H}CH_3$), 3.05 (s, 6H^1), 2.2–3.0 (br, CH_2NH_2 (4H)+4H^3), 3.0–3.3 (m, 4H^{12}+4H^2), 3.8 (q, $^3J_{HH} = 6.9$ Hz, 12H^{15}), 4.3 (br, 4H^8), 6.0 (br, 2H^9), 6.4 (br, 2H^{11}), 6.9–7.6 (m, 18H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 7.8 (s, C^{14}), 18.3 (s, C^{16}), 20.1 (s, $NH_2CH\mathit{C}H_3$), 24.0 (s, C^{13}), 26.2 (m, C^3), 43.0 (s, C^{12}), 43.2 (s, C^8), 49.5 (s, NH_2CH_2), 49.5 (s, NH_2CH), 58.0 (s, C^1), 58.4 (s, C^{15}), 69.2 (s, C^2), 133.0 (m, C^{18}), 141.4 (s, C^7), 159.4 (s, C^{10}), 125–160 (C_6H_5, C_6H_4). IR (KBr, cm^{-1}): ν(NH) 3339, ν(C=O) 1556.

*2.7.4. Preparation of **6d**(**T**^{o})*

5(**T**^{o}) (300 mg, 0.247 mmol) was reacted with the diamine **d** (28.1 mg, 0.260 mmol) to give 314 mg (96%) of **6d**(**T**^{o}) as a brown powder. FT ICR MS: *m*/*z* 1286.5 [M^+–Cl]. *Anal.* Calc. for $C_{58}H_{90}Cl_2N_6O_{10}P_2RuSi_2$ (1321.46): C, 52.72; H, 6.86; N, 6.36. Found: C, 52.88; H, 6.77; N, 6.63%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 40.9 (s). ^1H NMR ($CDCl_3$): δ (ppm) 0.64 (m, 4H^{14}), 1.20 (t, $^3J_{HH} = 7.0$ Hz, 18H^{16}), 1.61 (m, 4H^{13}), 2.47 (m, 4H^3), 3.11 (s, 6H^1), 3.16 (m, 4H^{12}), 3.31 (m, 4H^2), 3.80 (q, $^3J_{HH} = 7.0$ Hz, 12H^{15}), 4.3 (br, 4H^8), 4.5 (br, 4H, $C_6H_4(N\mathit{H}_2)_2$), 6.0 (br, 2H^{11}) 6.4 (br, 2H^9), 6.87–7.0 (m, 4H, C_6H_4), 7.0–7.6 (m, 18H, C_6H_4, C_6H_5), $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 8.0 (s, C^{14}), 18.6 (s, C^{16}), 24.3 (s, C^{13}), 26.6 (m, C^3), 43.3 (s, C^{12}), 43.5 (s, C^8), 58.4 (s, C^1), 58.7 (s, C^{15}), 69.5 (s, C^2), 116.5 (s, C^2-amine), 120.0 (s, C^3-amine) 131.9 (m, C^2-amine), 133.8 (m, C^{18}), 141.0 (s, C^7), 159.6 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, and C-amine). IR (KBr, cm^{-1}): ν(NH) 3308, ν(C=O) 1556.

*2.7.5. Preparation of **6e**(**T**^{o})*

5(**T**^{o}) (300 mg, 0.247 mmol) was reacted with the diamine **e** (41.1 mg, 0.260 mmol) to give 309 mg (91%) of **6e**(**T**^{o}) as a brown powder. FT ICR MS: *m*/*z* 1335.5 [M^+–Cl]. *Anal.* Calc. for $C_{62}H_{92}Cl_2N_6O_{10}P_2RuSi_2$ (1371.52): C, 54.30; H, 6.76; N, 6.13. Found: C, 54.03; H, 6.35; N, 6.08%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 44.0 (s). ^1H NMR (CD_2Cl_2): δ (ppm) 0.51 (m, 4H^{14}), 1.08 (t, $^3J_{HH} = 7.0$ Hz, 18H^{16}), 1.49 (m, 4H^{13}), 2.25 (m, 4H^3), 2.84 (s, 6H^1), 2.9–3.34 (m, 4H^{12}+4H^2), 3.69 (q, $^3J_{HH} = 7.0$ Hz, 2H^{15}), 4.0–5.5 (br, 4H^8, NH_2 (4H)), 6.0 (br, 2H^{11}), 6.4 (br, 2H^9), 6.2–7.0 (m, 6H-amine), 7.0–7.6 (m, 18H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 8.2 (s, C^{14}), 18.7 (s, C^{16}), 24.4 (s, C^{13}), 26.0 (m, C^3), 43.3 (br, C^{12}+C^8), 58.3 (s, C^1), 58.7 (s, C^{15}), 69.6 (s, C^2), 111.6 (s, C^2-amine), 119.5 (s, C^4-amine) 121.4 (s, C^3-amine), 136.9 (s, C^1-amine), 133.8 (m, C^{18}), 141.0 (s, C^7), 159.8 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, and C-amine). IR (KBr, cm^{-1}): ν(NH) 3307, ν(C = O) 1561.

