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Phosphorus Dendrimers and Dendrons Functionalized with the Cage Ligand Tris(1,2-dimethylhydrazino)diphosphane

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ABSTRACT: *The synthesis of a new phosphorus dendrimer peripherally functionalized with the cage ligand tris(1,2-dimethylhydrazino) diphosphane is described. In addition, dendrons (dendritic wedges) containing the same cage ligand at the focal point are also reported along with their corresponding ruthenium derivatives, which are thought to be potential catalysts in aqueous media.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:290–297, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20611

INTRODUCTION

Phosphorus "cage" compounds, as for example the proazaphosphatrane **1** [1], the triaza- or the trihydrazino- phosphoadamantanes **2** [2], or **3** [3], as well as the tris(1,2 dimethylhydrazino) diphosphane (THDP) **4** [4] (Fig. 1), are well known for their unique properties specially in catalysis allowing a number of reactions to take place in mild conditions and in high yields. Our interest in the use of dendrimers as ligands in catalysis already exemplified in several reports [5,6] leads us to investigate the possibility to graft some of these phosphorus cage compounds on the surface of dendrimers with the hope to observe a positive dendritic effect, i.e. an enhancement in the catalytic activity when moving from the monomer to dendrimers decorated with several monomer units. Indeed some examples of such a dendritic effect have been reported in the literature [7].

Recently, some of us [4a] described the preparation of several monomeric ruthenium, rhodium, and iridium complexes containing the cage ligand THDP **4** (Scheme 1) and their catalytic behavior in the atom-transfer radical addition of bromotrichloromethane to olefins (the Karasch reaction) in aqueous media.

The excellent catalytic results observed in such a process incited us to explore the possibility of synthesizing new species having the ligand **4** grafted on the surface of phosphorus dendritic systems to obtain multimetallic dendritic complexes

We report here the different synthetic strategies investigated for this purpose, as well as the synthesis of several new monomers incorporating **4** and

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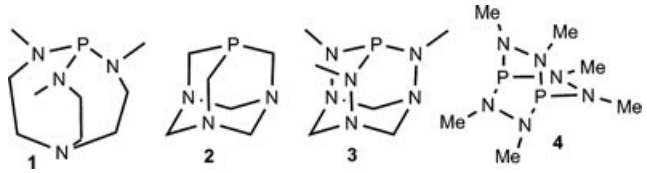


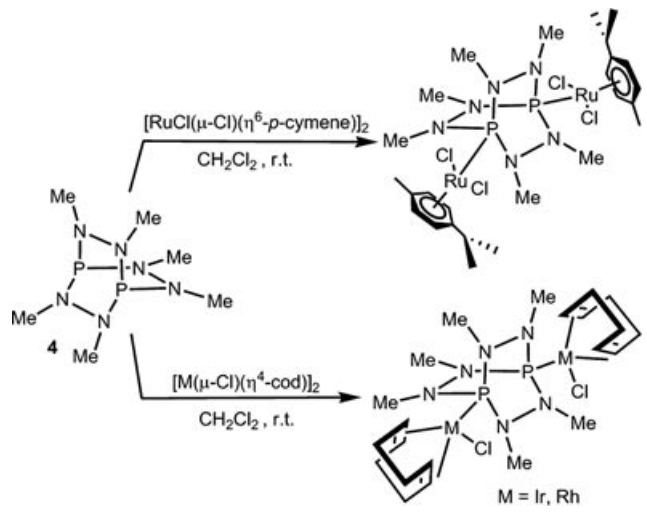
FIGURE 1 Examples of phosphorus cage compounds.

the preparation of dendron (dendritic wedge) and dendrimer ruthenium complexes.

