Organometallics **1993,** *12,* 2861-2863

Phosphorus-Containing Metallamacrocycles

Dominique Colombo-Khater, Anne-Marie Caminade, Béatrice Delavaux-Nicot, and Jean-Pierre Majoral*

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne,
31077 Toulouse Cédex, France

Received February 2, 1993

Summary: The four phosphorus–zirconium-containing macrocycles ***4a–d****, $PhP(Y)[N(Me)N{=}C(H)C_6H_4OM(Cp)_2OC_6H_4C(H){=}NNMe]_2P(Y)Ph$ (M = Zr), were prepared via [2 + 2] cycloaddition reactions involving dimethylzirconocene, Cp_2ZrMe_2, and phosphodihydrazones* ***2a,b*** *and* ***3a,b****, $PhP(Y)[N(Me)N{=}C(H)C_6H_4OH]_2$ (***2a***, meta OH, Y = S;* ***2b****, meta OH, Y = O;* ***3a****, para OH, Y = S;* ***3b****, para OH, Y = O). Addition of dimethyltitanocene, Cp_2TiMe_2, to* ***3a*** *led to the macrocyclic [2 + 2] cycloadduct* ***4e****. Phosphonium metallacycles* ***6c,d*** *possessing either P—SMe or P—$OSiMe_3$ groups were prepared by reacting* ***4c*** *or* ***4d*** *with methyl trifluoromethanesulfonate or trimethylsilyl trifluoromethanesulfonate respectively. p-Hydroxy phosphodihydrazones* ***3a,b*** *when reacted with dimethyl- or diphenyldichlorosilanes led to the phosphorus–silicon-containing macrocycles* ***8a–c****, $PhP(Y)[NMeN{=}C(H)C_6H_4OSiR_2\text{-}OC_6H_4C(H){=}NNMe]_2P(Y)Ph$ (R = Me, Ph), arising from [2 + 2] cyclocondensations.*

Phosphodihydrazides $RP(Y)[N(Me)NH_2]_2$ (1) or phosphodihydrazones $RP(Y)[N(Me)\text{-}N{=}C(H)C_6H_4OH]_2$ (2) appeared to be useful starting reagents for the preparation of a large variety of phosphorus-containing macrocycles when reacted with dialdehydes[1] or dichlorophosphine oxides or sulfides.[2] Some of these linear ligands or the resulting macrocycles exhibited interesting complexation properties toward a number of alkaline-earth or transition metals[1a,3,4] due to the presence of various donor atoms such as P, O, S, and N.

Previous reports have described the synthesis and structures of bimetallic macrocyclic zirconocene dialkoxide or dithiolate complexes.[5] While the dithiolate derivatives allowed complexation of silver, it appeared that the donor ability of the oxygen atoms in the alkoxy complexes diminished by π bonding to zirconium. As a consequence, dialkoxides seemed not to allow complexation.

The demonstrated stability and ability of our phosphorus ligands to form complexes prompted us to investigate the possibility of preparing early-transition-metal bimetallic macrocyclic species possessing numerous electron donors in order to enhance the ability of zirconium or titanium macrocycles to bind other metals. On the other hand, it was tempting to take advantage of the reactivity of phosphodihydrazones 2 and 3 to prepare macrocycles possessing both donor and acceptor atoms which might allow the simultaneous complexation of cations and anions. Our first efforts in this area were directed to the formation of phosphorus- and silicon-containing macrocycles. We report here the synthesis of the first phosphorus–zirconium- and phosphorus–titanium-containing macrocycles arising from [2 + 2] cyclocondensation reactions as well as preliminary experiments concerning their reactivity and leading to new bis(phosphonium) metallacycles. The preparation of some unique phosphorus- and silicon-containing macrocycles is also described.

