Published in Inorganic Chemistry Communications 12, issue 8, 716-719, 2009
which should be used for any reference to this work

Rhodium(I) iminophosphine poly(propyleneimine) dendrimers: Synthesis, characterization and molecular structure of a mononuclear analogue

Nathan C. Antonels [a], Bruno Therrien [b], John R. Moss [a], Gregory S. Smith [a,*]

[a] *Department of Chemistry, University of Cape Town, Rondebosch 7701, Cape Town, South Africa*
[b] *Service Analytique Facultaire, University of Neuchatel, Case postale 158, CH-2009 Neuchatel, Switzerland*

A B S T R A C T

First (G*1*)- and second-generation (G*2*) poly(propyleneimine) (PPI) dendrimers were reacted with 2-(diphenylphosphino)benzaldehyde, to form iminophosphine-functionalised dendritic ligands (**1**, **2**). The reaction of the dimeric precursor $[RhCl(CO)_2]_2$ with the heterobidentate dendritic ligands **1**, **2** gave the corresponding rhodium(I) complexes (**3**, **4**).

Keywords:
Dendrimers, Rhodium complexes, Poly(propyleneimine), Iminophosphine, *P,N*-heterobidentate

Dendrimers are highly branched, monodisperse, macromolecular constructs, that are often used as supports for homogeneous catalysts. Various examples of dendritic scaffolds have been used to immobilize homogeneous catalysts, including carbosilanes [1], polyamidoamines [2], polypropyleneimines [3] and polyarylethers [4], to name a few.

Dendritic ligands generally have an increased local concentration of similar functional groups at their periphery. These dendrimers may contain donor ligands capable of coordinating to various transition metals, thereby catalyzing various organic transformations with a range of metals, such as Kharasch-type addition reactions [5] (Ni), ethylene oligomerisations/norbornene polymerizations [6] (Ni), hydroformylation [7] (Rh), carbon–carbon cross-coupling reactions [8] (Pd), hydrogen transfer reductions [9] (Ru) and epoxidation of cyclohexene [10] (Ti).

There has been recent interest in the chemistry of polydentate ligands, especially those which combine "soft" and "hard" donor atoms [11]. The most used hemilabile ligands are the *P,N*-donor bidentate ligands, combining the distinct behaviour of a soft phosphorus atom which coordinates very strongly to a soft metal centre (e.g. palladium) and a hard nitrogen donor which is weakly bound. Non-rigid ligands, such as the widely studied iminophosphines, often act as chelating ligands that easily form five- or six-membered chelate rings. Iminophosphines display versatile coordination behaviour and are potentially hemilabile, making them useful for a variety of homogeneous processes, such as, C–C coupling reactions [12], oligomerisation and polymerization of ethylene [13], aminations [14], transfer hydrogenations [15] and hydroboration [16]. The steric and electronic properties of such ligands can also be fine-tuned and this can have a huge effect on the kinetics and thermodynamics of a chemical reaction [17].

Examples of metallodendritic chelating heterobidentate complexes are rare. For metallodendrimers containing *P* and *N* donor atoms, many transition metals are coordinated in a *P*-monodentate or *N*-monodentate fashion. In this communication, we report on the synthesis of first- and second-generation chelating, heterobidentate [*P*, *N*] iminophosphine dendritic ligands and their coordination chemistry with a Rh(I) precursor. The molecular structure of a mononuclear analogue is also presented and discussed.

The synthesis of the first- and second-generation iminophosphine-functionalised dendritic ligands **1** and **2** (Fig. 1) [19] was achieved by a Schiff-base condensation reaction of the commercially available DAB-dendr-$(NH_2)_n$ with 2-diphenylphosphinobenzaldehyde. Screttas et al. first reported the synthesis of a third generation iminophosphine dendritic ligand based on a poly(propyleneimine) scaffold [18]. These dendritic P,N ligands were used *in situ* in the presence of palladium acetate in the Heck cross-coupling of *p*-anisyl bromide with styrene.