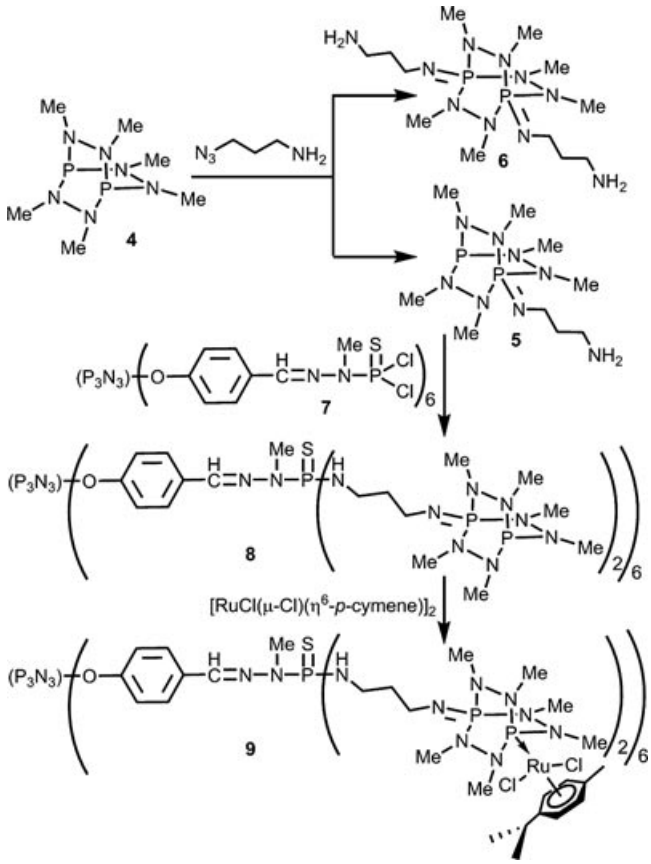
RESULTS AND DISCUSSION

Dendrimers Containing THDP Cage Units on the Surface

As can be seen in Scheme 1, the dinuclear THDP-based complexes recently reported [4] are the result of the simultaneous functionalization of both phosphorus atoms of the cage. However, the formation of the dendritic systems containing the THDP units on the periphery requires the functionalization of only one phosphorus atom while the other should remain available for coordination to the appropriate metal fragment. Our strategy to link the THDP cage to the dendrimer takes into account the report by Verkade and co-workers, which proved that the Staudinger reaction between **4** and different azides is possible [8]. In addition, it is interesting to note that the Staudinger reaction between an azide and a phosphorus PR_3 compound produces as a by-product just a N_2 molecule.



SCHEME 1 Synthesis of dinuclear THDP-based complexes.



SCHEME 2 Synthesis of dendrimers ended by phosphorus cage ligands.

In this paper, the chosen azide was $N_3(CH_2)_3NH_2$, since it possesses a $-NH_2$ group that can be used to anchor the fragment to a terminated $-P(S)Cl_2$ dendrimer. The reaction between **4** and $N_3(CH_2)_3NH_2$ was performed in toluene at different temperatures and molecular ratio to optimize the formation of the monosubstituted compound **5**. Even when the reaction was carried out at room temperature and an excess of **4** was used, a mixture of the disubstituted **6** and the desired monosubstituted **5** products was obtained (Scheme 2). The best reaction conditions found were 50°C and a **4**/azide ratio of 1:1.3. The monosubstituted compound **5** was isolated and purified by successive precipitation of the disubstituted product **6** at −30°C in *n*-heptane. The product **5** was obtained as a colorless oil with 53% of yield. The ^{31}P NMR spectrum of **5** showed two doublets at 95.1 ppm (free phosphorus atom) and 2.8 ppm (P=N atom) with a coupling constant of $^3J_{PP} = 74.6$ Hz. The methylene group located at the middle of the chain appeared as a quintuplet of doublets because of its coupling with the four protons of the methylene groups attached to it

($^3J_{HH}$ = 6.9 Hz) and with the P=N phosphorus atom ($^4J_{HP}$ = 1.5 Hz).

A two-dimensional ^{1}H ^{13}C HMQC experiment permitted to assign unequivocally the ^{13}C NMR spectrum of **5** and to correlate each carbon signal of the chain with its corresponding proton atoms. In addition, the ^{13}C NMR spectra with individual irradiation of the two phosphorus atoms were performed to assign unambiguously the two doublets corresponding to the two different methyl groups of the cage that appeared at 37.8 ($^2J_{CP}$ = 10.8 Hz) and 36.2 ppm ($^2J_{CP}$ = 2.2 Hz). Thus, the irradiation of the phosphorus nuclei P=N produced the disappearance of the coupling of the carbon signal at 36.2 ppm, indicating that this was the corresponding signal for the closest methyl groups. Both chemical ionization and electrospray ionization mass spectra showed the molecular peak of the compound, confirming the identity of the product.

Functionalization of the phosphorus dendrimer **7** (generation 1) [9] with the aminoderivative **5** proceeds nicely, in the presence of cesium carbonate as base to give the dendrimer **8** in 91% yield. As a result of the complete substitution of both chlorine atoms of the $-P(S)Cl_2$ branches, the ^{31}P NMR signal of this group appeared downfield as a unique signal (it shifted from 62.4 to 66.8 ppm). The phosphorus atoms of the cage resonated at 95.3 ppm (external P atom) and at 2.1 ppm (P=N), coupled to each other and with a coupling constant of $^3J_{PP}$ = 74.6 Hz, whereas the equivalent phosphorus atoms of the core appeared as a broad singlet at 8.5 ppm. ^{1}H and ^{13}C NMR spectra were collected to complete the characterization of this compound. As in the case of **5**, ^{13}C NMR spectra with selective irradiation of phosphorus nuclei and two-dimensional ^{1}H-^{13}C HMQC spectrum were essential to complete the assignment of the signals. Unfortunately, neither MALDI nor ES mass spectra confirmed the identity of the compound, due to its high degree of fragmentation, well known for phosphorhydrazone-containing dendrimers [10].