*2.7.6. Preparation of **6f**(**T**^{o})*

5(**T**^{o}) (300 mg, 0.247 mmol) was reacted with the diamine **f** (40.5 mg, 0.259 mmol) to give 193 mg (57%) of **6f**(**T**^{o}) as a brown powder. FT ICR MS: *m*/*z* 1334.5 [M^+–Cl]. *Anal.* Calc. for $C_{62}H_{90}Cl_2N_6O_{10}P_2RuSi_2$ (1369.51): C, 54.37; H, 6.62; N, 6.14. Found: C, 53.98; H, 6.35; N, 5.98%. $^1P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 27.3 (s). ^1H NMR (CD_2Cl_2): δ (ppm) 0.48 (m, 4H^{14}), 1.07 (t, $^3J_{HH} = 7.0$ Hz, 18H^{16}), 1.44 (m, 4H^{13}), 2.67 (m,

$4H^3$), 2.95 (s, $6H^1$), 2.9–3.3 (m, $4H^{12}+4H^2$), 3.68 (q, $^3J_{HH}=7.0$ Hz, $12H^{15}$), 4.0–4.4 (br, $4H^8$), 5.7 (br, $2H^{11}$) 6.0 (br, $2H^9$), 7.0–7.8 (m, 18H, C_6H_4, C_6H_5), 7.8–8.7 (m, 6H, ($2H^1+2H^3+2H^4$, amine)), $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 8.0 (s, C^{14}), 18.6 (s, C^{16}), 24.3 (s, C^{13}), 26.4 (m, C^3), 43.3, 43.4 (2s, $C^{12}+C^8$), 58.3 (s, C^1), 58.7 (s, C^{15}), 69.6 (s, C^2), 121.2 (s, C^2-amine), 122.5 (s, C^4-amine), 137.3 (s, C^4-amine), 149.5 (s, C^1-amine), 158.8 (s, C^5-amine), 136.9 (s, C^1-amine), 133.8 (m, C^{18}), 141.0 (s, C^7), 159.4 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, C-amine). IR (KBr, cm^{-1}): ν(NH) 3345, ν(C=O) 1560.

2.7.7. Preparation of 6g(T°)

5(**T**°) (300 mg, 0.247 mmol) was reacted with the diamine **g** (46.7 mg, 0.259 mmol) to give 285 mg (83%) of **6g**(**T**°) as a red powder. FT ICR MS: *m*/*z* 1357.5 [M^+–Cl]. *Anal.* Calc. for $C_{64}H_{90}Cl_2N_6O_{10}P_2RuSi_2$ (1393.52): C, 55.16; H, 6.51; N, 6.03. Found: C, 54.82; H, 6.39; N, 6.01%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 27.3 (s). ^1H NMR (CD_2Cl_2): δ (ppm) 0.47 (m, $4H^{14}$), 1.2 (t, $^3J_{HH}=6.9$ Hz, $18H^{16}$) 1.4 (m, $4H^{13}$), 2.5–3.8 (m, $4H^3+6H^1+4H^{12}+4H^2$), 2.97 (s, $6H^1$), 3.8 (q, $^3J_{HH}=$ 6.9 Hz, $12H^{15}$), 3.8–4.4 (br, $4H^8$), 5.8 (br, $2H^{11}$), 6.2 (br, $2H^9$), 6.7–8.4 (m, 24H, C_6H_4, $C_6H_5+(2H^2+2H^3+2H^4$, amine)), 8.9 (m, ($2H^1$, amine)), $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 8.1 (s, C^{14}), 18.7 (s, C^{16}), 24.4 (s, C^{13}), 26.6 (m, C^3), 43.3 (br, $C^{12}+C^8$), 58.4 (s, C^1), 58.7 (s, C^{15}), 69.6 (s, C^2), 123.4 (s, C^2-amine), 126.5 (s, C^4-amine), 134.7 (s, C^3-amine), 149.5 (s, C^1-amine), 158.8 (s, C^6-amine), 133.8 (m, C^{18}), 141.0 (s, C^7), 159.4 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, and C-amine). IR (KBr, cm^{-1}): ν(NH) 3350, ν(C=O) 1555.

2.8. General procedure for the preparation of the cationic complexes 7a(T°)–7g(T°)

$AgBF_4$ or $TlPF_6$ (5% excess) was added to a solution of the neutral complexes in 25 ml of dichloromethane and stirred for 4 h. After filtration through silica gel the solution was concentrated to about 5 ml under reduced pressure. The cationic complex was precipitated by addition of 100 ml of diethyl ether, filtered off (P3) and washed three times with 25 ml of diethyl ether and dried under vacuum.