The dendritic ligands (**1**, **2**) were isolated as pale yellow solids in moderate yields (65–68%). These compounds were characterized by elemental analysis (C, H, N), and by IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectra of **1** and **2** show the aliphatic protons for the dendritic core occurring in the range between 1 and 4 ppm, and the aromatic and imine resonances occurring between 6 and 9 ppm. The CH_2 protons adjacent to the

* Corresponding author. Tel.: +27 21 6505279; fax: +27 21 6897499.
E-mail address: Gregory.Smith@uct.ac.za (G.S. Smith).

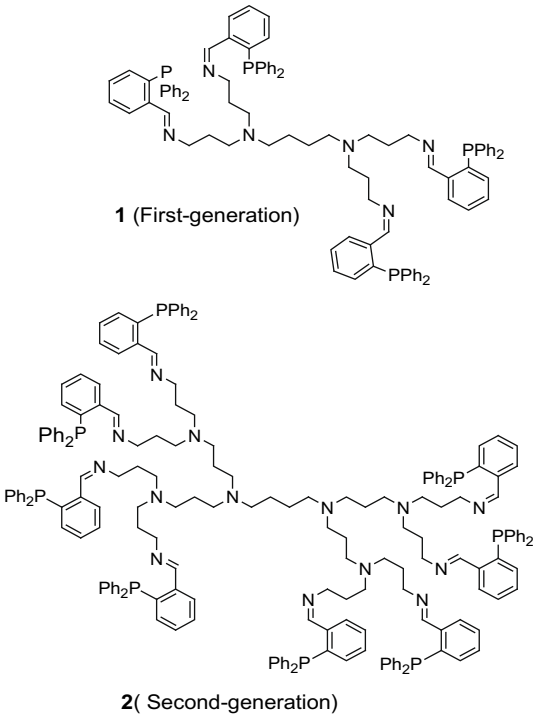
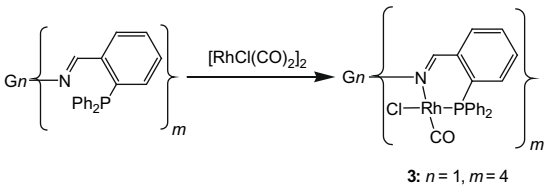


Fig. 1. First- and second-generation iminophosphine dendrimers.

imine moiety are observed as a triplet around 3.69 ppm, for **1** and **2**. The appearance of a singlet at ca. 8.37 ppm, assigned to the imine proton (–CH_2N=C*H*–CH_2–) establishes that the condensation reaction has occurred. As was the case for Screttas and co-workers, it is important to consider *syn* and *anti* isomerism about the imine double bond [18]. One resonance is noted for the imine proton in both ligands, assigned to the *trans* isomer for steric reasons. The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** show a singlet at −13.35 and −13.43 ppm, respectively. Infrared spectroscopy confirms the formation of the imine functionality. In the IR spectrum of **1** and **2**, the absorption bands associated with the imine functionality (ν(C=N)) occur at 1637 cm^{-1}. This corroborates the evidence for imine formation observed in the ^1H NMR spectra. The composition and purity of the dendritic ligands were further confirmed by elemental analysis and ESI-mass spectrometry.

Reaction of the iminophosphine dendrimers **1** and **2** with the dimeric rhodium(I) precursor $[RhCl(CO)_2]_2$ (Scheme 1) gave the tetranuclear (**3**) and octanuclear (**4**), six-membered chelate ring, rhodium(I) metallodendrimers, respectively [20].

The metallodendrimers (**3**, **4**) were isolated as orange powders in moderate to good yields, stable at room temperature and soluble in toluene, THF and chlorinated solvents but insoluble in hydrocarbons. Generally, the IR spectra for **3** and **4** show a wavelength shift of the C=N absorption band towards lower wavenumbers, as compared to the uncomplexed dendritic Schiff-base (ca. 1630 vs 1637 cm^{-1}), indicative of coordination of rhodium to the nitrogen



Scheme 1.

of the imine functionality. The stretching frequency for the terminal carbonyl is observed at about 2000 cm^{-1}. The ^1H NMR spectrum shows a singlet at 8.49 ppm for the methine proton of the imino group, an upfield shift from 8.85 ppm for the free, uncomplexed dendritic ligand, providing further evidence of nitrogen coordination of the C=N group. The $^{31}P\{^1H\}$ NMR spectrum displays a doublet at 48.5 ppm with ^1J(RhP) = 163 Hz, consistent with rhodium coupling to phosphorus and is typical of phosphorus *trans* to chlorine [21,22]. This indicates the presence of a single isomer for each generation (complexes **3** and **4**). Elemental analyses correlates with solvent inclusion within the dendritic structures.