Results and Discussion

Phosphorus–Zirconium- and Phosphorus–Titanium-Containing Macrocycles. Addition of a THF solution of Cp_2ZrMe_2 (1 equiv) to a THF solution of meta or para phosphodihydrazones[2,6] **2a,b** or **3a,b** (1 equiv) was accompanied by rapid evolution of methane with the formation of [2 + 2] cycloadducts **4a–d** (Scheme I). ^{31}P NMR spectra of the resulting mixture showed, as expected, no $\Delta\delta(^{31}P)$ between the chemical shift of the starting phosphorus ligands and the final compounds **4a–d**.[1] Nevertheless, structures were deduced from ^1H and ^{13}C NMR, IR, and mass spectrometry as well as elemental analysis. For example, ^1H NMR spectra exhibited a singlet resonance arising from the cyclopentadienyl protons ($6.1 < \delta < 6.3$ ppm), while no signal corresponding to either the OH group of **2a,b** or **3a,b** or the methyl groups of Cp_2ZrMe_2 was detected. ^{13}C NMR spectra were fully consistent with the presence of the Cp groups, which appeared as a singlet ($110.4 < \delta < 112.6$ ppm). Fast atom bombardment mass spectrometry of **4a–d** showed molecular ion peaks corresponding to [2 + 2] cyclocondensations. No peak due to [1 + 1], [3 + 3], or other types of cyclocondensations between Cp_2ZrMe_2 and **2a,b** or **3a,b** was observed.

Note that the position of the hydroxyl groups in **2a,b** and **3a,b** is of the greatest importance since the reaction is significantly faster with **3a,b** (OH in para position) than with **2a,b** (OH in meta position): the reactions required 8 h of stirring at room temperature to go to completion in one case and 2 days in the other. Moreover, no reaction was observed with phosphodihydrazones **5a,b**, in which the OH groups are in ortho position.

In a similar manner, the reaction of Cp_2TiMe_2 with the phosphodihydrazone **3a** proceeded with methane liber-

---

(1) (a) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1988,** *27,* 3873. (b) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Gorgues, A.; Delmas, M.; Gaset, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990,** *49–50,* 143. (c) Badri, M.; Majoral, J.-P.; Caminade, A.-M.; Delmas, M.; Gaset, A.; Gorgues, A.; Jaud, J. *J. Am. Chem. Soc.* **1990,** *112,* 5618. (d) Badri, M.; Majoral, J-P.; Gonce, F.; Caminade, A.-M.; Sallé, M.; Gorgues, A. *Tetrahedron Lett.* **1990,** *31,* 6343. (e) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1991,** *30,* 344. (f) Majoral, J.-P.; Badri, M.; Caminade, A.-M. *Heteroat. Chem.* **1991,** *2,* 45. (g) Gonce, F.; Caminade, A.-M.; Majoral, J.-P. *Tetrahedron Lett.* **1991,** *32,* 203. (h) Gonce, F.; Caminade, A.-M.; Boutonnet, F.; Majoral, J.-P. *J. Org. Chem.* **1992,** *57,* 970. (i) Gonce, F.; Caminade, A.-M.; Majoral, J.-P.; Jaud, J.; Vignaux, P. *Bull. Soc. Chim. Fr.* **1992,** *129,* 237.

(2) Colombo, D.; Caminade, A.-M.; Majoral, J.-P. *Inorg. Chem.* **1991,** *30,* 3367.

(3) Delavaux-Nicot, B.; Lugan, N.; Majoral, J.-P.; Mathieu, R. *Inorg. Chem.* **1992,** *31,* 334.

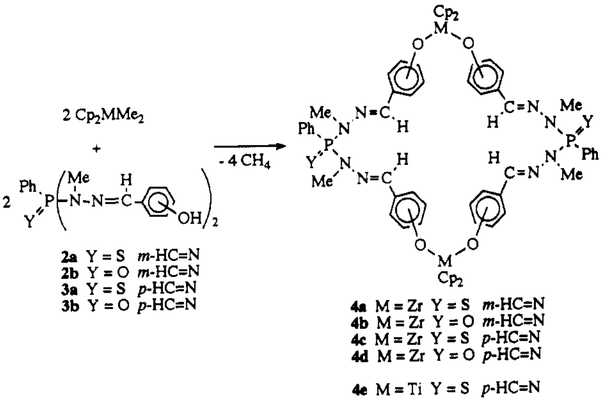
(4) Colombo-Khater, D.; Caminade, A.-M.; Jaud, J.; Majoral, J.-P. Submitted for publication.

