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ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 278–282
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Carbosilane dendrimers containing complexes *N*,*N*′-pyridylimine of molybdenum and platinum at their periphery

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Received 6 July 2006; received in revised form 30 October 2007; accepted 30 October 2007
Available online 4 November 2007

Abstract

Pyridylimine ligands of general formula CS-{O-4-(2,5-$C_6H_2R_2$)-N=CH-2-Py}$_n$, where CS is a trimethylsilyl group ($n = 1$, R = H, **Ia** or Me, **Ib**) or a carbosilane dendritic framework (**IIa**,**b**, $n = 4$; **IIIa**, $n = 8$), have been coordinated to platinum(II) and molybdenum(0) centers to give the mononuclear [(**Ia**,**b**){$PtCl_2$}], tetranuclear [(**IIb**){$PtCl_2$}$_4$] and [(**IIa**){$Mo(CO)_3(MeCN)$}$_4$], and octanuclear [(**IIIa**){$Mo(CO)_3(MeCN)$}$_8$] complexes. The poor solubility of the polymetallic platinum compounds impedes the preparation of higher-generation dendrimers, although such a limitation is not found in the case of the more soluble molybdenum dendrimers.

Keywords: N ligands; Dendrimers; Molybdenum; Platinum

1. Introduction

Dendrimers form a special type of materials because of the nanosized, hyperbranched, and well-defined nature of their macromolecular structures [1]. Functionalization of the core, branches, or periphery of such macromolecules with transition metals or organic synthons has attracted much attention for applications in areas such as catalysis [2,3] or in the biomedical arena [4]. In our ongoing program in this field, we have contributed to the chemistry of dendrimers, mostly of a carbosilane nature, that contain early transition metal complexes bonded to the dendritic periphery or focal point through aryloxy [5], siloxy [6], or cyclopentadienyl ligands [7], or using N-donor anchoring ligands such as diketiminato [8], imido [9], or scorpionate linkages [10]. Additionally, we have evidenced the good biocompatibility of ammonium-functionalized carbosilane dendrimers and their capability to form dendriplexes with oligonucleotides, making them potential candidates as drugs nanocarriers [11].

Nickel and palladium complexes with *N*,*N*′-pyridylimine ligands have been used as catalysts in different polymerization processes [12], and, recently, we have synthesized a series of dendrimers containing such metal complexes and found that the dendrimer generation affects the nature of the polymerization products [13]. Platinum complexes containing the same type or closely related ligands have played an important role in the study of C–H bond activation [14], or showed promising results as anticancer agents [15]. Other reported applications of *N*,*N*′-pyridylimine ligands include the immobilization of molybdenum carbonyls or copper halides for solid-phase organometallic synthesis and radical polymerization, respectively [16].

Since high metal loadings in metallodendrimers, together the presence of the dendritic matrix itself, might bring about uncovered behaviors in practical applications (e.g., therapeutic agents), we set out to explore the chemistry of platinum carbosilane dendrimers. Here, we describe the synthesis and characterization of new carbosilane dendrimers decorated with *N*,*N*′-pyridylimine complexes of molybdenum or platinum at their periphery. Related to this work, there are a few reports in the literature describing alkylpyridyliminopalladium moieties bound to the periphery of poly(propyleneimine) – also known as

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0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.10.050

DAB – dendrimers [17], or iron-bis(imino)pyridyl-terminated carbosilane dendrimers [18].