2.8.1. Preparation of 7a(T°)

6a(**T**°) (300 mg, 0.235 mmol) was reacted with $AgBF_4$ (48 mg, 0.247 mmol) to give 237 mg (76%) of **7a**(**T**°) as a yellow powder. FT ICR MS: *m*/*z* 1237.5 [M^+–BF_4]. *Anal.* Calc. for $C_{54}H_{90}BClF_4N_6O_{10}P_2RuSi_2$ (1324.77): C, 48.96; H, 6.85; N, 6.34. Found: C, 48.52; H, 6.48; N, 6.25%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) diastereomers a and b: (90%) 56.5 (d, $^2J_{PP}=37$ Hz, η^2-P∩O), 56.6 (d, $^2J_{PP}=36$ Hz, η^2-P∩O), 47.2 (d, $^2J_{PP}=36$ Hz, η^1-P∼O), 47.0 (d, $^2J_{PP}=37$ Hz, η^1-P∼O), diastereomer c: (10%) 57.4 (d, $^2J_{PP}=39$ Hz, η^2-P∩O), 50.7 (d, $^2J_{PP}=$ 39 Hz, η^1-P∼O). ^1H NMR ($CDCl_3$): δ (ppm) 0.54 (m, $4H^{14}$), 1.1 (m, $18H^{16}$), 1.52 (m, $4H^{13}$), 2.3–3.2 (br m, $4H^{12}+4H^2+CH_2NH_2$ (8H)), 3.08 (s, $3H^1$), 3.5 (s, $3H^1$), 3.7 (m, $12H^{15}$), 3.9–4.5 (br, $4H^8$), 6.1–6.4 (br, $2H^{11}+2H^9$), 6.9–7.6 (m, 18H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 7.8 (s, C^{14}), 18.4 (s, C^{16}), 23.9 (s, C^{13}), 31.1 (m, C^3), 43.0, 43.5, and 43.46 (m, C^{12}, C^8, CH_2NH_2), 58.6 (s, C^{15}), 58.2 (s, C^1), 68.5 (s, C^2), 69.3 (s, C^2), 133.0 (m, C^{18}), 141.0 (s, C^7), 158.0 (s, C^{10}), 125–160 (C_6H_5, C_6H_4). IR (KBr, cm^{-1}): ν(NH) 3340, ν(C=O) 1558. For this and the following complexes the ^1H and ^{13}C NMR data for only one diastereoisomer is given.

2.8.2. Preparation of 7b(T°)

6b(**T**°) (300 mg, 0.233 mmol) was reacted with $AgBF_4$ (48 mg, 0.247 mmol) to give 202 mg (65%) of **7b**(**T**°) as a yellow powder. FT ICR MS: *m*/*z* 1251.5 [M^+–BF_4]. *Anal.* Calc. for $C_{55}H_{92}BClF_4N_6O_{10}P_2RuSi_2$ (1338.8): C, 49.34; H, 6.93; N, 6.28. Found: C, 49.14; H, 6.90; N, 6.10%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 2 diastereomers, 53.5 (d, $^2J_{PP}=36$ Hz, η^2-P∩O), 52.9 (d, $^2J_{PP}=37$ Hz, η^2-P∩O), 45.7 (d, $^2J_{PP}=36$ Hz, η^1-P∼O), 45.1 (d, $^2J_{PP}=37$ Hz, η^1-P∼O). ^1H NMR ($CDCl_3$): δ (ppm) 0.57 (m, $4H^{14}$), (m, $18H^{16}$), 1.5 (m, $4H^{13}$), 2.1 (br m, $2H^3$), 2.3–3.3 (br, $2H^3+4H^{12}+4H^2+CH_2CH_2CH_2$-$(NH_2)_2$ (10H)), 3.05 (s, $3H^1$), 3.7 (br, $3H^1+12H^{15}$), 4.0–4.6 (br, $4H^8$), 5.3 (br, $2H^9$), 6.3 (br, $2H^{11}$), 6.7–8.2 (m, 18H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 8.0 (s, C^{14}), 18.6 (s, C^{16}), 24.3 (s, C^{13}), 26.3 (m, C^3), 28.5 (s, $NH_2CH_2\mathit{C}H_2$), 30.6 (m, C^3), 40.6 (s, $NH_2\mathit{C}H_2CH_2$), 42.9 (s, C^{12}), 43.3 (s, C^8), 58.4 (s, C^1), 58.6 (s, C^{15}), 60.9 (s, C^1), 68.3 (s, C^2), 73.9 (s, C^2), 133.0 (m, C^{18}), 141.0 (s, C^7), 159.2 (s, C^{10}), 125–160 (C_6H_5, C_6H_4). IR (KBr, cm^{-1}): ν(NH) 3313, ν(C=O) 1576.