To gain further insight into the coordination environment of the Rh(I) atoms in the metallodendrimers, the analogous mononuclear compound (**5**) was synthesized [20] from the known compound o-$Ph_2PC_6H_4CH$=NPr^n [22] and $[RhCl(CO)_2]_2$. Spectroscopic data (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, IR) for **5** are similar to that observed for the rhodium metallodendrimers (**3**, **4**), providing evidence of metal coordination for the respective metallodendrimers, indicative of the formation of six-membered chelate rings with rhodium on the periphery of the dendrimers.

The molecular structure of **5** was confirmed by X-ray crystallography [23]. An ORTEP drawing [24] with the corresponding atom labelling scheme is shown in Fig. 2 together with selected bond lengths and angles. The molecular structure shows the rhodium atom to be in a square-planar geometry surrounded by the imino nitrogen atom *trans* to the carbonyl ligand and the chloro ligand *trans* to phosphorus. The geometrical parameters around the rhodium atom are comparable to those found in the analogous complexes [Rh(PyP)(CO)Cl] (PyP = 1-(2-diphenylphosphino)ethylpyrazole) [25], [Rh(P–N)(CO)Cl] (P–N = diphenylphosphino(phenyl pyridine-2-yl methylene)amine) [26] and [Rh(P–N*)(CO)Cl] (P–N* = (2*S*, 3*S*)-2-{4-(dimethylamino)benzylideneamino} + -3-methylpentyl bis(2,6-dimethylphenyl) phosphite) [27]. The formation of a six-membered chelate ring imposes distortion around the rhodium atom. The P–Rh–Cl angle [170.60(11)] is smaller than the expected value of 180°. The atoms Rh, Cl, N, C(23) and O are essentially coplanar with an average deviation of 0.0218 Å from the mean plane, while the P atom is 0.39(1) Å away from this plane.

In conclusion, first- and second-generation iminophosphine rhodium(I) metallodendrimers were synthesized, based on a

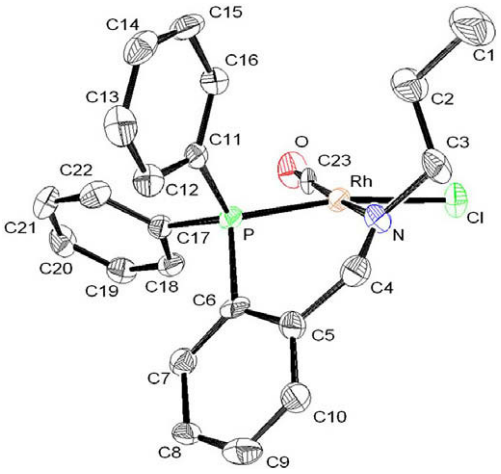


Fig. 2. Molecular structure of the mononuclear rhodium(I) iminophosphine complex **5** showing ellipsoids at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Rh–P 2.188(4), Rh–Cl 2.394(4), Rh–N 2.118(11), Rh–C(23) 1.806(14), N–C(4) 1.284(16), N–C(3) 1.468(15); P–Rh–Cl 170.60(11), P–Rh–N 86.1(3), P–Rh–C(23) 93.7(4), Cl–Rh–N 90.0(3), Cl–Rh–C(23) 90.6(4), N–Rh–C(23) 177.1(5), C(3)–N–C(4) 116.9(11).

poly(propyleneimine) dendritic scaffold. We are currently exploring the coordination of other rhodium(I) homogeneous catalysts to similar dendrimeric scaffolds, and the use of these complexes in alkene hydroformylation reactions.