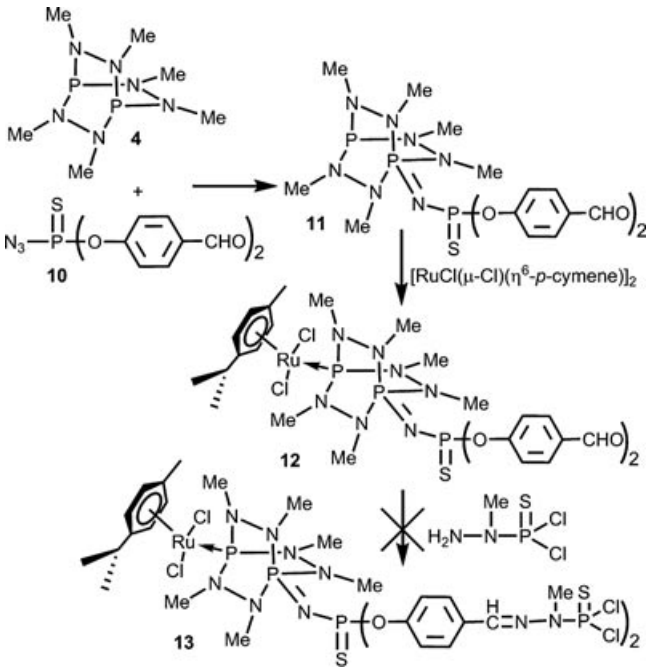
The functionalization of the external phosphorus atoms of the dendrimer **8** was attempted by using two different metal complexes, $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ and $[Ir(\mu\text{-}Cl)(\eta^4\text{-cod})]_2$. When trying to complex the dendrimer with the dimer $[Ir(\mu\text{-}Cl)(\eta^4\text{-cod})]_2$, a dark brown solid was observed. No characterization of this product was obtained due to the high degree of insolubility of the solid in all the organic solvents tested. However, the ruthenium metallodendrimer **9** could be obtained as shown in Scheme 2. The process was monitored by ^{31}P NMR spectroscopy, which evidenced the complete coordination of all the external phosphorus atoms, showing the expected deshielding effect (from 95.3 for **8** to 114.5 ppm for **9**). The metallodendrimer was isolated as a red solid in high yield (93%), and its characterization was completed with ^{1}H and ^{13}C NMR spectra. The new compound is air-stable and soluble in common polar organic solvents such as $CHCl_3$, CH_2Cl_2, and acetone.

Dendrons Containing a THDP Unit at the Focal Point

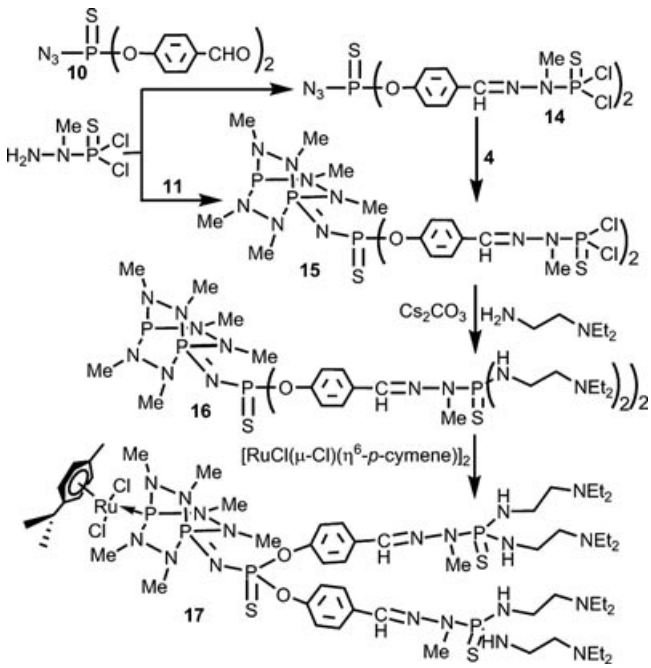
As discussed earlier, a number of metallodendrimers have been reported to show "dendritic effects," which can be relevant in catalysis. This effect can be particularly strong in metallodendrons, in which the catalytic site is at the focal point. In such kind of species, due to the steric hindrance, the access to the metal center can be restricted in increasing the dendron generation. Thus, in many cases, the reactivity and selectivity of metallodendrons depend on their particular generation [11]. With this in mind, we envisaged the construction of metallodendrons in which the metal/THDP unit is localized at the focal point. Furthermore, we wanted to functionalize the dendron with amino groups at the periphery. It is well known that the incorporation of hydrophilic groups into different dendritic structures is a good strategy for enhancing water solubility in the system. Protonated amines, carboxylate, sulfonate, phosphonic, or bisphosphonic groups are examples of the surface functionalities used for this purpose [12].

Several strategies were investigated to prepare diversely functionalized metallodendrons. The reaction of **4** with the azide **10** [13] yielded **11** after 2 days of reaction (Scheme 3). In spite of the fact that the reaction taking place through both phosphorus atoms of **4** was always observed whatever the experimental conditions used, the dendron **11** was isolated in 66% yield. Complexation of **11** with the ruthenium dimer $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ resulted in the formation of the desired complex **12** in 90% yield as a red solid. Unfortunately, **12** was not a suitable complex for the growing of the dendron since addition of the monomethylhydrazono-dichloro-thiophosphine on the terminal aldehyde groups (a classical reaction for the preparation of phosphorus dendrons and dendrimers [9]) provokes the degradation of **12** and not the formation of the metallodendron **13** as it was expected.