2.8.3. Preparation of 7c(T°)

6c(**T**°) (300 mg, 0.233 mmol) was reacted with $AgBF_4$ (48 mg, 0.247 mmol) to give 218 mg (70%) of **7c**(**T**°) as a yellow powder. FT ICR MS: *m*/*z* 1251.5 [M^+–BF_4]. *Anal.* Calc. for $C_{55}H_{92}BClF_4N_6O_{10}P_2RuSi_2$ (1338.8): C, 49.34; H, 6.93; N, 6.28. Found: C, 49.10; H, 6.80; N, 6.20%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 58.0 (d, $^2J_{PP}=36$ Hz, η^2-P∩O), 56.3 (d, $^2J_{PP}=37$ Hz, η^2-P∩O), 56.1 (d, $^2J_{PP}=37$ Hz, η^2-P∩O), 46.0 (m, η^1-P∼O). ^1H NMR (CD_2Cl_2): δ (ppm) 0.51 (m, $4H^{14}$), 0.64 (br, 3H, $CHC\mathit{H}_3$), 1.18 (m, $18H^{16}$), 1.48 (m, $4H^{13}$), 2.8–3.0 (br, $C\mathit{H}CH_3+CH_2(NH_2)_2$ (6H)$+3H^1+4H^3+4H^{12}+4H^2$), 3.6 (br m, $3H^1+12H^{15}$), 4.2 (br s, $4H^8$), 6.2 (br m, $2H^9+2H^{11}$), 6.8–8.3 (m, 18H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 8.0 (s, C^{14}), 18.6 (m, C^{16}), 19.7 (s, $NH_2CH\mathit{C}H_3$), 24.3 (s, C^{13}), 30.2 (m, C^3), 32.1 (m, C^3), 43.3 (s, C^{12}), 43.6 (s, C^8), 51.2 (s, NH_2CH_2), 53.6 (s, NH_2CH), 58.2 (s, C^1), 58.7 (s, C^{15}), 60.6 (d, $^3J_{PC}=22.4$ Hz, C^2), 69.2 (s, C^2), 133.0 (m, C^{18}), 140.4 (s, C^7), 158.3 (s, C^{10}), 125–160 (C_6H_5, C_6H_4). IR (KBr, cm^{-1}): ν(NH) 3333, ν(C=O) 1572.

2.8.4. Preparation of 7d(T°)

6d(**T**°) (300 mg, 0.227 mmol) was reacted with $AgBF_4$ (47 mg, 0.241 mmol) to give 249 mg (80%) of **7d**(**T**°) as a brown powder. FT ICR MS: *m/z* 1286.5 [M^+–BF_4]. *Anal.* Calc. for $C_{58}H_{90}BClF_4N_6O_{10}P_2RuSi_2$ (1372.8): C, 50.74; H, 6.61; N, 6.12. Found: C, 50.34; H, 6.53; N, 6.01%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 38.6 (m, η^2-P∩O), 35.0 (d, $^2J_{PP}=30$ Hz, η^1-P∼O), 34.8 (d, $^2J_{PP}=31$ Hz, η^1-P∼O). ^1H NMR ($CDCl_3$): δ (ppm) 0.53 (m, $4H^{14}$), 1.13 (m, $18H^{16}$), 1.5 (m, $4H^{13}$), 2.6–3.2 (br m, $4H^3+3H^1+4H^{12}+4H^2$), 3.5 (m, $3H^1$), 3.7 (m, $12H^{15}$), 4.3 (br, $4H^8$), 6.1–6.8 (br, $C_6H_4(NH_2)_2$ (4H)+$2H^{11}$+$2H^9$), 6.8–8.0 (br, 22H, C_6H_4 (amine), C_6H_4, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 8.1(s, C^{14}), 18.7 (s, C^{16}), 23.8 (s, C^{13}), 24.3 (m, C^3), 43.6 (br, C+C8+C12), 58.4 (s, C^1), 58.8 (s, C^{15}), 61.5 (s, C^1), 59.5 (s, C^2), 68.1 (s, C^2), 123–136 (C_6H_5, C_6H_4, $C_6H_4(NH_2)_2$), 159.5 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, and C-amine). IR (KBr, cm^{-1}): ν(NH) 3336, ν(C=O) 1558.

2.8.5. Preparation of 7e(T°)

6e(**T**°) (300 mg, 0.219 mmol) was reacted with $AgBF_4$ (45 mg, 0.231 mmol) of to give 242 mg (78%) of **7e**(**T**°) as a brown powder. FT ICR MS: *m/z* 1335.5 [M^+–BF_4]. *Anal.* Calc. for $C_{62}H_{92}BClF_4N_6O_{10}P_2RuSi_2$ (1422.9): C, 52.34; H, 6.52; N, 5.91. Found: C, 51.96; H, 6.50; N, 5.93%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 61.5 (m, η^2-P∩O), 51.1 (m, η^1-P∼O), 49.1 (m, η^1-P∼O). ^1H NMR (CD_2Cl_2): δ (ppm) 0.44 (m, $4H^{14}$), 1.08 (m, $18H^{16}$), 1.36 (m, $4H^{13}$), 2.3–3.0 (br, $4H^3+3H^1+4H^{12}+4H^2$), 3.69 (m, $15H^{15}+3H^1$), 3.85–4.4 (br, $4H^8$), 6.0 (br, $2H^{11}$), 6.4 (br, $2H^9$), 6.1–6.8 (br, $C_{10}H_6(NH_2)_2$ (4H)+$2H^{11}$+$2H^9$), 7.0–7.6 (m, $C_{10}H_6(NH_2)_2$ (6H)+C_6H_4 (8H)+C_6H_5 (10H)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 8.0 (s, C^{14}), 18.6 (s, C^{16}), 24.1 (s, C^{13}), 26.7 (m, C^3), 30.9 (m, C^3), 43.3 (br, $C^{12}+C^8$), 58.3 (s, C^1), 58.8 (s, C^{15}), 62.6 (s, C^1), 69.6 (s, C^2), 72.3 (s, C^2), 120–138 (C_6H_5, C_6H_4, $C_{10}H_6(NH_2)_2$), 159.17 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, and C-amine). IR (KBr, cm^{-1}): ν(NH) 3351, ν(C=O) 1569.