(5) Stephan, D. *Organometallics* **1990,** *9,* 2718; **1991,** *10,* 2037.

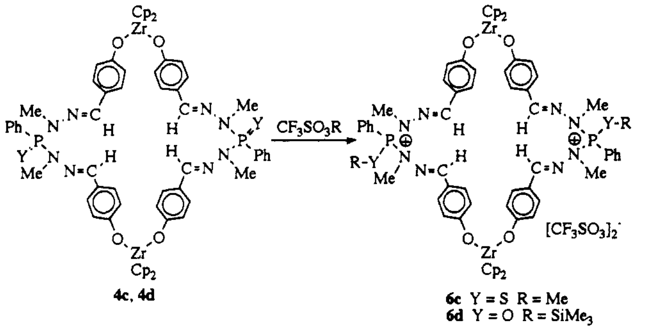
(6) Colombo, D.; Caminade, A.-M.; Majoral, J.-P. *Synthesis*, in press.

0276-7333/93/2312-2861$04.00/0

Scheme I



Scheme II



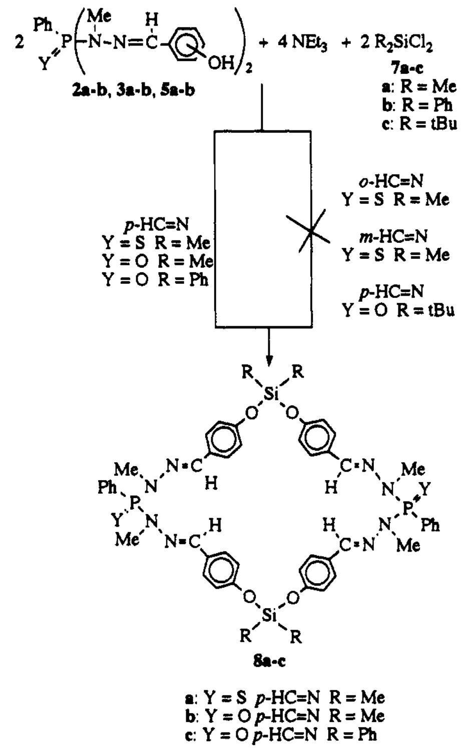
ation and formation of the titanium-containing macrocycle **4e**. This extremely unstable derivative was also fully characterized by NMR, IR, mass spectrometry, and elemental analysis.

The 32- or 36-membered rings **4a–e** represent the first examples of phosphorus-containing early-transition-metal macrocycles. These compounds slowly decomposed in solution and were extremely sensitive to hydrolysis.

We tried to obtain macrocyclic salts by reacting some of these derivatives with either methyl or trimethylsilyl trifluoromethanesulfonate. Indeed, addition of 2 equiv of methyl trifluoromethanesulfonate to a dichloromethane solution of **4c** (1 equiv) at 0 °C led to the bis(phosphonium) salt **6c** (Scheme II). A deshielding effect of 5 ppm is observed in ^{31}P NMR (**4c**, δ 78.4 ppm; **6c**, δ 73.0 ppm).[1e,7] ^{1}H NMR implicated that methylation occurred exclusively on sulfur: the SMe groups appeared as a doublet at 2.6 ppm with a hydrogen–phosphorus coupling constant of 16 Hz, which is larger than that observed for the NMe groups ($^{3}J_{HP}$ = 9–10 Hz). IR spectroscopy showed a shift of the $\nu_{P=S}$ vibration from 780 to 640 cm^{-1}, consistent with the methylation of sulfur atoms. Conductometric measurements in acetonitrile (0.01 M) confirmed the ionic character of **6c** (Λ_{eq} = 151 Ω^{-1} cm^{2} mol^{-1}).