To overcome these difficulties, another way of preparation of dendrons was defined. It consists first on the reaction of **4** with the azide **14**, which was prepared in 83% yield from the azide **10**, and the monomethylhydrazono-dichloro-thiophosphine using a slight modification of the previously reported



SCHEME 3 Synthesis of a small dendron complex.



SCHEME 4 Synthesis of multifunctional dendrons.

synthesis [14]. To avoid the formation of the P=N bond at both sides of compound **4**, a slight excess of the diphosphane was added (**4/14** ratio 1.2:1). After 14 h of reaction at room temperature, the ^{31}P NMR spectrum showed the disappearance of the signal due to the $N_3P(S)$ group ($\delta = 57.9$ ppm) of the starting compound **14** on behalf of a doublet at 44.0 ppm ($^2J_{PP} = 66.9$ Hz) characteristic for the P=S unit of a P=N–P=S linkage and of a doublet of doublets for the P=N unit ($\delta = 1.5$ ppm, $^3J_{PP} = 86.7$ Hz, $^2J_{PP} = 66.9$ Hz), as it was also coupled with the external phosphorus atom, now acting as the focal point of the resulting dendron **15**. Alternatively, compound **15** was also obtained from the reaction of dendron **11** with $H_2NNMeP(S)Cl_2$ (Scheme 4).

The second step of the construction of a dendron bearing a free phosphino group at the focal point was the substitution of the terminal chlorine atom of **15** with *N,N′*-diethylethylenediamine. The reaction was performed in CH_2Cl_2 and in the presence of cesium carbonate leading to the dendron **16** stable for months under inert atmosphere (Scheme 4).

The ^{31}P NMR spectrum of the reaction mixture showed, after 14 h, no signal for the initial $-P(S)Cl_2$ group ($\delta = 63.2$ ppm) and the appearance in its place of a singlet at 68.0 ppm. The other ^{31}P shift values remained almost unchanged. In the ^{13}C NMR spectrum, one methylene carbon appeared coupled with the phosphorus atom (53.5 ppm, *d*, $^2J_{CP} = 7.9$ Hz) corroborating again the substitution of the chlorine atoms.

Compound **16** was purified by washing the product with pentane at -30°C. The ^1H NMR spectrum showed no evidence of amine in excess, confirming the purity of the compound, which was obtained as yellow oil in 82% yield. Characterization of the dendron included two-dimensional HSQC ^1H ^{13}C spectra to assign unambiguously all the proton and carbon signals. ES mass spectroscopy showed the molecular peak $[M]^+$ of **16**.

As in the case of **8** and **11**, dendron **16** was functionalized with the ruthenium fragment $RuCl_2(\eta^6$-*p*-cymene). The reaction was carried out in a molar ratio **16**/$[RuCl(\mu\text{-}Cl)(\eta^6$-*p*-cymene$)]_2$ 2:1 to guarantee complete coordination and, at the same time, to avoid the presence of ruthenium dimer in excess. However, ^{31}P NMR spectrum of the reaction mixture revealed that the complexation of **16** was not complete. The ^1H NMR spectrum showed the signals corresponding to the *p*-cymene ligand of the organometallic fragment coordinated to the dendron, as well as a new set of signals in the same region, which did not correspond either to **17** or to free dimer. Probably, this was due to the existence of a competition in the complexation of the ruthenium fragment between the amine groups of the dendron and the phosphorus atom located at the focal point. Therefore, these signals could be attributed to a partial coordination of the organometallic unit to

the amine groups of compound **16**. Monitoring by ^{31}P NMR was necessary to complete the functionalization at the focal point of **16** by successive addition of the ruthenium dimer. Finally, the ^{31}P NMR spectrum of the reaction mixture showed no signals corresponding to **16** but the expected deshielding of the external phosphorus atom from 99.1 ppm (*d*, $^3J_{PP} = 87.4$ Hz) to 118.8 ppm (*d*, $^3J_{PP} = 99.0$ Hz). The ^1H NMR spectrum revealed that approximately 20% of the total amount of the organometallic fragment present in the sample was presumably coordinated to the amine groups.

CONCLUSION

We have described the methodology for preparing phosphorous dendrimers bearing on the surface the cage like THDP ligand. The metallation of the species occurs by the coordination of the $RuCl_2(\eta^6$-*p*-cymene) fragment to the free phosphorous atom of the cage. On the other hand, we have also reported the synthetic procedure for phosphorous ruthenadendrons bearing a Ru/THDP unit localized at the focal point. Both types of species are thought to be potential precursors for catalysts in the Karasch reaction in both organic and aqueous media. These studies are currently in progress.

EXPERIMENTAL SECTION

General Data

All manipulations were performed under purified nitrogen using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and two-dimensional NMR spectra were recorded on a Bruker 300 (DPX300), 200 (AC200) MHz, and Varian Mercury 400 spectrometers. Chemical shifts are reported in ppm relative to external standards (TMS for ^1H and ^{13}C and 85% H_3PO_4 for ^{31}P), and coupling constants are given in hertz. The numbering used for NMR assignment is shown in Fig. 2. MS ESI(+) spectra were recorded using a LC/MSD-TOF (Agilent technologies) spectrometer. Mass spectrometry was recorded on a Thermo Fisher DS QII or Neromag R10-10. Compounds **4** [8b–d], **10** [13], and **14** [14] were prepared as previously described. Other reagents were used as received from commercial suppliers.