Acknowledgements

We would like to thank the Anglo Platinum Corporation, University of Cape Town, the National Research Foundation (NRF) of South Africa and NRF-DST Centre of Excellence in Catalysis (c* change) for financial support.

Appendix A. Supplementary material

CCDC 716316 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.05.026.

References

[1] (a) D. de Groot, E.B. Eggeling, J.C. de Wilde, H. Kooijman, R.J. van Haaren, A.W. van der Made, A.L. Spek, D. Vogt, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Chem. Commun. (1999) 1623;
(b) D. Groot, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Eur. J. Org. Chem. (2002) 1085;
(c) 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.

[2] S.C. Bourque, H. Alper, L.E. Manzer, P. Arya, J. Am. Chem. Soc. 122 (2000) 956.

[3] (a) M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem., Int. Ed. Engl. 36 (1997) 1526;
(b) L. Busseto, M.C. Cassani, P.W.N.M. van Leeuwen, R. Mazzoni, Dalton Trans. (2004) 2767;
(c) G.S. Smith, R. Chen, S.F. Mapolie, J. Organomet. Chem. 673 (2003) 111.

[4] (a) T. Fujihara, Y. Obora, M. Tokunaga, H. Sato, Y. Tsuji, Chem. Commun. (2005) 4526;
(b) W.-J. Tang, Y.-Y. Huang, Y.-M. He, Q.-H. Fan, Tetrahedron: Asymmetry 17 (2006) 536.

[5] J. March, Advanced Organic Chemistry, fourth ed., John Wiley and Sons, London, 1992. pp. 5–33.

[6] (a) R. Malgas, S.F. Mapolie, S.O. Ojwach, G.S. Smith, J. Darkwa, Catal. Commun. 9 (2008) 1612;
(b) R. Malgas-Enus, S.F. Mapolie, G.S. Smith, J. Organomet. Chem. 693 (2008) 2279.

[7] (a) L. Ropartz, D.F. Foster, R.E. Morris, A.M.Z. Slawin, D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans. (2002) 1997;
(b) L. Ropartz, R.E. Morris, D.F. Foster, D.J. Cole-Hamilton, Chem. Commun. (2001);
(c) L. Ropartz, R.E. Morris, G.P. Schwartz, D.F. Foster, D.J. Cole-Hamilton, Inorg. Chem. Commun. 3 (2000) 714.

[8] (a) D.P. Catsoulacos, B.R. Steele, G.A. Heropoulos, M. Micha-Screttas, C.G. Screttas, Tetrahedron Lett. 44 (2003) 4575;
(b) M. Beller, A. Zapf, T.H. Riermeier, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, Wiley/VCH, Weinheim, Germany, 2004;
(c) G.S. Smith, S.F. Mapolie, J. Mol. Cat. A.: Chem. 213 (2004) 187.

[9] I. Angurell, G. Muller, M. Rocamora, O. Rossell, M. Seco, Dalton Trans. (2004) 2450.

[10] (a) J.W. Kriesel, T.D. Tilley, Chem. Mater. 11 (1999) 1190;
(b) J.W. Kriesel, T.D. Tilley, Polym. Prepr. 41 (2000) 566;
(c) J.W. Kriesel, T.D. Tilley, Chem. Mater. 12 (2000) 1171;
(d) J.W. Kriesel, T.D. Tilley, Adv. Mater. 13 (2001) 1645.

[11] (a) J.R. Dilworth, S.D. Howe, A.J. Hutson, J.R. Miller, J. Silver, R.M. Thomson, M. Harman, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1994) 3553;
(b) J.R. Dilworth, A.J. Hutson, J.S. Lewis, J.R. Miller, Y. Zheng, Q. Chen, J. Zubieta, J. Chem. Soc., Dalton Trans. (1995) 1093;
(c) G.R. Newkome, Chem. Rev. 93 (1993) 2067;
(d) G. Sanchez, J.L. Serrano, M.A. Moral, J. Perez, E. Mollins, G. Lopez, Polyhedron 18 (1999) 3057.

