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Divergent Route to Organoplatinum or Platinum−Palladium Dendrimers

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Summary: A new divergent route to organotransition-metal dendrimers is described, in which a key step involves oxidative addition. The product dendrimers contain organoplatinum(IV) centers in each inner generational layer and either platinum(II) or palladium(II) centers in the outermost layer.

There continue to be exciting advances in the synthesis of dendrimers and in the development of their chemistry.[1] For example, new methods have been found for synthesis of dendrimers containing transition-metal centers in each generation, at the core only or at the periphery only.[1−8] They may be grown in a stepwise generation-by-generation manner[1−8] or by self-assembly,[4,9] and some organotransition-metal dendrimers have been shown to have useful catalytic properties.[1,5] A convergent approach to organoplatinum dendrimers was reported earlier, based on the reagent 4,4′-bis(bromomethyl)-2,2′-bipyridine (**A**).[9] The bipyridine unit serves to coordinate to a dimethylplatinum(II) unit to begin each new generation, while the branching in each generation is achieved by oxidative addition of the C−Br bonds to the platinum(II) center. This article reports a new divergent route to organometallic dendrimers, based on the new reagent **B**,[10] which contains a single bromomethyl group and two 2,2′-bipyridine groups.

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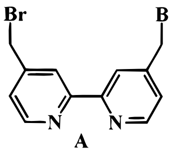
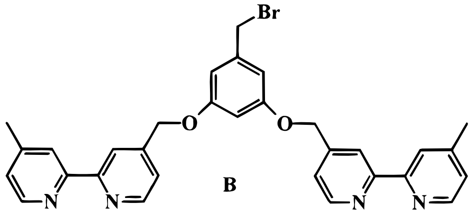
[10] Ligand **B** was prepared by reaction of 4-methyl-4′-(bromomethyl)-2,2′-bipyridine (2 equiv) with 3,5-dihydroxybenzyl alcohol in the presence of K_2CO_3 and 18-crown-6 to give 3,5-(4-MeC_5H_4N-4′-C_5H_4N-$CH_2O)_2C_6H_3CH_2OH$, followed by reaction with CBr_4/PPh_3 to give **B**. ^1H NMR data (300 MHz): δ 2.44 [s, 6H, Me]; 4.39 [s, 2H, CH_2Br]; 5.13 [s, 4H, CH_2O]; 6.56−8.66 [15H, aryl]. Ligand **C** was prepared by reaction of 4-methyl-4′-bromomethyl-2,2′-bipyridine (3 equiv) with 1,1,1-tris(4-hydroxyphenyl)ethane in the presence of K_2CO_3 and 18-crown-6. NMR: $\delta(^1H)$ 2.09 [s, 3H, Me central]; 2.45 [s, 9H, Me (bpy)]; 5.14 [s, 6H, CH_2O]; 6.86 and 6.98 [m, 12H, C_6H_4]; 7.17−8.67 [18H, aryl (bpy)].