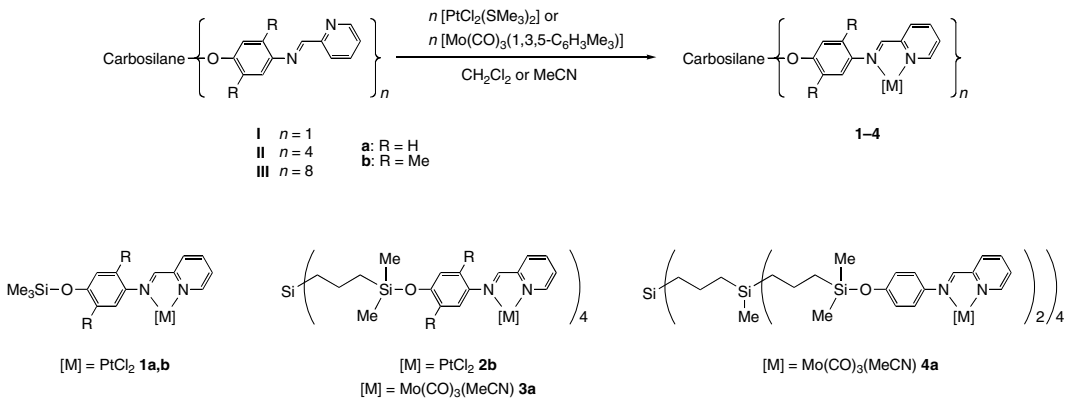
2. Results and discussion

The dichloroplatinum complexes **1a**,**b** were prepared in good yields by reaction of the corresponding pyridylimine ligand **Ia**,**b** with a mixture of *cis* and *trans* isomers of $[PtCl_2(SMe_2)_2]$ in dichloromethane (Scheme 1) [19]. They were isolated as orange or red solids, that are quite air-stable but that should be stored under an inert atmosphere for prolonged storage. Complex **1a** is slightly whereas **1b** is scarcely soluble in chlorinated solvents but both complexes are insoluble in alkanes, diethyl ether, or toluene. The positive-ion electrospray mass spectra (ESI+/MS) of compounds **1a**,**b** were measured in acetonitrile and exhibit the fragments due to the replacement of a chloride by an acetonitrile molecule $[M-Cl+MeCN]^+$, thus showing the characteristic ionization reported for related group 10 metal complexes [13,20]. While related palladium complexes were previously prepared by the displacement of a coordinated COD ligand (COD = 1,5-cyclooctadiene) [13c], the reaction of $[PtX_2(COD)]$ (X = Cl, I) with **Ia**,**b** afforded complicated mixtures of compounds in agreement with the relative resistance toward diolefin dissociation of platinum(II) compared with palladium(II) complexes [21].

In the reaction of **IIb** and $[PtCl_2(SMe_2)_2]$, the tetranuclear platinum **2b** precipitated out from the CH_2Cl_2 solution as a red solid insoluble in all common solvents. The elemental analysis and IR spectrum of the solid are consistent with the coordination of four platinum moieties per molecule. The solubility of these pyridylimine complexes and dendrimers generally decreases when the number of methyl substituents at the pyridylimine ligand is reduced or the dendrimer generation is increased [13]. The lack of solubility rends complete metalation of the dendrimer periphery difficult, as observed in our attempts to prepare **2a** or higher-generation derivatives.

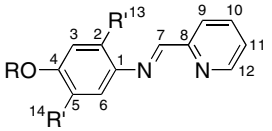
The molybdenum(0) complex $[Mo(CO)_3(MeCN)(\mathbf{Ia})]$, reported by Heinze, is much more soluble in polar solvents and polymetallated polymers derived from this type of complexes have already been prepared [16a]. Accordingly, molybdenum dendrimers **3a** and **4a** were efficiently prepared by treatment of $[Mo(CO)_3(1,3,5\text{-}C_6H_3Me_3)]$ in acetonitrile with the dendritic ligands **IIa** or **IIIa**. The initial pale-yellow solutions turned deep blue immediately and complexes **3a** and **4a** were isolated from these solutions as purple solids that are soluble in polar solvents such as acetonitrile and fairly air-stable, although decomposing in long exposures to air. The complete metalation of the dendritic branches was confirmed by ^1H and ^{13}C NMR spectroscopy in CD_3CN. Only resonances of uncoordinated CH_3CN molecules are observed in the ^1H and ^{13}C NMR spectra, indicating exchange between the coordinated acetonitrile and the deuterated solvent. The three carbonyl ligands are coordinated *fac* to the octahedral metal center as demonstrated by the appearance of three carbonyl resonances in the ^{13}C NMR spectra and the observation of two $\nu(CO)$ IR absorptions at around 1900 and 1780 cm^{-1} ($a_1 + e$ modes). The IR spectra of complexes **1**–**4** in KBr pellets also show a medium-to-strong absorption at around 1575 cm^{-1}, together with a much weaker band at around 1610 cm^{-1} for Pt, or 1590 cm^{-1} for Mo instead of the group of three intense absorptions observed in the range 1565–1627 cm^{-1} for the corresponding free ligands **I**–**III**. The disappearance or shift of the C=N vibration in the IR spectra of related complexes have been attributed to a reduction of electron density in the C=N bonds after coordination of the ligand to the metal center [12d].

Important CIS effects (CIS = coordination-induced shift) are observed for the proton and carbon-13 NMR resonances of the pyridylimine ligands after coordination to the metal centers, especially for the imine group and the pyridine ring (Table 1). The negative CIS effect observed for H^9 ($\Delta\delta \approx -0.2$ to -0.4 ppm) is a result of the change from the *transoid* conformation of the free ligands in solution, where H^9 is in the proximity of the imine lone-pair, to the *cisoid* conformation required to coordinate to the metal center (Scheme 1) [16a,22]. The negative CIS effect observed for the imine proton (H^7) in the palladium ana-



Scheme 1.