2.8.6. Preparation of 7f(T°)

6f(**T**°) (300 mg, 0.219 mmol) was reacted with $TlPF_6$ (81 mg, 0.232 mmol) to give 232 mg (63%) of **7f**(**T**°) as a brown powder. FT ICR MS: *m/z* 1334.5 [M^+–PF_6]. *Anal.* Calc. for $C_{62}H_{90}ClF_6N_6O_{10}P_3RuSi_2$ (1479.02): C, 50.35; H, 6.13; N, 5.68. Found: C, 49.93; H, 5.82; N, 5.25%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) diastereomer a: (16%) 45.1 (d, $^2J_{PP}=33$ Hz, η^2-P∩O), 39.7 (d, $^2J_{PP}=33$ Hz, η^1-P∼O), diastereomer b: (84%) 44.8 (d, $^2J_{PP}=33$ Hz, η^2-P∩O), 40.5 (d, $^2J_{PP}=33$ Hz, η^1-P∼O). H^1 NMR (CD_2Cl_2): δ (ppm) 0.58 (m, $4H^{14}$), 1.07 (m, $18H^{16}$), 1.44 (m, $4H^{13}$), 2.3–3.4 (m, $4H^3+3H^1+4H^{12}+4H^2$), 3.68 (m, $12H^{15}+3H^1$), 3.75 (m, $15H^{15}+3H^1$), 4.0–4.5 (br, $4H^8$), 5.5–6.6 (br, $2H^{11}+2H^9$), 6.6–7.9 (m, 18H, C_6H_4, C_6H_5), 7.9–8.7 (m, $2H^1+2H^3+2H^4$, amine). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 8.0 (s, C^{14}), 18.6 (s, C^{16}), 24.2 (s, C^{13}), 28.0 (d, $^1J_{PC}=29$ Hz, C^3), 32.4 (m, C^3), 44.3, 44.6 (2s, $C^{12}+C^8$), 59.3 (s, C^1), 59.7 (s, C^{15}), 62.4 (s, C^1), 69.2 (s, C^2), 75.0 (s, C^2), 120–157 (C_6H_5, C_6H_4, $C_{10}H_{11}N_2$), 152.2 (s, C^1-amine) 158.8 (s, C^5-amine), 140.0 (s, C^7), 159.2 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, and C-amine). IR (KBr, cm^{-1}): ν(NH) 3418, ν(C=O) 1568.

2.8.7. Preparation of 7g(T°)

6g(**T**°) (300 mg, 0.215 mmol) was reacted with $TlPF_6$ (80 mg, 0.229 mmol) to give 224 mg (61%) of **7g**(**T**°) as a red powder. FT ICR MS: *m/z* 1357.5 [M^+–PF_6]. *Anal.* Calc. for $C_{64}H_{90}ClF_6N_6O_{10}P_3RuSi_2$ (1503.0): C, 51.14; H, 6.04; N, 5.59. Found: C, 50.82; H, 5.84; N, 5.28%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) diastereomer a: (12%) 45.7 (d, $^2J_{PP}=34$ Hz, η^2-P∩O), 39.9 (d, $^2J_{PP}=34$ Hz, η^1-P∼O), diastereomer b: (88%) 44.5 (d, $^2J_{PP}=34$ Hz, η^2-P∩O), 41.1 (d, $^2J_{PP}=34$ Hz, η^1-P∼O), ^1H NMR (CD_2Cl_2): δ (ppm) 0.52 (m, $4H^{14}$), 1.1 (m, $18H^{16}$), 1.5 (m, $4H^{13}$), 2.3–3.2 (br m, $4H^3+3H^1+4H^{12}+4H^2$), 3.7 (m, $12H^{15}+3H^1$), 3.8–4.6 (m, $4H^8$), 6.2 (m, $2H^{11}$), 6.4 (m, $2H^9$), 6.7–8.4 (m, C_6H_4 (8H)+C_6H_5 (10H)+$2H^2$+$2H^3+2H^4$, amine) 8.6 (m, $2H^1$, amine). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 7.9 (s, C^{14}), 18.6 (s, C^{16}), 24.3 (s, C^{13}), 29.3 (d, $^1J_{PC}=25.0$ Hz, C^3), 31.1 (d, $^1J_{PC}=29.0$ Hz, C^3), 43.4 (s, C^{12}), 43.2 (s, C^8), 58.2 (s, C^1), 58.7 (s, C^{15}), 61.4 (s, C^1), 68.0 (m, C^2), 73.9 (s, C^2), 126.5 (s, C^4-amine), 134.7 (s, C^3-amine), 149.6 (s, C^1-amine), 159.2 (s, C^6-amine), 133.8 (m, C^{18}), 141.0 (s, C^7), 159.7 (s, C^{10}), 125–160 (C_6H_5, C_6H_4, and C-amine). IR (KBr, cm^{-1}): ν(NH) 3412, ν(C=O) 1557.