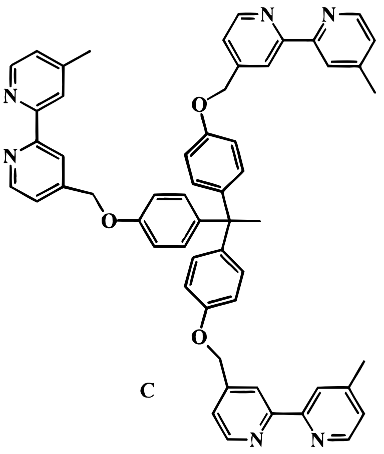
S0276-7333(96)00716-9 CCC: $12.00



A

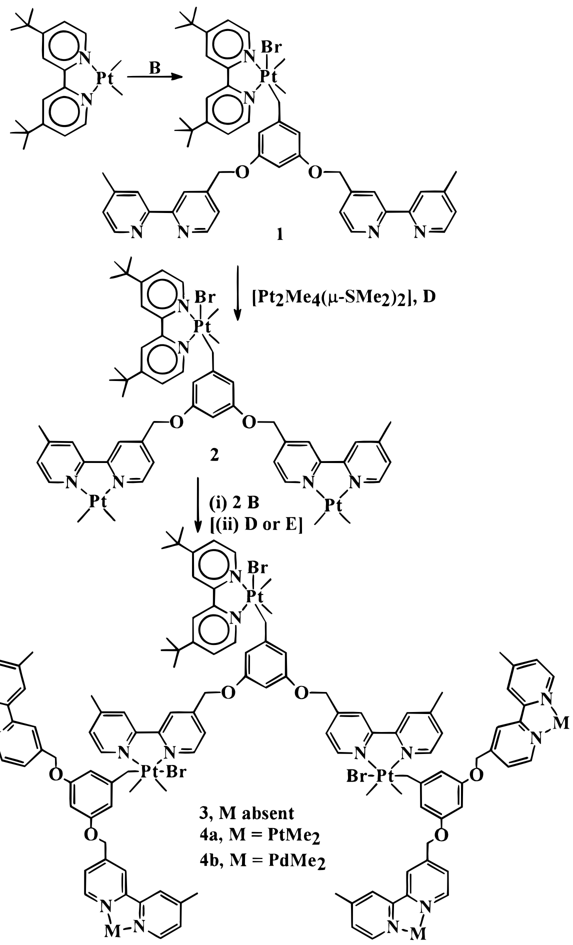


B



C

Scheme 1



Since the branching occurs at the bipyridine complexation step, this naturally leads to divergent growth. Hence, in combination with the previous convergent route, the synthesis of a particularly wide range of organometallic dendrimers, including mixed-metal dendrimers, becomes possible.

As shown in Scheme 1, the oxidative addition of the C−Br bond of **B** to [$PtMe_2(bu_2bpy)$], bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) gave the Pt(IV) complex **1**, which reacted with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**D**)[11] to form the $Pt^{IV}Pt^{II}_2$ complex **2** by displacement of the weakly bound SMe_2 ligands. This completes the first generation of dendrimer growth, since two new dimethylplatinum(II) centers are present in **2**, ready for further oxidative addition.

Reaction of **2** with **B** gave the Pt^{IV}_3 complex **3** and further reaction of **3** with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] then gave the $Pt^{IV}_3Pt^{II}_4$ complex **4a**. In principle, this process could be repeated to give larger dendrimers, but complex **4a** is only sparingly soluble in common organic solvents, thus making further reactions difficult. However, the mixed-metal $Pt^{IV}_3Pd^{II}_4$ dendrimer **4b** was easily prepared by reaction of **3** with [$Pd_2Me_4(\mu$-pyridazine$)_2$] (**E**).[12]

Another useful reagent is the tris(2,2′-bipyridyl) reagent **C**,[10] which can act as a core for dendrimer growth as shown in Scheme 2. Reaction of **C** with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**D**) gave the triplatinum(II) complex **5a** while reaction with [$Pd_2Me_4(\mu$-pyridazine$)_2$] (**E**) gave the corresponding palladium complex **5b**. Each of the platinum(II) centers in **5a** reacted with **B** to give the Pt^{IV}_3 complex **6**, which contains six free bipyridine donors. Finally, complex **6** reacted with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] or [$Pd_2Me_4(\mu$-pyridazine$)_2$] to give the $Pt^{IV}_3Pt^{II}_6$ or $Pt^{IV}_3Pd^{II}_6$ complex **7a** or **7b**, respectively. Since the