Table 1
Relevant CIS effects observed by NMR spectroscopy for compounds **1**, **3** and **4**[a]



R' = H (**1a, 3a**, **4a**), Me (**1b**)

Complex	$\Delta\delta$[b]									
	H^{12}	C^{12}	H^{11}	C^{11}	H^{10}	C^{10}	H^{9}	C^{9}	H^{7}	C^{7}
1a	+1.03	+0.2	+0.34	+3.2	+0.43	+2.7	−0.36	+6.7	+0.00	+8.2
1b	+1.05	+0.9	+0.42	+4.3	+0.43	+2.9	−0.27	+6.5	+0.25	+10.5
3a	+0.31	+3.1	+0.18	+2.9	+0.22	+2.0	−0.22	+7.7	+0.04	+4.8
4a	+0.31	+3.2	+0.18	+2.8	+0.21	+2.2	−0.23	+7.7	+0.01	+4.8

[a] In $CDCl_3$ at 20 °C.
[b] $\Delta\delta$ in ppm with respect to the corresponding free ligands **I**–**III**.

logues ($\Delta\delta \approx -0.3$ ppm) [13c] becomes zero or positive in the platinum and molybdenum complexes **1**–**4**. On the other hand, the largest coordination shifts of the H^{12} proton in platinum complexes ($\Delta\delta \approx +1.0$) is ascribed to the strong deshielding effect of the chloro ligand *cis* to the pyridyl ring. The most affected protons in the molybdenum complexes are H^{12} and $H^{2,6}$ ($\Delta\delta \approx +0.3$ ppm) probably as a result of a deshielding contribution of the carbonyl groups coplanar with the chelate ligand. The most significant CIS effects in the ^{13}C NMR spectra are found for C^9, and the imine carbon C^7 (Table 1).

3. Conclusion

We have described the preparation of carbosilane dendrimers containing $PtCl_2$ and $Mo(CO)_3(MeCN)$ moieties coordinated to pyridylimine ligands linked at the dendritic periphery. We have previously reported the synthesis of $NiBr_2$, $PdCl_2$, and PdClMe analogues. The procedures used for the preparation of metal-pyridylimine dendrimers are efficient, with the only limitation being the solubility of the final products. Thus, pure dendrimers of the less soluble complexes, for example platinum compounds, can only be obtained in the lowest generations, however, such an obstacle is not met for carbonyl molybdenum dendrimers described here. Therefore, modification of the ligand and/or the complex, or the dendritic matrix itself, will be required to obtain more soluble compounds in the case of platinum.

4. Experimental

4.1. Reagents and general techniques

All operations were performed under argon using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[Mo(CO)_3(1,3,5\text{-}C_6H_3Me_3)]$ [23], $[PtCl_2(SMe_2)_2]$ [24], $[PtX_2(COD)]$ (X = Cl, I) [25], and the pyridylimine ligands **I**–**III** [13,16a] were prepared according to the literature procedures. Solvents were dried prior to use and distilled under argon as described elsewhere [26]. NMR spectra were recorded with Varian Unity VR-300 or Varian Unity 200 NMR spectrometers. Chemical shifts (δ) are reported in ppm relative to $SiMe_4$, and were measured relative to the ^{13}C and residual ^1H resonances of the deuterated solvents. Assignments for the pyridylimine fragments are given according to the numbering of the positions depicted in Table 1. For dendrimers, ^1H NMR integrals are given relative to one of the four arms of the molecule. IR spectra were recorded with a Perkin–Elmer FT-IR Spectrum-2000 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratories of the University of Alcalá with a Heraeus CHN-O-Rapid or a Perkin–Elmer 2400 Serie II C, H, N, S/O microanalyzer. Mass spectra were recorded with a Thermo Quest Finningan Automass Multi mass spectrometer.