[12] (a) K.R. Reddy, K. Sureka, G.-H. Lee, S.-M. Peng, S.-T. Liu, Organometallics 19 (2000) 2637;
(b) M. Koprowski, R.-M. Sebastian, V. Maraval, M. Zablocka, V. Cadierno, B. Donnadieu, A. Igau, A.-M. Caminade, J.-P. Majoral, Organometallics 21 (2002) 4680;
(c) B. Crociani, S. Antoneroli, V. Beghetto, U. Matteoli, A. Scrivanti, Dalton Trans. (2003) 2194.

[13] (a) E.K. van den Beuken, B.L. Feringa, W.J.J. Smeets, A.L. Spek, Chem. Commun. (1998) 223;
(b) G.L. Crossetti, M.L. Dias, B.T. Queiroz, L.P. Silva, C.M. Ziglio, J.A.S. Bomfim, C.A.L. Filgueiras, Appl. Organomet. Chem. 18 (2004) 331;
(c) F. Speriser, P. Braunstein, L. Saussine, Acc. Chem. Res. 38 (2005) 784.

[14] [a] B. Crociani, S. Antonaroli, G. Bandoli, L. Canovese, F. Visentin, P. Uguagliati, Organometallics 18 (1999) 1137;
(b) B. Crociani, S. Antonaroli, L. Canovese, F. Visentin, P. Uguagliati, Inorg. Chim. Acta 315 (2001) 172.

[15] (a) P. Crochet, J. Gimeno, S. Garcia-Granda, J. Borge, Organometallics 20 (2001) 4369;
(b) P. Crochet, J. Gimeno, J. Borge, S. Garcia-Granda, New J. Chem. 27 (2003) 414.

[16] D.I. McIsaac, S.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott, Inorg. Chim. Acta 359 (2006) 2771.

[17] J. Best, J.M. Wilson, H. Adams, L. Gonsalvi, M. Peruzzini, A. Haynes, Organometallics 26 (2007) 1960.

[18] D.P. Catsoulacos, B.R. Steele, G.A. Heropoulos, M. Micha-Screttas, C.G. Screttas, Tetrahedron Lett. 44 (2003) 4575.

[19] General Procedure for the synthesis of **1**–**2**: A mixture of 2-(diphenylphosphino)benzaldehyde and DAB-$(NH_2)_n$ in dichloromethane/ethanol (50:50 v/v%) (60 cm^3) was stirred at room temperature (48 h). Anhydrous $MgSO_4$ was transferred to the stirred solution. The mixture was filtered by gravity, and the solvent removed from the filtrate collected. The residue was dissolved in dichloromethane (3–5 cm^3) and pentane added to precipitate a pale yellow solid. Compound **1**: Yield = 1.27 g (76%). M.p. = 56–58 °C. IR (CH_2Cl_2, cm^{-1}): 1637 (s, C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.29 (br qn, 4H, $CH_2CH_2N((CH_2)_3N)_2$), 1.59 (br qn, 8H, $CH_2N(CH_2CH_2CH_2N)_2$), 2.28 (br m, 12H, $CH_2N(CH_2CH_2CH_2N)_2$), 3.44 (br t, 8H, CH_2NCH), 6.86 (m, 4H, $P(C_6H_5)CCH$), 7.29 (br m, 48H, phenyl), 7.94 (m, 4H, NCHCC*H*), 8.85 (d, 4H, NC*H*C, $^4J_{PH}$ = 4.5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.4, 28.4, 51.8, 54.3, 59.8 (aliphatic), 127.9–140.0 (aromatic), 159.5 (d, $^4J_{PC}$ = 20.7 Hz, −C=N); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ (ppm) = −13.4 (s). Elemental analysis (%): Calc. for $C_{92}H_{92}N_6P_4$.0.25 CH_2Cl_2: C, 77.65; H, 6.53; N, 5.89; Found: C, 77.40; H, 6.86; N, 5.79. ESI-MS: *m*/*z* 703 $[M]^{2+}$ (doubly charged ion). Compound **2**: Yield = 0.362 g (68%). M.p. = 61–63 °C. IR (CH_2Cl_2, cm^{-1}): 1637 (s, C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.55 (br qn, 4H, $CH_2CH_2N((CH_2)_3N)_2$), 1.59 (br qn, 24H, $NCH_2CH_2CH_2NCH_2CH_2$), 2.29–2.39 (2 × br s, 36H, $CH_2N(CH_2CH_2CH_2N)_2(CH_2)_4$), 3.42 (m, 16H, CH_2NCHC), 6.85 (m, 8H, $P(C_6H_5)CCH$), 7.27–7.39 (br m, 96H, phenyl), 7.94 (m, 8H, NCHCC*H*), 8.84 (d, 8H, NC*H*C, $^4J_{PH}$ = 4.5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 23.7, 24.2, 27.2, 50.6, 51.3, 53.4, 58.6 (aliphatic), 126.7–138.8 (aromatic), 158.2 (d, $^4J_{PC}$ = 20.7 Hz, −C=N). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ (ppm) = −13.4 (s). Elemental analysis (%): Calc. for $C_{192}H_{200}N_{14}P_8$·3CH_2Cl_2: C, 73.09; H, 6.46; N, 6.13; Found: C, 73.05; H, 6.48; N, 6.12.