Similarly, addition of 2 equiv of trimethylsilyl trifluoromethanesulfonate to the macrocycle **4d** (1 equiv) in dichloromethane afforded the bis(phosphonium) salt **6d** (Scheme II), which exhibited a $\delta(^{31}P)$ value of +31.6 ppm (**4d**, δ 24.2 ppm), indicating that silylation occurred selectively on the oxygen atoms of the two phosphoryl groups. Its ^{1}H NMR spectrum showed a signal at 0.3 ppm due to the SiMe$_3$ groups. As in the case of **6c**, conductometric measurements in acetonitrile (0.01 M) corroborated the ionic character of **6d** (Λ_{eq} = 193 Ω^{-1} cm^{2} mol^{-1}).

Scheme III



Phosphorus- and Silicon-Containing Macrocycles. Reactions involved slow addition of a THF solution of the dichlorosilane R$_2$SiCl$_2$ (**7a**, R = Me; **7b**, R = Ph) (1 equiv) to a THF solution of the difunctionalized phosphodihydrazone **3a** or **3b** (1 equiv) and triethylamine (2 equiv) (Scheme III). Formation of macrocycles **8a** and **8b** was significantly faster than that of **8c**: 1 day to go to completion in the first case and 3 days in the second case. Moreover, no reaction occurred with a more bulky dichlorosilane such as *tert*-Bu$_2$SiCl$_2$ (**7c**).

Besides the ^{1}H NMR signals of the phosphodihydrazone part of the molecule (i.e., C$_6$H$_5$, NCH$_3$, CH=N, C$_6$H$_4$) macrocycles **8a,b** showed singlets at 0.2 (**8a**) and 0.3 ppm (**8b**) in their ^{1}H NMR spectra and at −2.7 (**8a**) and −2.8 ppm (**8b**) in their ^{13}C{^{1}H} NMR spectra for the (CH$_3$)$_2$Si groups. These chemical shifts are typical for protons and carbons of methyl groups in an OSi(CH$_3$)$_2$O environment. Characteristic singlets are also observed in the ^{29}Si NMR spectra: δ −4.5 ppm for **8a** and **8b**, δ −37 ppm for **8c**. Mass spectrometry provided a direct confirmation of the structures, pointing out the presence of only [2 + 2] cycloadducts.

As in the case of the formation of metallacycles **4a–e**, phosphodihydrazones **2a,b** (OH in meta position) and **5a,b** (OH in ortho position) reacted very slowly with **7a** or **7b**. Thus, reactions did not go to completion after 1 week in refluxing THF and hydrolysis of Si–O bonds took place under these conditions.

We are currently extending the generality of these cyclocondensation reactions using not only a variety of other phosphodihydrazones but also new phosphotrihydrazones, (Y)P(NCH$_3$N=CHR)$_3$. Reactivity studies of these phosphorus–zirconium-, phosphorus–titanium-, and phosphorus–silicon-containing macrocycles, including complexation properties, are also underway.

---

[7] Hudson, H. R.; Dillon, K. B.; Walker, B. J. In *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press: Boca Raton, FL, 1990; pp 181–226.

Experimental Section

General Procedures. All experiments were performed under a dry argon atmosphere. Dry, oxygen-free solvents were used at all times. ^{31}P NMR spectra were obtained on a Bruker AC 80 spectrometer. Downfield shifts are expressed with a positive sign in ppm relative to external 85% H_3PO_4. ^{1}H NMR spectra were recorded on a Bruker WM 250 or a Bruker AC 80. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. Downfield shifts are expressed with a positive sign. IR spectra were recorded on a Beckman IR 10 spectrometer and a Perkin-Elmer lattice spectrometer (Mol 598), using a polystyrene film for calibration. Mass spectra were obtained on a Ribermag R 10 10E instrument or a Varian MAT 311 A instrument.