Syntheses

Synthesis of **5**. To a solution of **4** (0.382 g, 3.804 mmol) in 10 mL of toluene, 8.595 g of a solution in toluene of N_3-$(CH_2)_3$-NH_2 (4.44% w/w, 0.382 g, 3.804 mmol) was added. After stirring the resulting solution at 50°C for 24 h, the solvent was removed in vacuo. **5** was obtained as a colorless oil after purification by successive precipitation of the disubstituted **6** product at −30°C in heptane. Yield: 0.478 g (53%). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K, δ, ppm): 95.1 (*d*, $^3J_{PP} = 74.6$ Hz, P), 2.8 (*d*, $^3J_{PP} = 74.6$ Hz, P=N). ^1H NMR (300.1 MHz, $CDCl_3$, 298 K, δ, ppm): 3.30 (t, $^3J_{HH} = 6.9$ Hz, 2H, $^1CH_2$), 3.26 (t, $^3J_{HH} = 6.9$ Hz, 2H, $^3CH_2$), 1.65 (*qd*, $^3J_{HH} = 6.9$ Hz, $^4J_{HP} = 1.5$ Hz, 2H, $^2CH_2$), 1.44 (*s*, 2H, NH_2). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K, δ, ppm): 41.2 (*s*, $^1CH_2$), 40.6 (*s*, $^3CH_2$), 38.8 (*d*, $^3J_{CP} = 15.1$ Hz, $^2CH_2$), 37.8 (*d*, $^2J_{CP} = 10.8$ Hz, $^2CH_3$), 36.2 (*d*, $^2J_{CP} = 2.2$ Hz, $^1CH_3$). MS (CI, NH_3), *m/z*: 309.2 (309.3 calculated) $[M + H]^+$. MS (EI, NH_3), *m/z*: 308.3 (308.3 calculated) $[M]^+$.

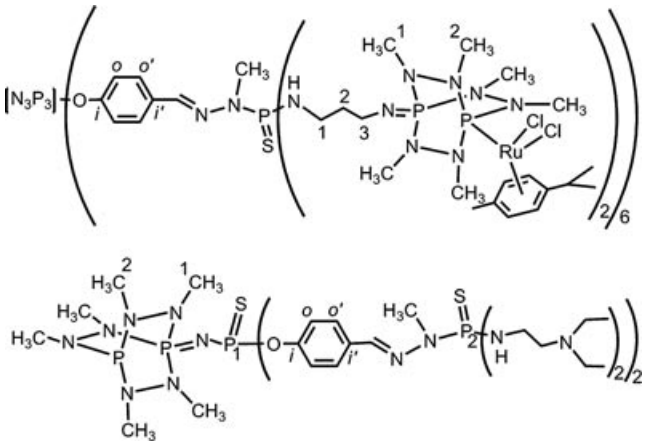


FIGURE 2 Numbering used for NMR assignment.

Synthesis of **8**. To a mixture of **7** (0.104 g 0.057 mmol) and Cs_2CO_3 (0.666 g, 2.052 mmol) in THF (20 mL), a solution of **5** (0.210 g, 0.684 mmol) in THF (5 mL) was added dropwise at 0°C. The mixture was allowed to reach room temperature; and after 3 days of stirring, completion was achieved. Cs_2CO_3 was filtered through celite and the solution was concentrated to 5 mL. The product was precipitated as a white solid by addition of pentane. Yield: 0.262 g (91%). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K, δ, ppm): 95.3 (*d*, $^3J_{PP} = 74.6$ Hz, P), 66.8 (*s*, P(S)), 8.5 (*s* (*br*), $[N_3P_3]$), 2.1 (*d*, $^3J_{PP} = 74.6$ Hz, P=N). ^1H NMR (300.1 MHz, CD_2Cl_2, 298 K, δ, ppm): 7.70–7.30 (*m*, 18H, *o'*-C_6H_4 + CH=N), 7.30–6.80 (*m*, 12H, *o*-C_6H_4), 4.52 (*s* (*br*), 12H, NH), 3.40–3.25 (m, 24H, $^1CH_2$), 3.25–3.10 (m, 42H, $^3CH_2$ + $P(S)NCH_3$), 2.90–2.65 (*m*, 216H, $^1CH_3 + ^2CH_3$), 1.66 (*s*, 24H, $^2CH_2$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 298 K, δ, ppm): 150.4 (*s* (*br*), *i*-C_6H_4), 135.0 (*s* (*br*),

CH=N), 133.4 (*s*(*br*), *i*′-C_6H_4), 127.4 (*s*, *o*′-C_6H_4), 121.1 (*s*, *o*-C_6H_4), 42.0 (*s*, $^1CH_2$), 41.3 (*s*, $^3CH_2$), 37.7 (*d*, $^2J_{CP}$ = 2.1 Hz, $^2CH_3$), 36.0 (*d*, $^2J_{CP}$ = 2.8 Hz, $^1CH_3$), 34.9 (*dd*, $^3J_{CP}$ = 16.5 Hz, $^3J_{CP}$ = 7.8 Hz, $^2CH_2$), 32.0 (d, $^2J_{CP}$ = 12 Hz, P(S)NCH_3). Anal. Calcd for $C_{156}H_{348}N_{111}O_6P_{33}S_6$ (5089.7): C, 36.81; H, 6.89; N, 30.55. Found: C, 36.98; H, 6.94; N, 30.39.