4.2. Preparation of $[PtCl_2(Me_3SiO\text{-}4\text{-}C_6H_4\text{-}N{=}CH\text{-}2\text{-}Py)]$ (*1a*)

$[PtCl_2(SMe_2)_2]$ (80 mg, 0.20 mmol) was added to a solution of ligand **Ia** (60 mg, 0.22 mmol) in dichloromethane (10 mL), and the resulting reaction mixture was stirred at room temperature for 12 h. Removal of the solvent, followed by washing of the residue with pentane (4 × 10 mL) gave compound **1a** as an orange solid. Yield: 85 mg (80%). Anal. Calc. for $C_{15}H_{18}Cl_2N_2OPtSi$ (536.39): C, 33.59; H, 3.38; N, 5.22. Found: C, 33.89; H, 3.50; N, 5.44%. ^1H NMR ($CDCl_3$): δ 0.28 (s, 9H, $SiMe_3$), 6.89 (AA′ part of an AA′XX′ spin system, 2H, $H^{3,5}$), 7.40 (XX′ part of an AA′XX′ spin system, 2H, $H^{2,6}$), 7.64 (*pt*, 1H, H^{11}), 7.80 (d, $J_{H,H} = 7.9$ Hz, 1H, H^9), 8.19 (*pt*, 1H, H^{10}), 8.60 (s, 1H, H^7), 9.70 ppm (d, $J_{H,H} = 6.3$ Hz, 1H, H^{12}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.4 ($SiMe_3$), 119.4 ($C^{3,5}$), 125.9 ($C^{2,6}$), 128.3 (C^9), 128.4 (C^{11}), 139.6 (C^{10}), 140.7 (C^1), 149.7 (C^{12}), 154.6 (C^4), 157.1 (C^8), 167.3 ppm (C^7). IR (KBr): *v* 1610 (w), 1570 cm^{-1} (s, C=N). MS (ESI+ in CH_3CN): *m/z* 542 $[M-Cl+CH_3CN]^+$.

4.3. Preparation of [$PtCl_2$\{(Me_3SiO-4-(2,5-$C_6H_2Me_2$)-N=CH-2-Py)\}] (**1b**)

Compound **1b** was synthesized as described for **1a** from **Ib** (144 mg, 0.48 mmol) and [$PtCl_2(SMe_2)_2$] (173 mg, 0.44 mmol) as starting substrates, and was isolated as a red solid. Yield: 195 mg (78%). Anal. Calc. for $C_{17}H_{22}Cl_2N_2OPtSi$ (564.45): C, 36.17; H, 3.93; N, 4.96. Found: C, 36.61; H, 3.89; N, 5.44%. ^{1}H NMR ($CDCl_3$): δ 0.27 (s, 9H, $SiMe_3$), 2.09 (s, 3H, Me^{14}), 2.33 (s, 3H, Me^{13}), 6.60 (s, 1H, H^3), 6.93 (s, 1H, H^6), 7.73 (*p*t, 1H, H^{11}), 7.94 (d, $J_{H,H} = 7.7$ Hz, 1H, H^9), 8.20 (*p*t, 1H, H^{10}), 8.76 (s, 1H, H^7), 9.71 ppm (d, $J_{H,H} = 6.6$ Hz, 1H, H^{12}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.7 ($SiMe_3$), 16.2 and 18.4 ($Me^{13,14}$), 120.3 (C^3), 125.5 (C^6), 126.8 (C^5), 127.7 (C^9), 128.8 (C^{11}), 130.2 (C^2), 139.3 (C^{10}), 140.2 (C^1), 150.3 (C^{12}), 154.0 (C^4), 156.4 (C^8), 168.0 ppm (C^7). IR (KBr): *v* 1615 (w), 1580 cm^{-1} (m, C=N). MS (ESI+ in CH_3CN): *m/z* 570 [M−Cl+CH_3CN]$^+$.

4.4. Preparation of [(**IIb**)($PtCl_2$)$_4$] (**2b**)

[$PtCl_2(SMe_2)_2$] (70 mg, 0.18 mmol) was added to a solution of the carbosilane dendrimer **IIb** (60 mg, 0.045 mmol) in dichloromethane (15 mL), and the reaction mixture was stirred at room temperature for 18 h. A red solid precipitated during the course of the reaction. Removal of the solvent was followed by washing of the crude residue with pentane (2 × 30 mL) to yield compound **2b** as a red solid that is insoluble in common solvents. Yield: 80 mg (74%). Anal. Calc. for $C_{76}H_{100}Cl_8N_8O_4Pt_4Si_5$ (2394.1): C, 38.13; H, 4.21; N, 4.68. Found: C, 38.30; H, 4.21; N, 5.06%. IR (KBr): *v* 1615 (w), 1571 cm^{-1} (m, C=N).