Typical Procedure for the Preparation of Macrocycles 4a–e. To a solution of phosphodihydrazone (1.98 mmol) **2a,b** or **3a,b**[6] in 20 mL of THF at room temperature was added dropwise a solution of Cp_2ZrMe_2 (1.98 mmol) in 10 mL of THF. Methane evolution was readily apparent, and the reaction mixture was allowed to stand for 8–24 h, depending on the starting phosphodihydrazone. Removal of the solvent gave a white powder which was washed with THF/pentane (1/1). The same reaction involving Cp_2TiMe_2 was performed at −60 °C.

4a: 56% yield; ^{1}H NMR ($CDCl_3$) δ 3.4 (d, $^{3}J_{HP} = 9.8$ Hz, 12H, P—N—CH_3), 6.1 (s, 20H, C_5H_5), 6.6–8.2 (m, 30H, C_6H_5, C_6H_4 and HC=N); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 31.4 (d, $^{2}J_{CP} = 7.4$ Hz, P—N—CH_3), 111.4 (s, C_5H_5), 112.8–135.9 (m, C_6H_5 and C_6H_4), 136.8 (m, HC=N), 162.1 (s, C—O—Zr); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 78.2 (s); IR (KBr) 1685 ($\nu_{C=N}$), 862 (ν_{Zr-O}), 720 ($\nu_{P=S}$) cm^{-1}; mass spectrum (FAB) *m/e* 1317 [M + 1]$^+$. Anal. Calcd for $C_{64}H_{62}N_8O_4P_2S_2Zr_2$: C, 58.42; H, 4.75; N, 8.52. Found: C, 58.30; H, 4.61; N, 8.39.

4b: 54% yield; ^{1}H NMR ($CDCl_3$) δ 2.9 (d, $^{3}J_{HP} = 6.9$ Hz, 12H, P—N—CH_3), 6.3 (s, 20H, C_5H_5), 6.6–8.1 (m, 30H, C_6H_5, C_6H_4 and HC=N); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 24.6 (s). Anal. Calcd for $C_{64}H_{62}N_8O_6P_2Zr_2$: C, 59.89; H, 4.87; N, 8.73. Found: C, 59.71; H, 4.77; N, 8.61.

4c: 75% yield; ^{1}H NMR ($CDCl_3$) δ 3.2 (d, $^{3}J_{HP} = 9.6$ Hz, 12H, P—N—CH_3), 6.2 (s, 20H, C_5H_5), 6.4–8.0 (m, 30H, C_6H_5, C_6H_4, and HC=N); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 30.4 (d, $^{2}J_{CP} = 7.8$ Hz, P—N—CH_3), 112.6 (s, C_5H_5), 113.8–134.7 (m, C_6H_5 and C_6H_4), 137.9 (m, HC=N), 165.5 (s, C—O—Zr); $^{31}P\{^{1}H\}$ NMR (CD_3CN) δ 78.4 (s); IR (KBr) 1690 ($\nu_{C=N}$) 850 (ν_{Zr-O}), 780 ($\delta_{P=S}$) cm^{-1}; mass spectrum (FAB) *m/e* 1317 [M + 1]$^+$. Anal. Calcd for $C_{64}H_{62}N_8O_4P_2S_2Zr_2$: C, 58.42; H, 4.75; N, 8.52. Found: C, 58.31; H, 4.71; N, 8.46.

4d: 64% yield; ^{1}H NMR ($CDCl_3$) δ 3.1 (d, $^{3}J_{HP} = 6.8$ Hz, 12H, P—N—CH_3), 6.1 (s, 20H, C_5H_5), 6.8–8.1 (m, 30H, C_6H_5, C_6H_4, and HC=N); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 31.2 (d, $^{2}J_{CP} = 7.2$ Hz, P—N—CH_3), 110.4 (s, C_5H_5), 113.7–134.9 (m, C_6H_5 and C_6H_4), 138.8 (m, HC=N), 160.1 (s, C—O—Zr); $^{31}P\{^{1}H\}$ NMR (CD_3CN) δ 24.2 (s); IR (KBr) 1665 ($\nu_{C=N}$), 1255 ($\nu_{P=O}$), 872 (ν_{Zr-O}) cm^{-1}; mass spectrum (FAB) *m/e* 1285 [M + 1]$^+$. Anal. Calcd for $C_{64}H_{62}N_8O_6P_2Zr_2$: C, 59.89; H, 4.87; N, 8.73. Found: C, 59.61; H, 4.61; N, 8.64.