Synthesis of **9**. To a solution of **8** (0.090 g, 0.018 mmol) in CH_2Cl_2 (10 mL), 0.065 g (0.108 mmol) of [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$ was added. After 30 min, the solvent was removed in vacuo and the crude product was washed three times with pentane. The desired product was obtained as a red solid. Yield: 0.144 g (93%). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K, δ, ppm): 114.5 (*s* (*br*), P-Ru), 67.1 (*s*, P(S)), 8.5 (*s* (*br*), [N_3P_3]), 1.5 (*s* (*br*), P=N). ^1H NMR (300.1 MHz, CD_2Cl_2, 298 K, δ ppm): 7.70–7.30 (*m*, 18H, *o*′-C_6H_4 + CH=N), 7.30–6.80 (*m*, 12H, *o*-C_6H_4), 5.65 (*s* (*br*), 24H, C_6H_4 cymene), 5.28 (*s* (*br*), 24H, C_6H_4 cymene), 4.44 (*s* (*br*), 12H, NH), 3.45–3.25 (m, 24H, $^1CH_2$), 3.25–3.05 (m, 42H, $^3CH_2$ + P(S)NCH_3), 3.06–2.80 (*m*, 228H, $^1CH_3$ + $^2CH_3$ + C*H*$(CH_3)_2$), 2.20 (*s*, 36H, C*H*$_3$-C_6H_4), 1.73 (*s* (*br*), 24H, $^2CH_2$), 1.36 (*d*, 72H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 298 K, δ, ppm): 150.3 (*s* (*br*), *i*-C_6H_4), 135.0 (*s* (*br*), CH=N), 133.0 (*s* (*br*), *i*′-C_6H_4), 127.7 (*s*, *o*′-C_6H_4), 121.0 (*s*, *o*-C_6H_4), 113.6 (*s*, *C*-CH$(CH_3)_2$), 100.3 (*s*, *C*-CH_3), 91.5 (*s* (*br*), C_6H_4 cymene), 87.9 (*s*, C_6H_4 cymene), 41.7 (*s*, $^1CH_2$), 40.9 (*s*, $^3CH_2$), 38.3 (*d*, $^2J_{CP}$ = 15.1 Hz, $^2CH_3$), 36.1 (*s*, $^1CH_3$), 34.8 (*s* (*br*), $^2CH_2$), 32.0 (*s* (*br*), P(S)NCH_3), 30.6 (*s*, *C*H$(CH_3)_2$), 22.0 (*s* (*br*), CH(*C*H$_3$)$_2$), 17.5 (*s*, *C*H$_3$-C_6H_4). Anal. Calcd for $C_{276}H_{516}Cl_{24}N_{111}O_6P_{33}Ru_{12}S_6$ (8764.1): C, 37.83; H, 5.93; N, 17.74. Found: C, 37.95; H, 5.99; N, 17.58.

Synthesis of **11**. To a solution of **4** (0.392 g, 0.166 mmol) in CH_2Cl_2 and at 0°C, a solution of **10** (0.577 g, 0.166 mmol) in 15 mL of CH_2Cl_2 was added dropwise. The temperature and stirring were maintained for 2 days. The desired product was obtained as a colorless oil after purification by successive precipitation of the by-products with diethylether at 0°C. Yield: 0.607 g (66%). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K, δ, ppm): 99.3 (*d*, $^3J_{PP}$ = 87.6 Hz, P), 42.5 (*d*, $^2J_{PP}$ = 67.1 Hz, P(S)), 1.8 (*dd*, $^3J_{PP}$ = 87.6 Hz, $^2J_{PP}$ = 67.1 Hz, P=N). ^1H NMR (200.1 MHz, CD_2Cl_2, 298 K, δ, ppm): 9.96 (*s*, 2H, CHO), 7.87 (*d*, $^3J_{HH}$ = 8.3 Hz, 4H, *o*′-C_6H_4), 7.40 (*dd*, $^3J_{HH}$ = 8.3 Hz, $^4J_{HP}$ = 1.5 Hz, 4H, *o*-C_6H_4), 2.85–2.76 (*m*, 18H, $^1CH_3$ + $^2CH_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 298 K, δ, ppm): 191.6 (*s*, CHO), 157.3 (*s*, *i*-C_6H_4), 133.8 (*s*, *i*′-C_6H_4), 131.9 (*s*, *o*′-C_6H_4), 122.7 (*d*, $^3J_{CP}$ = 5.4 Hz, *o*-C_6H_4), 38.3 (*d*, $^2J_{CP}$ = 10.1 Hz, $^2CH_3$), 36.7 (*d*, $^2J_{CP}$ = 4.1 Hz, $^1CH_3$). Anal. Calcd for $C_{20}H_{28}N_7O_4P_3S$ (555.5): C, 43.25; H, 5.08; N, 17.65. Found: C, 43.32; H, 5.11; N, 17.58.