[20] General Procedure for the synthesis of **3**–**5**: A solution of the iminophosphine and $[RhCl(CO)_2]_2$ in THF was stirred for 2 h at room temperature. The solvent was reduced and *n*-pentane added to precipitate the product as an orange solid. Compound **3**: Yield = 0.168 g (63%). M.p.: does not melt <300 °C. IR (CH_2Cl_2, cm^{-1}): 1630 (m, C=N); 2001 (s, C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.45 (br s, 4H, $CH_2CH_2N((CH_2)_3N)_2$), 1.84 (br s, 8H, $CH_2N(CH_2CH_2CH_2N)_2$), 2.27 (br s, 12H, $CH_2N(CH_2CH_2CH_2N)_2$), 4.07 (br s, 8H, CH_2NCH), 6.82 (m, 4H, $P(C_6H_5)CCH$), 7.43 (br m, 48H, phenyl), 7.91 (m, 4H, NCHCC*H*), 8.49(s, 4H, NCHC). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 25.8 (br), 62.0 (br), 68.2, 125.6–136.6 (aromatic), 167.1 (br, C=N), 189.4. (dd, $^2J_{PC}$ = 17.0 Hz, $^1J_{RhC}$ = 72.0 Hz, CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ (ppm) = 48.5 (d, PPh_2, $^1J_{RhP}$ = 163 Hz). Elemental analysis (%): Calc. for $C_{96}H_{92}N_6P_4Rh_4Cl_4O_4$·2.5$CH_2Cl_2$: C, 51.81; H, 4.28; N, 3.68; Found: C, 51.83; H, 4.38; N, 3.61. ESI-MS: *m*/*z* 1038 $[M]^{2+}$ (doubly charged ion). Compound **4**: Yield = 0.348 g (88%). M.p.: does not melt <300 °C. IR (CH_2Cl_2, cm^{-1}): 1630 (m, C=N); 1996 (s, C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.64 (br s, 28H, $CH_2CH_2N(CH_2CH_2CH_2N)_2(CH_2CH_2CH_2N)_4$), 2.35 (br s, 36H, $CH_2N(CH_2CH_2CH_2N)_2(CH_2)_4$), 4.11 (m, 16H, CH_2NCH), 6.79 (m, 8H, NCHCC*H*CH), 7.92 (br m, 96H, phenyl), 7.92 (m, 8H, $CHP(C_6H_5)$), 8.54 (br s, 8H, CH_2NCHC). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 22.4 (br), 51.4 (br) 62.1, 125.9–136.3 (aromatic), 166.2 (br, C=N), 190.0 (dd, $^2J_{PC}$ = 17.0 Hz, $^1J_{RhC}$ = 72.0 Hz, CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ (ppm) = 48.5 (d, PPh_2, J_{RhP} = 164 Hz). Elemental analysis (%): Calc. for $C_{200}H_{200}N_{14}P_8Rh_8Cl_8O_8$·7$CH_2Cl_2$: C, 50.98; H, 4.42; N, 4.02; Found: C, 50.57; H, 4.54; N, 3.62. Compound **5**: Yield = 0.040 g (54%). M.p.: dec. without melting >250 °C. IR (CH_2Cl_2, cm^{-1}): 1631 (m, C=N), 2001 (s, C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.47 (t, 3H, $(CH_2)_2CH_3$), 1.68 (sx, 2H, $CH_2CH_2CH_3$), 4.11 (t, 2H, NCH_2), 6.90 (t, 1H, $P(C_6H_5)CCH$), 7.47 (m, 13H, phenyl, NCHCC*H*), 7.93 (s, 1H, NCHC). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 10.8, 24.3, 66.9, 128.8–135.4 (aromatic), 163.8 (s, C=N), 189.5 (dd, $^2J_{PC}$ = 17.0 Hz, $^1J_{RhC}$ = 72.0 Hz, CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ (ppm) = 48.3 (d, PPh_2, J_{RhP} = 167 Hz). Elemental analysis (%): Calc. for $C_{23}H_{22}NOPClRh$: C, 55.49; H, 4.45; N, 2.81; Found: C, 55.49; H, 4.10; N, 2.58.