4.5. Preparation of [(**IIa**)\{$Mo(CO)_3(MeCN)$\}$_4$] (**3a**)

Solid [$Mo(CO)_3$\{1,3,5-$C_6H_3Me_3$\}] (642 mg, 2.14 mmol) was added to a solution of compound **IIa** (652 mg, 0.53 mmol) in acetonitrile (30 mL). The yellow solution turned blue immediately. Stirring was maintained for 48 h at room temperature, then the solvent was removed under reduced pressure and the resulting purple powder washed with hexane (5 × 15 mL). Compound **3a** was found to be soluble in acetonitrile and insoluble in alkanes, aromatic, or chlorinated solvents. Yield: 750 mg (67%). Anal. Calc. for $C_{88}H_{96}Mo_4N_{12}O_{16}Si_5$ (2102.0): C, 50.28; H, 4.60; N, 8.00. Found: C, 50.02; H, 4.64; N, 8.15%. ^{1}H NMR (CD_3CN): δ 0.25 (s, 6H, $SiMe_2$), 0.64 (m, 2H, $SiCH_2$), 0.84 (m, 2H, CH_2SiMe_2), 1.49 (m, 2H, $CH_2CH_2CH_2$), 1.93 (s, 3H, CH_3CN), 6.90 (AA′ part of an AA′XX′ spin system, 2H, $H^{3,5}$), 7.49 (m, 1H, H^{11}), 7.55 (XX′ part of an AA′XX′ spin system, 2H, $H^{2,6}$), 7.92 (d, $J_{H,H} = 7.1$ Hz, 1H, H^9), 7.97 (m, 1H, H^{10}), 8.62 (bs, 1H, H^7), 8.97 ppm (bs, 1H, H^{12}). ^{13}C{^{1}H} NMR (CD_3CN): δ −1.0 ($SiMe_2$), 17.5, 18.6, and 21.9 (CH_2), 120.9 ($C^{3,5}$), 124.5 ($C^{2,6}$), 127.7 (C^{11}), 129.3 (C^9), 138.6 (C^{10}), 146.5 (C^1), 152.6 (C^{12}), 155.5 (C^4), 156.5 (C^8), 163.0 (C^7), 218.6 (CO *trans* to MeCN), 228,6 and 230.8 ppm (CO *cis*). ^{29}Si{^{1}H} NMR (CD_3CN): δ 21.5 ($SiMe_2$), 2.1 ppm (central Si). IR (KBr): *v* 1903 and 1774 (vs. CO), 1593 cm^{-1} (s, C=N and py-ring).

4.6. Preparation of [(**IIIa**)\{$Mo(CO)_3(MeCN)$\}$_8$] (**4a**)

Compound **4a** was synthesized as described above for **3a**, starting from dendrimer **IIIa** (275 mg, 0.10 mol) and [$Mo(CO)_3$\{1,3,5-$C_6H_3Me_3$\}] (241 mg, 0.80 mmol), and was isolated as a purple solid. Yield: 307 mg (68%). Anal. Calc. for $C_{192}H_{228}Mo_8N_{24}O_{32}Si_{13}$ (4516.7): C, 51.06; H, 5.09; N, 7.44. Found: C, 50.03; H, 5.50; N, 6.99%. ^{1}H NMR (CD_3CN): δ −0.08 (s, 3H, SiMe), 0.23 (s, 12H, $SiMe_2$), 0.59 (m, 8H, $SiCH_2$), 0.84 (m, 4H, CH_2SiMe_2), 1.27 and 1.42 (2 × m, 2H and 4H, $CH_2CH_2CH_2$), 1.93 (s, 3H, CH_3CN), 6.90 (AA′ part of an AA′XX′ spin system, 2H, $H^{3,5}$), 7.48 (m, 1H, H^{11}), 7.54 (XX′ part of an AA′XX′ spin system, 2H, $H^{2,6}$), 7.91 (m, 1H, H^9), 7.96 (m, 1H, H^{10}), 8.59 (bs, 1H, H^7), 8.98 ppm (bs, 1H, H^{12}). ^{13}C{^{1}H} NMR (CD_3CN): δ −4.4 (SiMe), −0.9 ($SiMe_2$), 18.5, 19.1, 19.6, 21.2 and 21.9 (CH_2), 120.9 ($C^{3,5}$), 124.5 ($C^{2,6}$), 127.5 (C^{11}), 129.2 (C^9), 138.6 (C^{10}), 146.5 (C^1), 152.6 (C^{12}), 155.5 (C^4), 156.5 (C^8), 162.9 (C^7), 218.5 (CO *trans* to MeCN), 228.6 and 230.8 ppm (CO *cis*). ^{29}Si{^{1}H} NMR (CD_3CN): silent after 48 h. IR (KBr): *v* 1903 and 1789 (vs, CO), 1593 cm^{-1} (s, C=N and py-ring).

Acknowledgements

We gratefully acknowledge financial support from the Spanish Ministerio de Educación y Ciencia (Project CTQ2005-00795/BQU) and the Comunidad de Madrid (Project S-0505/PPQ/0328-03).

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