Synthesis of **12**. The procedure was analogous to that used for product **6**. Starting with 0.200 g (0.360 mmol) of **11** and 0.110 g (0.180 mmol) of the ruthenium dimer, **12** was obtained as a red solid. Yield: 0.279 g (90%). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K, δ, ppm): 118.7 (*d*, $^3J_{PP}$ = 98.8 Hz, P-Ru), 43.7 (*d*, $^2J_{PP}$ = 67.1 Hz, P(S)), 1.5 (*dd*, $^3J_{PP}$ = 98.8 Hz, $^2J_{PP}$ = 67.1 Hz, P=N). ^1H NMR (250.1 MHz, $CDCl_3$, 298 K, δ, ppm): 10.0 (*s*, 2H, CHO), 7.91 (*d*, $^3J_{HH}$ = 8.2 Hz, 4H, *o*′-C_6H_4), 7.44 (*dd*, $^3J_{HH}$ = 8.2 Hz, $^4J_{HP}$ = 1.3 Hz, 4H, *o*-C_6H_4), 5.77–5.26 (*m*, 4H, C_6H_4 *p*-cymene), 3.03 (*m*, 1H, C*H*$(CH_3)_2$), 2.77 (*d*, $^3J_{HP}$ = 9.7 Hz, 18H, $^1CH_3$ + $^2CH_3$), 2.26 (*s*, 3H, C*H*$_3$-C_6H_4), 1.39 (*d*, $^3J_{HH}$ = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (62.9 MHz, CD_2Cl_2, 298 K, δ, ppm): 190.8 (*s*, CHO), 157.0 (*s*, *i*-C_6H_4), 133.3 (*s*, *i*′-C_6H_4), 131.2 (*s*, *o*′-C_6H_4), 122.0 (*d*, $^3J_{CP}$ = 5.7 Hz, *o*-C_6H_4), 114.4 (*s*, *C*-CH$(CH_3)_2$), 100.6 (*s*, *C*-CH_3), 91.5 (*m*, C_6H_4 *p*-cymene), 88.3 (*m*, C_6H_4 *p*-cymene), 38.3 (*d*, $^2J_{CP}$ = 6.9 Hz, $^2CH_3$), 35.9 (*d*, $^2J_{CP}$ = 6.3 Hz, $^1CH_3$), 30.7 (*s*, *C*H$(CH_3)_2$), 22.0 (*s* (*br*), CH(*C*H$_3$)$_2$), 17.6 (*s*, *C*H$_3$-C_6H_4). Anal. Calcd for $C_{30}H_{42}Cl_2N_7O_4P_3RuS$ (861.7): C, 41.82; H, 4.91; N, 11.38. Found: C, 41.91; H, 4.95; N, 11.30.

Synthesis of **15**. This product was prepared using two different procedures. In both cases, the reaction were quantitative and followed by $^{31}P\{^1H\}$ NMR. (a) 0.175 g (0.262 mmol) of compound **14** was dissolved in 5 mL of CH_2Cl_2 and added to a solution of **4** (0.075 g, 0.314 mmol) in 10 mL of CH_2Cl_2 at 0°C. The resulting solution was stirred overnight. (b) 3.3 mL of a solution of $H_2NNMeP(S)Cl_2$ 2.0 M in $CHCl_3$ (0.660 mmol) were added dropwise to a solution of **11** (0.183 g, 0.329 mmol) in CH_2Cl_2 (10 mL) in the presence of molecular sieves. The mixture was stirred for 2 days at room temperature. $^{31}P\{^1H\}$ NMR (121.5 MHz, CH_2Cl_2/C_6D_6, 298 K, δ, ppm): 99.1 (*d*, $^3J_{PP}$ = 86.7 Hz, P), 63.2 (*s*, P(S)Cl_2), 44.0 (*d*, $^2J_{PP}$ = 66.9 Hz, P(S)), 1.5 (*dd*, $^3J_{PP}$ = 86.7 Hz, $^2J_{PP}$ = 66.9 Hz, P=N). ^1H NMR (250.1 MHz, $CDCl_3$, 298 K, δ, ppm): 7.59 (*d*, $^3J_{HH}$ = 8.0 Hz, 4H, *o*′-C_6H_4), 7.48 (*s*, 2H, CH=N), 7.25 (*d*, $^3J_{HH}$ = 8.0 Hz, 4H, *o*-C_6H_4), 3.19 (*d*, $^3J_{HP}$ = 10.3 Hz, 6H, P(S)NCH_3), 2.85–2.70 (*m*, 18H, $^1CH_3$ + $^2CH_3$). Anal. Calcd for $C_{22}H_{34}Cl_4N_{11}O_2P_5S_3$ (877.5): C, 30.11; H, 3.91; N, 17.56. Found: C, 30.20; H, 3.96; N, 17.45.