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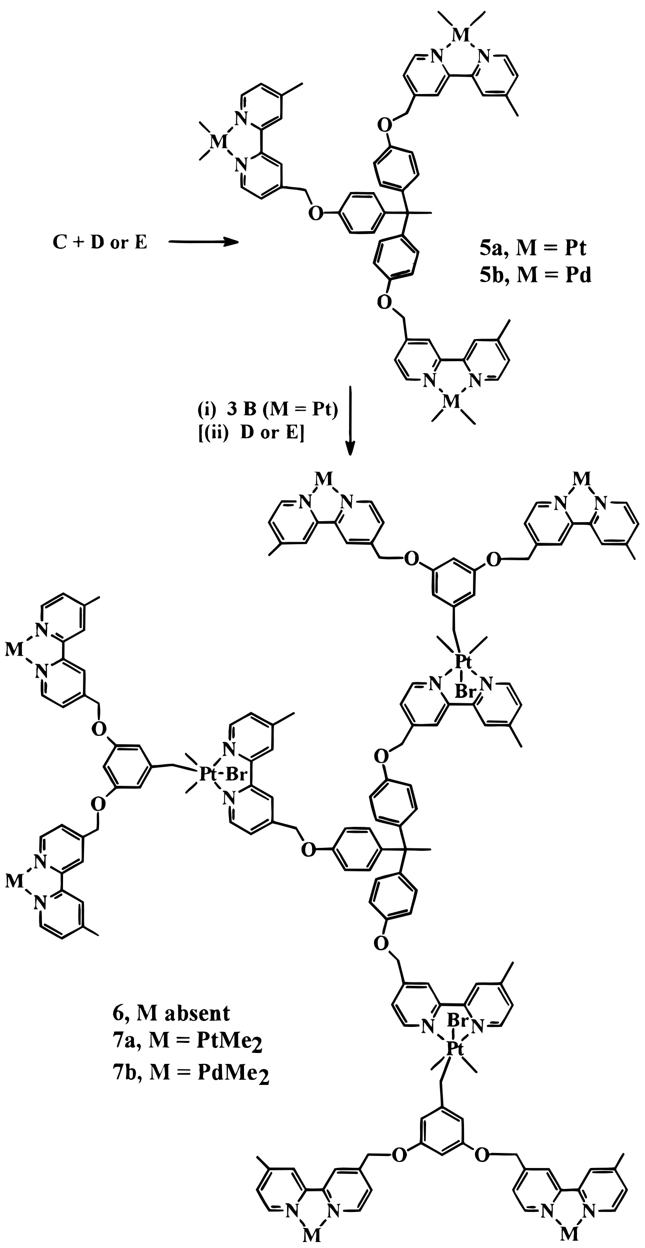
[12] Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210. Organopalladium groups can be introduced only in the outermost generational layer, since palladium(IV) centers are not sufficiently stable to support further growth by oxidative addition to palladium(II).