4e: 52% yield; ^{1}H NMR ($CDCl_3$) δ 3.4 (d, $^{3}J_{HP} = 7.9$ Hz, 12H, P—N—CH_3), 6.1 (s, 20H, C_5H_5), 6.8–8.0 (m, 30H, C_6H_5, C_6H_4, and HC=N); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 78.6 (s); mass spectrum (FAB) *m/e* 1273 [M + 1]$^+$. Anal. Calcd for $C_{64}H_{62}N_8O_4P_2S_2Ti_2$: C, 62.54; H, 5.08; N, 9.12. Found: C, 62.49; H, 5.12; N, 8.97.

Synthesis of the Bis(phosphonium) Compound 6c. To a solution of the macrocycle **4c** (0.45 mmol) in 20 mL of dichloromethane at 0 °C was added methyl trifluoromethanesulfonate (0.9 mmol). The reaction mixture was stirred for 1 h at room temperature. Evaporation of the solvent gave an unstable orange oily residue, which was purified by extraction with acetonitrile (2 × 10 mL). Removal of acetonitrile gave a pure sample of **6c** (orange oil).

6c: 95% yield; ^{1}H NMR (CD_3CN) δ 2.6 (d, $^{3}J_{HP} = 16$ Hz, 6H, S—CH_3), 3.4 (d, $^{3}J_{HP} = 10.4$ Hz, 12H, P—N—CH_3), 6.4 (s, 20H, C_5H_5), 6.7–8.2 (m, 30H, C_6H_5, C_6H_4, and CH=N); $^{31}P\{^{1}H\}$ (CD_3CN) δ 73.0 (s); IR (KBr) 640 ($\nu_{P=S}$) cm^{-1}. Anal. Calcd for $C_{68}H_{68}F_6N_8O_{10}P_2S_4Zr_2$: C, 49.68; H, 4.17; N, 6.82. Found: C, 49.46; H, 4.12; N, 6.71.

Synthesis of the Bis(phosphonium) Compound 6d. Trimethylsilyl trifluoromethanesulfonate (0.9 mmol) was added to a solution of the macrocycle **4d** (0.45 mmol) in 20 mL of dichloromethane maintained at 0 °C. The reaction mixture was stirred for 1 h at room temperature. Evaporation of the solvent gave crude **6d** as an orange oil, which was purified by extraction with acetonitrile (20 mL). Removal of acetonitrile gave a pure sample of **6d**.

6d: 93% yield; ^{1}H NMR (CD_3CN) δ 0.3 (s, 18H, $OSiMe_3$), 3.4 (d, $^{3}J_{PH} = 7.4$ Hz, 12H, P—N—CH_3) 6.2 (s, 20H, C_5H_5), 6.8–8.1 (m, 30H, C_6H_5, C_6H_4, and CH=N); $^{31}P\{^{1}H\}$ NMR (CD_3CN) δ 31.6 (s). Anal. Calcd for $C_{72}H_{80}F_6N_8O_{12}P_2S_2Si_2Zr_2$: C, 50.04; H, 4.67; N, 6.48. Found: C, 49.81; H, 4.57; N, 6.32.

Synthesis of Phosphorus–Silicon Macrocycles 8a–c. To a solution of phosphodihydrazone **3a** or **3b** (1.14 mmol, 0.50 g of **3a** or 0.48 g of **3b**) in 20 mL of THF was added triethylamine (2.28 mmol, 318 μL). The mixture was stirred for 20 min at 0 °C. Dichlorodimethylsilane (1.14 mmol, 138 μL) or dichlorodiphenylsilane (1.14 mmol, 240 μL) was added. The mixture was stirred for 1 day (compound **8a,b**) or 3 days (compound **8c**) and then filtered. Evaporation of the solvent led to white powders.