2.9. Preparation of the dicationic complex 8a(T°)

6a(**T**°) (300 mg, 0.235 mmol) was added to $TlPF_6$ (1.235 g, 3.54 mmol) in 25 ml of dichloromethane and the mixture was refluxed for 24 h. After filtration through silica gel the solvent was reduced under vacuum to 5 ml. The dicationic complex was precipitated by addition of 100 ml of diethyl ether, filtered off (P3) and washed three times with 25 ml of diethyl ether. FT ICR MS: *m/z* 601 [M^{2+}–$2PF_6$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) dicationic complex **8a**(**T**°) (75%), 50.5 (d, $^2J_{PP}=36$ Hz, η^2-P∩O), 50.7 (d, $^2J_{PP}=35$ Hz, η^2-P∩O), 51.5 (d, $^2J_{PP}=35$ Hz, η^2-P∩O), 64.1 (d, $^2J_{PP}=36$ Hz, η^2-P∩O), 65.0 (d, $^2J_{PP}=36$ Hz, η^2-P∩O), 65.1 (d, $^2J_{PP}=35$ Hz, η^2-P∩O), **6a**(**T**°): (25%) 38.2 (s).

3. Results and discussion

3.1. Synthesis of the ligand 4(T°)

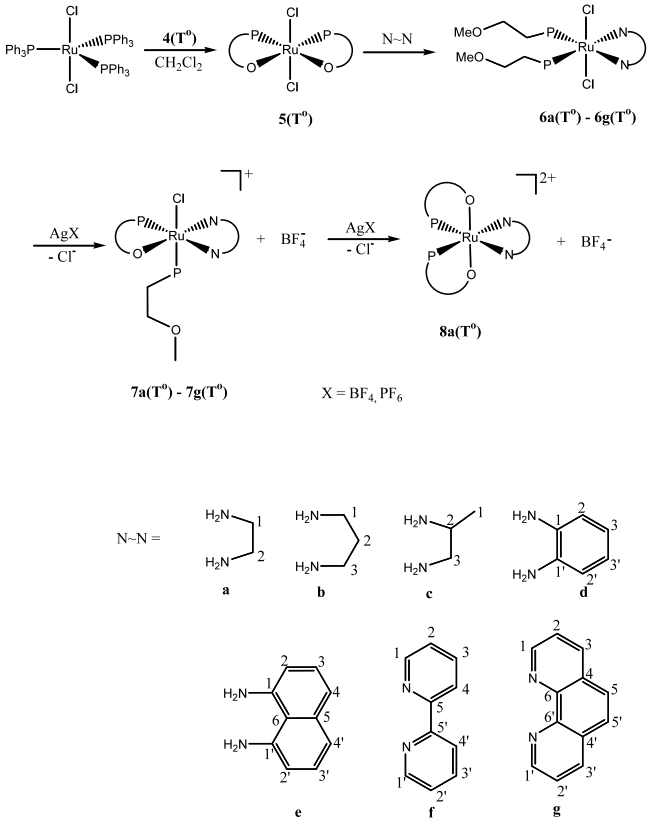
Starting compound is the phenylphosphine **1** which is easily obtained by thermolysis of phenylphosphinic acid

[21] (Scheme 2). With some modifications the synthesis of the ether–phosphine **2** was carried out according to a known procedure [20]. Reaction of **2** with potassium in diethoxyethane affords the corresponding phosphide, which in the presence of 4-fluorobenzylamine is transformed, to the ether–phosphine ligand **3**. Slow addition of the intermediate potassium phosphide to 4-fluorobenzylamine at 50 °C reduces the formation of by-products. The fluorine atom in the *para*-position of the benzylamine enhances the nucleophilic substitution at the aromatic ring [22]. Compound **3** is obtained as a colorless air sensitive liquid in high yields. The amine group provides an excellent substituent to introduce a spacer unit with a terminal T-silyl function. This step is realized if the ether–phosphine **3** is treated with 3-(triethoxysilyl)propylisocyanate in dichloromethane. The modified phosphine **4**($\mathbf{T^o}$) is isolated as colorless solid which readily dissolves in medium polar organic solvents and is sensitive to air and moisture.