(13) ^1H NMR data (300 MHz) for the organometallic derivatives are as follows: **1**: δ 1.25 [s, 18H, *t*-Bu]; 1.44 [s, 6H, $^2J(Pt-H) = 69$ Hz, Me_2Pt^{IV}]; 2.48 [s, 6H, MeC]; 2.73 [s, 2H, $^2J(Pt-H) = 98$ Hz, CH_2Pt^{IV}]; 4.82 [s, 4H, CH_2O]; 5.53−8.68 [21H, aryl]. **2**: δ 0.94, 0.96 [s, 12H, $_2J(Pt-H) = 87$ Hz, Me_2Pt^{II}]; 1.38 [s, 36H, t-Bu]; 1.45 [s, 6H, $^2J(Pt-H) = 69$ Hz, Me_2Pt^{IV}]; 2.37 [s, 6H, MeC]; 2.76 [s, 2H, $^2J(Pt-H) = 96$ Hz, CH_2Pt^{IV}]; 4.70 [s, 4H, CH_2O]; 5.68−9.15 [21H, aryl]. **3**: δ 1.00−1.45 [54H, *t*-Bu and Me_2Pt^{IV}]; 2.30 [s, 6H, MeC in first generation]; 2.39 [s, 12H, MeC in second generation]; 2.50−2.73 [6H, CH_2Pt^{IV}]; 4.76 [s, 4H, CH_2O in first generation]; 4.86 [s, 8H, CH_2O in second generation]; 5.77−8.62 [51H, aryl]. **4a**: δ 0.80 [s, 24H, Me_2Pt^{II}]; 1.10−1.50 [36H, *t*-Bu and Me_2Pt^{IV}]; 2.26 [s, 12H, MeC of second generation]; 2.42 [s, 6H, MeC of first generation]; 2.50−2.70 [6H, CH_2Pt^{IV}]; 4.60−4.75 [8H, CH_2O in second generation]; 4.80−4.95 [4H, CH_2O in first generation]; 5.50−9.10 [51H, aryl]. **4b**: δ 0.10 [s, 24H, Me_2Pd^{II}]; 1.00−1.50 [36H, *t*-Bu and Me_2Pt^{IV}]; 2.30−2.70 [24H, MeC and CH_2Pt^{IV}]; 4.70−5.00 [12H, CH_2O in second generation]; 5.20−8.70 [51H, aryl]. **5a**: δ 0.94 and 0.96 [s, 18H, $^2J(Pt-H) = 85.5$ Hz, Me_2Pt^{II}]; 2.10 [s, 3H, Me central]; 2.37 [s, 9H, Me (bpy)]; 5.04 [s, 6H, CH_2O]; 6.91 and 7.02 [m, 12H, C_6H_4]; 7.35−9.16 [18H, aryl (bpy)]. **6**: δ 1.23 and 1.25 [s, 18H, $^2J(Pt-H) = 70$ Hz, Me_2Pt^{IV}]; 1.90 [s, 3H, Me central]; 2.33 [18H, Me (bpy), second generation]; 2.35 [s, 9H, Me (bpy), first generation]; 2.59 [s, 6H, CH_2Pt^{IV}]; 4.84 [s, 12H, CH_2O, second generation]; 5.10 [s, 6H, CH_2O, first generation]; 5.44−6.80 [21H, C_6H_4 and C_6H_3]; 7.21−8.60 [54H, aryl (bpy)]. **7a**: δ 0.60−0.90 [36H, Me_2Pt^{II}]; 1.00−1.40 [18H, Me_2Pt^{IV}]; 1.90−2.0 [s, 3H, Me central]; 2.15−2.50 [27H, Me (bpy)]; 2.72 [6H, CH_2Pt^{IV}]; 4.7−4.9 [18H, CH_2O]; 5.7−7.1 [21H, C_6H_4 and C_6H_3]; 7.4−9.2 [54H, aryl (bpy)]. **7b**: δ 0.06 [36H, Me_2Pd^{II}]; 1.2−1.5 [18H, Me_2Pt^{IV}]; 1.92 [s, 3H, Me central]; 2.3−2.5 [27H, Me(bpy)]; 2.7[6H, CH_2Pt^{IV}]; 4.85 [12H, CH_2O, second generation]; 5.20 [6H, CH_2O, first generation]; 5.5−7.0 [21H, C_6H_4 and C_6H_3]; 7.3−8.8 [54H, aryl (bpy)].

Scheme 2



5a, M = Pt
5b, M = Pd

6, M absent
7a, M = PtMe$_2$
7b, M = PdMe$_2$

complexes **7** are sparingly soluble, no attempt has been made to extend the growth reactions further. Of course, this method of dendrimer formation is a modified divergent growth strategy.

The new dendrimers reported above were formed in >90% yield as monitored by NMR; they were purified by dissolution in dichloromethane followed by precipitation with hexane, and repetition of this procedure several times, and were isolated in 60−80% yield. All gave satisfactory C, H, N analyses, and the mixed Pt/Pd dendrimers all gave the expected Pt:Pd ratios as determined by energy dispersive X-ray analysis. Structural characterization of the smaller dendrimers **1**, **2**, and **5** by ^{1}H NMR is unambiguous, but as expected,[9] the spectra become progressively more complex and broad as the dendrimers become larger.[13] Dendrimers containing only platinum(IV) centers are very pale yellow, while those containing platinum(II) or palladium(II) are red or yellow, respectively, due to intense metal to ligand charge transfer transitions.

In terms of strategies for dendrimer growth, it should be clear that a mixed convergent−divergent method is possible by using the two key reagents **A** and **B** in sequence and applications of this approach will be described elsewhere. The limit to growth in the present divergent growth system is due to decreasing solubility with increasing dendrimer size, whereas in the previous convergent growth system, where the dendrimers contain more bu$_2$bpy groups, the solubilities increased with increasing dendrimer size and the limit to growth was due to increasing steric congestion.[9]

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Supporting Information Available: Text giving details of the synthesis and analytical data for the compounds prepared in this paper (5 pages). Ordering information is given on any current masthead page.

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