8a: 78% yield; ^{1}H NMR (C_6D_6) δ 0.2 (s, 12H, CH_3—Si), 3.0 (d, $^{3}J_{HP} = 9.4$ Hz, 12H, P—N—CH_3), 6.8–8.2 (m, 30H, C_6H_5, C_6H_4, and HC=N); ^{13}C NMR (C_6D_6) δ −2.7 (q, $^{1}J_{CH} = 120.1$ Hz, CH_3—Si), 31.2 (dq, $^{2}J_{CP} = 7.9$ Hz, $^{1}J_{CH} = 135.8$ Hz, P—N—CH_3), 116.4–131.9 (m, C_6H_5 and C_6H_4), 136.9 (dd, $^{3}J_{CP} = 13.6$ Hz, $^{1}J_{CH} = 159.9$ Hz, HC=N), 156.1 (t, $^{2}J_{CH} = 8.8$ Hz, C—O—Si); $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 78.2 (s); $^{29}Si\{^{1}H\}$ NMR (C_6D_6) δ −4.6 (s); mass spectrum (FAB) *m/e* 989 [M + 1]· Anal. Calcd for $C_{48}H_{54}N_8O_4P_2S_2Si_2$: C, 58.28; H, 5.50; N, 11.33. Found: C, 58.17; H, 5.22; N, 11.58.

8b: 69% yield; ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 12H, CH_3—Si), 3.1 (d, $^{3}J_{HP} = 7.1$ Hz, 12H, P—N—CH_3), 6.7–8.1 (m, 30H, C_6H_5, C_6H_4, and HC=N); ^{13}C NMR ($CDCl_3$) δ −2.8 (q, $^{1}J_{CH} = 119.8$ Hz, CH_3—Si), 30.2 (dq, $^{2}J_{CP} = 7.8$ Hz, $^{1}J_{CH} = 139.0$ Hz, P—N—CH_3), 115.3–132.8 (m, C_6H_5 and C_6H_4), 136.6 (dd, $^{3}J_{CP} = 13.7$ Hz, $^{1}J_{CH} = 161$ Hz, HC=N), 154.0 (t, $^{2}J_{CH} = 9.8$ Hz, C—O—Si); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 24.4 (s); $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$) δ −4.5 (s); mass spectrum (FAB) *m/e* 957 [M + 1]$^+$. Anal. Calcd for $C_{48}H_{54}N_8O_6P_2Si_2$: C, 60.24; H, 5.69; N, 11.71. Found: C, 60.75; H, 5.22; N, 11.26.

8c: 75% yield; ^{1}H NMR ($CDCl_3$) δ 3.1 (d, $^{3}J_{HP} = 7.1$ Hz, 12H, P—N—CH_3), 6.7–8.0 (m, 50H, C_6H_5, C_6H_4, and HC=N); ^{13}C NMR ($CDCl_3$) δ 30.1 (dq, $^{2}J_{CP} = 7.6$ Hz, $^{1}J_{CH} = 138.8$ Hz; P—N—CH_3) 115.2–133.1 (m, C_6H_5 and C_6H_4), 136.1 (dd, $^{3}J_{PC} = 13.4$ Hz, $^{1}J_{CH} = 159$ Hz, HC=N), 153.8 (t, $^{2}J_{CH} = 9.9$ Hz, C—O—Si); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 25.0 (s); $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$) δ −37.0 (s); mass spectrum (FAB) *m/e* 1205 [M + 1]$^+$. Anal. Calcd for $C_{68}H_{62}N_8O_6P_2Si_2$: C, 67.76; H, 5.18; N, 9.30. Found: C, 67.62; H, 5.07; N, 9.21.

OM930059X