Both the intermediate **3** and the ligand **4**($\mathbf{T^o}$) were completely characterized by NMR, IR, and mass spectroscopy. In the $^{31}P\{^1H\}$ NMR spectra a singlet each at $\delta = -22.2$ and -22.1 is observed. This indicates that the *para*-positioned spacer function exerts nearly no influence on the ^{31}P chemical shift. In the ^1H NMR spectrum of **3** a characteristic peak at $\delta = 1.26$ is assigned to the amino group. It disappears in the case of **4**($\mathbf{T^o}$) and because of $^3J_{HH}$ coupling two new triplets at $\delta = 4.9$ and 5.1 occur which correspond to the NH functions of the urea linkage. The $^{13}C\{^1H\}$ NMR spectrum of **4**($\mathbf{T^o}$) reveals a singlet at $\delta = 159.0$ which is attributed to the carbonyl group of the spacer unit. For a complete assignment of the ^1H and ^{13}C signals 2D ^1H COSY, $^{13}C\{^1H\}$ DEPT, and $^1H,^{13}C\{^1H\}$ HMQC NMR spectra were recorded (see Experimental). A characteristic absorption at 3378 cm^{-1} in the IR spectrum of **3** is assigned to the NH_2 substituent. Concerning the ligand **4**($\mathbf{T^o}$) two bands at 3329 and 1624 cm^{-1} are assigned to the NH and C=O stretching vibrations, respectively. The composition of the T-silyl functionalized ligand **4**($\mathbf{T^o}$) was corroborated by its EI mass spectrum, showing the molecular peak at $m/z =$ 520.2.

3.2. Synthesis and characterization of the $Cl_2Ru(P\sim O)_2$(diamine) complexes **6a**($\mathbf{T^o}$)–**6g**($\mathbf{T^o}$)

According to Scheme 3 the chelated bis(ether-phosphine)ruthenium(II) complex **5**($\mathbf{T^o}$) is synthesized by addition of the ligand **4**($\mathbf{T^o}$) to $Cl_2Ru(PPh_3)_3$ in CH_2Cl_2. The red air-sensitive solid **5**($\mathbf{T^o}$) was obtained after precipitation and separation of PPh_3. It is soluble in most organic media, but not in diethyl ether. A FAB mass spectrum of **5**($\mathbf{T^o}$) shows the isotopic distribution of the molecular ion, which is in agreement with the calculated spectrum. The $^{31}P\{^1H\}$ NMR spectrum of



Scheme 3.

5($\mathbf{T^o}$) in CH_2Cl_2 displays a singlet at $\delta = 68.6$ which is markedly downfield shifted compared with that of the ligand **4**($\mathbf{T^o}$). Such a behavior is typical for a phosphorus atom, which is incorporated into a five-membered ring [23]. For the same reason the ^1H ($\delta = 3.7$ ppm) and ^{13}C ($\delta = 72.6$) resonance of the OCH_3 group in the ^1H and $^{13}C\{^1H\}$ NMR spectrum, respectively, is also shifted to lower field.

Complex **5**($\mathbf{T^o}$) is provided with two weak ruthenium–oxygen bonds, which are easily cleaved by the strong nitrogen donors of the bidentate diamine ligands. If the bis(chelate)ruthenium(II) complex **5**($\mathbf{T^o}$) is treated with a slight excess of the corresponding diamine **a**–**g** the η^1-P coordinated mixed ligand complexes **6a**($\mathbf{T^o}$)–**6g**($\mathbf{T^o}$) are formed (Scheme 3). The yellow **[6a**($\mathbf{T^o}$)–**6c**($\mathbf{T^o}$)**]**, brown **[6d**($\mathbf{T^o}$)–**6f**($\mathbf{T^o}$)**]** and red **[6g**($\mathbf{T^o}$)**]** solids show similar solubility as **5**($\mathbf{T^o}$). Electron spray mass spectra were carried out and they give evidence of the molecular composition. Expectedly the ^{31}P singlets in the $^{31}P\{^1H\}$ NMR spectra of **6d**($\mathbf{T^o}$)–**6g**($\mathbf{T^o}$) are high field shifted compared to **5**($\mathbf{T^o}$) indicating that the phosphines are monodentately coordinated via the P atoms. These singlet peaks indicate that the phosphine groups are chemically equivalent. In principle three different structural isomers **A**–**C** are possible (Chart 1). From the NMR data presented here and the literature it is concluded that only structure **B** is realized

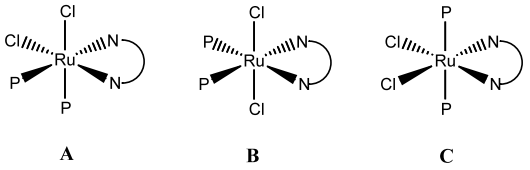


Chart 1.

in solution [10,11]. Since the spacer unit exerts nearly no influence on the ^{31}P chemical shift, the $^{31}P\{^1H\}$ NMR spectra of **6a**(**T**^{o})–**6g**(**T**^{o}) are comparable with those of the corresponding complexes without this spacer group [10]. In the ^1H NMR spectra of **6a**(**T**^{o})–**6g**(**T**^{o}) characteristic sets of signals occur which are assigned to the aliphatic and aromatic protons of the phosphine and diamine ligands, respectively, (Section 2). Furthermore the ^1H signals of the methoxy protons experience a considerable high field shift compared with **5**(**T**^{o}) which is in agreement with an η^1-P ~ O coordination. The $^{13}C\{^1H\}$ NMR spectra are consistent with these findings. As a typical example the ^{13}C resonance of the OCH_3 substituent is also high field shifted compared with **5**(**T**^{o}). Altogether it is emphasized that all NMR data are in close agreement with the analogous complexes for the homogeneous phase.