Synthesis of **16**. To a mixture of **15** (0.229 g, 0.262 mmol) and Cs_2CO_3 (1.022 g, 3.138 mmol) in CH_2Cl_2 (15 mL) and at 0°C, a solution of

diethylethylenediamine (0.148 mL, 1.048 mmol, 15 mL of CH_2Cl_2) was added dropwise. The mixture was stirred overnight and, afterwards, Cs_2CO_3 was filtered through celite and the solvent was removed in vacuo. The crude product was washed three times with pentane at −30°C. The desired product was obtained as a pale yellow oil. Yield: 0.256 g (82%). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K, δ, ppm): 99.1 (*d*, $^3J_{PP}$ = 87.4 Hz, P), 68.0 (*s*, $P_2(S)$), 44.1 (*d*, $^2J_{PP}$ = 66.8 Hz, $P_1(S)$), 1.3 (*dd*, $^3J_{PP}$ = 87.4 Hz, $^2J_{PP}$ = 66.8 Hz, P=N). ^1H NMR (400.1 MHz, $CDCl_3$, 298 K, δ, ppm): 7.57 (*d*, $^3J_{HH}$ = 8.1 Hz, 4H, *o*′-C_6H_4), 7.47 (*s*, 2H, CH=N), 7.23 (*d*, $^3J_{HH}$ = 8.1 Hz, 4H, *o*-C_6H_4), 4.07 (*s* (*br*), 4H, NH), 3.16 (*d*, $^3J_{HP}$ = 9.3 Hz, 6H, P(S)NCH_3), 3.14–2.90 (*m*, 8H, $NCH_2CH_2NEt_2$), 2.85–2.70 (*m*, 18H, $^1CH_3 + {}^2CH_3$), 2.70–2.54 (*m*, 24H, $NCH_2CH_2N(CH_2CH_3)_2$), 1.00 (*t*, $^3J_{HH}$ = 6.9 Hz, 24H, $N(CH_2CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K, δ, ppm): 152.2 (*d*, $^2J_{CP}$ = 9.4 Hz, *i*-C_6H_4), 136.1 (*d*, $^3J_{CP}$ = 12.4 Hz, CH=N), 132.4 (*s*, *i*′-C_6H_4), 127.5 (*s*, *o*′-C_6H_4), 121.8 (*d*, $^3J_{CP}$ = 4.9 Hz, *o*-C_6H_4), 53.5 (*d*, $^2J_{CP}$ = 7.9 Hz, $NCH_2CH_2NEt_2$), 46.9 (*s*, $N(CH_2CH_3)_2$), 38.8 (*s*, $NCH_2CH_2NEt_2$), 38.0 (*d*, $^2J_{CP}$ = 10.2 Hz, $^2CH_3$), 36.3 (*d*, $^2J_{CP}$ = 4.2 Hz, $^1CH_3$), 31.0 (*d*, $^2J_{CP}$ = 11.0 Hz, P(S)NCH_3), 11.7 (*s*, $N(CH_2CH_3)_2$). EM (ESI(+)), *m*/*z*: 1197.3 (1197.1 calculated) $[M]^+$.

Synthesis of **17**. To a solution of **16** (0.130 g, 0.109 mmol) in CH_2Cl_2 (15 mL), $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ was added until total disappearance of the signal at δ = 99.1 ppm in the $^{31}P\{^1H\}$ NMR was observed. The solution was concentrated to 5 mL, and 15 mL of pentane was added to precipitate the desired product that was washed three times with pentane (3 × 15 mL) and obtained as a dark red solid. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K, δ, ppm): 118.8 (*d*, $^3J_{PP}$ = 99.0 Hz, P-Ru), 68.0 (*s*, $P_2(S)$), 44.1 (*d*, $^2J_{PP}$ = 63.7 Hz, $P_1(S)$), 0.7 (*dd*, $^3J_{PP}$ = 99.0 Hz, $^2J_{PP}$ = 63.7 Hz, P=N). ^1H NMR (300.1 MHz, $CDCl_3$, 298 K, δ, ppm): 7.62 (*d*, $^3J_{HH}$ = 8.4 Hz, 4H, *o*′-C_6H_4), 7.50 (*s*, 2H, CH=N), 7.27 (*d*, $^3J_{HH}$ = 8.4 Hz, 4H, *o*-C_6H_4), 5.69–5.64 (*m*, 2H, C_6H_4 cymene), 5.34–5.24 (*m*, 2H, C_6H_4 cymene), 4.20 (*s* (*br*), 4H, NH), 3.20 (*d*, $^3J_{HP}$ = 9.3 Hz, 6H, P(S)NCH_3), 3.40 (*m*, 1H, $CH(CH_3)_2$), 3.18–2.50 (*m*, 50H, $^1CH_3 + {}^2CH_3 + NCH_2CH_2N(CH_2CH_3)_2$), 2.24 (*s*, 3H, CH_3-C_6H_4), 1.37 (*d*, $^3J_{HH}$ = 5.1 Hz, 6H, $CH(CH_3)_2$), 1.07 (*s*(*br*), 24H, $N(CH_2CH_3)_2$). **17** was not stable enough to allow us to register ^{13}C NMR data.

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