[21] (a) D.M. Roundhill, R.A. Bechtold, S.G.N. Roundhill, Inorg. Chem. 19 (1980) 284;
(b) M.P. Anderson, A.L. Casalnuovo, B.J. Johnson, B.M. Mattson, A.M. Mueting, L.H. Pignolet, Inorg. Chem. 27 (1988) 1649;
(c) V.V.S. Reddy, A. Varshney, G.M. Gray, J. Organomet. Chem. 391 (1990) 259;
(d) D.A. Slack, I. Greveling, M.C. Baird, Inorg. Chem. 18 (1979) 3125;
(e) E. Rotondo, G. Battaglia, G. Giordano, F.P. Cusmano, J. Organomet. Chem. 450 (1993) 245.

[22] C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci, J. Chem. Soc., Dalton Trans. (1992) 3371.

[23] Orange crystals of **5** ($0.15 \times 0.14 \times 0.10$ mm) suitable for X-ray diffraction analysis were grown by layering pentane on a concentrated solution of **5** in dichloromethane. Crystal data for **5**; $C_{23}H_{22}ClNOPRh$, triclinic space group $P-1$ (No. 2), cell parameters $a = 8.7765(12)$ Å, $b = 10.218(2)$ Å, $c = 13.180(2)$ Å, $\alpha = 109.90(2)$, $\beta = 101.83(2)$, $\gamma = 90.90(2)^\circ$, $V = 1083.0(3)$ Å^3, $T = 173(2)$ K, $Z = 2$, $D_c = 1.526$ g cm^{-3}, $F(0\,0\,0)$ 504, λ (Mo Kα) = 0.71073 Å, 8534 reflections measured, 3962 unique ($R_{int} = 0.0720$) which were used in all calculations. The structure was solved by direct method (SHELXS-97) and refined (SHELXL-97) [28] by full-matrix least-squares methods on F^2 with 254 parameters. $R_1 = 0.0697$ ($I > 2\sigma(I)$) and $wR_2 = 0.2565$, GOF = 1.143; max./min. residual density 2.005/−1.185 eÅ^{-3} located at less than 1 Å from the rhodium atom.

[24] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
[25] S. Burling, L.D. Field, B.A. Messerle, K.Q. Vuong, P. Turner, Dalton Trans. (2003) 4181.
[26] P.W. Dyer, J. Fawcett, M.J. Hanton, J. Organomet. Chem. 690 (2005) 5264.
[27] K.N. Gavrilov, O.G. Bondarev, R.V. Lebedev, A.A. Shiryaev, S.E. Lyubimov, A.I. Polosukhin, G.V. Grintselev-Knyazev, K.A. Lyssenko, S.K. Moiseev, N.S. Ikonnikov, V.N. Kalinin, V.A. Davankov, A.V. Korostylev, H.-J. Gais, Eur. J. Inorg. Chem. (2002) 1367.
[28] G.M. Sheldrick, SHELXS-97, SHELXL-97, University of Göttingen, Göttingen, Germany, 1999.