3.3. Synthesis and characterization of the mono and dicationic ruthenium(II) complexes 7a(T^o)–7g(T^o) and 8a(T^o), respectively

Complexes **6a**(**T**^{o})–**6g**(**T**^{o}) react in dichloromethane with different chloride scavengers such as $AgBF_4$ or $TlPF_6$ to give solutions from which the mono- and dicationic complexes **7a**(**T**^{o})–**7g**(**T**^{o}) and **8a**(**T**^{o}) can be isolated (Scheme 3). One chloride is abstracted with the simultaneous formation of a five-membered ring via ether coordination (η^2-P ∩ O coordination) by using an equivalent amount of one of the scavengers. Only in the case of **6a**(**T**^{o}) it was possible to abstract both chlorides in the presence of a large excess of $TlPF_6$ at 40 °C in CH_2Cl_2. But the reaction did not proceed quantitatively and the yield of **8a**(**T**^{o}) was low. It was not possible to transfer these reaction conditions to the other complexes **6b**(**T**^{o})–**6g**(**T**^{o}) due to the instability of the dicationic species. Electron spray mass spectra were recorded for **7a**(**T**^{o})–**7g**(**T**^{o}) which are in agreement with the expected values. In the transformation of compounds **6a**(**T**^{o})–**6g**(**T**^{o}) to **7a**(**T**^{o})–**7g**(**T**^{o}) the advantage of ether–phosphines becomes obvious since they protect the vacant coordination site. Hence further weakly coordinating ligands like acetonitrile, THF, or acetone are not necessary. In the solid state the cationic complexes **7a**(**T**^{o})–**7g**(**T**^{o}) are relatively insensitive while in solution they decompose in the presence of air and moisture. Due to their polar character they readily dissolve in solvents of medium polarity like dichloromethane.

Due to the existence of three chiral centers resulting from the two different phosphorus atoms and the metal center, eight isomers are to be expected. However, up to three diastereomers can be distinguished in the $^{31}P\{^1H\}$ NMR spectra. In all cases the resonances caused by the chelated ether–posphine are downfield shifted compared with those of the η^1-P ~ O bonded ligand. In particular this is the case for nuclei belonging to groups which are in direct vicinity of the ruthenium coordinated oxygen. Thus two sets of resonances are observed in the ^1H and $^{13}C\{H\}$ NMR spectra of **7a**(**T**^{o})–**7g**(**T**^{o}) which are caused by the CH_2OCH_3 moieties. Each diastereomer give rise to an AX pattern in the $^{31}P\{^1H\}$ NMR spectrum. The signals at lower field are attributed to the phosphorus atom, which is incorporated into the five-membered ring [24]. The size of the $^2J_{PP}$ coupling (35 Hz) indicates a *cis*-arrangement of the phosphine groups [25].

Both of the ^{31}P resonances for the two different phosphorus atoms in **8a**(**T**^{o}) are shifted to lower field compared with **7a**(**T**^{o}). Again each diastereomer is characterized by an AX spin system with a $^2J_{PP}$ coupling constant of 35 Hz which is typical for *cis*-phosphines. These spectral data are consistent for two η^2-P ∩ O bonded ligands. The molecular ion of the dicationic complex **8a**(**T**^{o}) was detected by electron spray mass spectroscopy and gives evidence for the molecular composition.

4. Conclusion

A small library of neutral and cationic diamine(ether-phosphine)ruthenium(II) complexes was obtained. The complexes are provided with T-silyl functions at the periphery of a novel phosphine ligand system. By this means they can later be subjected to a sol–gel process to create new stationary phases for chemistry in interphases. Complexes of this type represent potential catalysts for the hydrogenation of conjugated ketones [11]. Due to the reasonable effect of the co-ligand on the catalytic activity of such complexes, a series of different aliphatic and aromatic amines was selected to vary the electronic and steric character of the metal center and the complex, respectively. By the employment of ether–phosphines the introduction of amines is kinetically controlled and the formation of by-products is avoided. The weak ruthenium–oxygen bonds are easily cleaved during the reaction with the amines. Three important items were achieved with these investigations, (i) the cationic complexes **7a**(**T**^{o})–**7g**(**T**^{o}) can be applied for the parallel testing as homogeneous and heterogeneous catalysts; (ii) the presence of hemilabile ligands is responsible for a greater stability of coordinatively unsaturated metal centers in protecting vacant coordination sites and (iii) the weak metal–oxygen bond is

easily cleaved to activate unsaturated molecules in the hydrogenation process.

Acknowledgements

The support of this research by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg, Grant GK-GRK 441/1-00), Bonn/Bad Godesberg, by the Fonds der Chemischen Industrie, Frankfurt/Main, and by the Wilhelm Schuler-Stiftung is gratefully acknowledged. We also thank Dipl.-Chem. D. Schmid (Professor Jung), University of Tübingen for the electron spray mass spectroscopic measurements.

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