Convergent Synthesis of Alkynylbis(bidentate phosphine)ruthenium Dendrimers

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The "first-generation" alkynylruthenium dendrimers 1,3,5-C_6H_3(4-C≡CC_6H_4C≡C-*trans*-[Ru(dppe)$_2$]C≡C-3,5-C_6H_3{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡CC_6H_4R)(dppe)$_2$]}$_2$)$_3$ [R = H (**19**), NO_2 (**20**)], containing nine dialkynylruthenium centers, have been prepared by convergent synthesis. Reaction of 3 equiv of 1-iodo-4-trimethylsilylethynylbenzene with triethynylbenzene, under Sonogashira coupling conditions, followed by deprotection with tetra-*n*-butylammonium fluoride affords 1,3,5-C_6H_3(4-C≡CC_6H_4C≡CH)$_3$ (**2**), which is reacted with *cis*-[$RuCl_2(L)_2$] (L = dppe, dppm) to afford the octopolar, triruthenium dendritic cores 1,3,5-C_6H_3{4-C≡CC_6H_4C≡C-*trans*-[RuCl(L)$_2$]}$_3$ [L = dppe (**5**), L = dppm (**6**)] via the vinylidene intermediates [1,3,5-C_6H_3{4-C≡CC_6H_4CH=C-*trans*-[RuCl(L)$_2$]}$_3$](PF_6)$_3$ [L = dppe (**3**), L = dppm (**4**)]. Reaction of **5** with terminal alkynes 4-HC≡CC_6H_4R (R = H, NO_2, NEt_2) affords a series of related dialkynylruthenium zero-generation dendrimers 1,3,5-C_6H_3{4-C≡CC_6H_4-C≡C-*trans*-[Ru(4-C≡CC_6H_4R)(dppe)$_2$]}$_3$ [R = H (**7**), NO_2 (**8**), NEt_2 (**9**)]. Reaction of 3 equiv of *trans*-[Ru(4-C≡CC_6H_4C≡CH)(C≡CPh)(dppe)$_2$] with 1,3,5-triiodobenzene under Sonogashira coupling conditions also affords **7**, together with the homo-coupled *trans,trans*-[(dppe)$_2$(PhC≡C)Ru(4,4′-C≡CC_6H_4C≡CC≡CC_6H_4C≡C)Ru(C≡CPh)(dppe)$_2$]. The first-generation dendrimers **19** and **20** are prepared by coupling core **5** with the dendrons 1-(HC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡CC_6H_4R)(dppe)$_2$]}$_2$ [R = H (**17**), NO_2 (**18**)]. Thus, reaction of 1-(Me_3SiC≡C)C_6H_3-3,5-(4-C≡CC_6H_4C≡CH)$_2$ (**12**), obtained from 1-iodo-3,5-dibromobenzene through a series of Sonogashira coupling and transhalogenation reactions, with *cis*-[$RuCl_2$(dppe)$_2$] affords 1-(Me_3SiC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[RuCl(dppe)$_2$]}$_2$ (**13**), which can be reacted with appropriately functionalized terminal alkynes to afford the series 1-(Me_3SiC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡CC_6H_4R)(dppe)$_2$]}$_2$ [R = H (**14**), NO_2 (**15**), NEt_2 (**16**)]. Desilylation of **16** proceeds with decomposition; in contrast, treatment of **14** and **15** with tetra-*n*-butylammonium fluoride gives **17** and **18**, which are coupled with **5** under basic conditions to afford the dendritic complexes **19** and **20** via in situ deprotonation of the vinylidene complex intermediates. A transmission electron micrograph of **19** supported on alumina reveals molecules that are approximately 6 nm in diameter, in agreement with molecular modeling studies.

Introduction

Dendrimers are monodisperse hyperbranched molecules that have attracted significant interest recently as novel materials with uses in medical diagnostics and possible applications in areas such as molecular recognition, catalysis, and photoactive device engineering.[1−3] Although the first examples of dendrimers were purely organic in composition, and organic dendrimers continue to dominate the field, organometallic dendrimers have been the focus of considerable interest because the metal may imbue the dendritic material with specific optical, electronic, magnetic, catalytic, and other properties. For reviews of metal-containing dendrimers, see refs 4−10. The great majority of metal-containing dendrimers are peripherally metalated organic dendrimers,[11−38] par-

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ticular interest being shown in their potential in multielectron transfer redox reactions/catalysis, as precursors to metallic films, as mediators in amperometric biosensors, as inert frameworks carrying catalytically active transition metal complexes, as gas detection sensors, and in double-strand DNA cleavage. In contrast, considerably fewer core-metalated and other-shell-metalated dendrimers and dendrons have been reported.[39−42]

Organometallic dendrimers with transition metals in every generation are comparatively rare;[38,43−52] this scarcity has been suggested to derive from the intrinsically lower stability of most organometallic complexes compared to organic compounds, coupled to the need to build up the dendrimer by successive organometallic reactions.[48] Puddephatt[44] and Catalano[45] and their co-workers have constructed group 10 metal-containing dendrimers by a strategy involving oxidative addition as a key step, to afford dendrimers with metal-alkyl linkages, and Majoral and co-workers prepared ferrocene-containing dendrimers linked by CH═NNMeP(═S)$(OC_6H_4\text{-}4)_2$ groups.[50] Rigid π-delocalizable organometallic dendrimers incorporating 16-electron group 10 metals within an arylalkynyl branched structure have been constructed by Takahashi[43,47,48,51] and Stang.[46]

We have been examining the nonlinear optical (NLO) properties of alkynylmetal complexes and have noted an enhancement of NLO response upon increasing the metal valence electron count in linear (rodlike) alkynylmetal complexes.[53] NLO materials with a dendritic construction may have enhanced nonlinearities coupled to favorable transparency and processing characteristics, because the 1,3,5-trisubstituted benzene branching points in arylalkynyl dendrimers may permit extensive π-delocalization without appreciable red-shift of the important linear optical absorption band(s). We therefore desired access to 18-valence-electron metal-containing dendrimers, but despite their potential significance in materials applications, no electron-rich π-delocalizable organometallic dendrimers are extant. We report herein synthetic procedures to bis(diphosphine)ruthenium-containing arylalkynyl dendrimers, including examples peripherally functionalized by electron-donating (NEt_2) or electron-withdrawing (NO_2) substituents. The peripherally decorated phenylethynyl examples have been described very briefly in a preliminary form.[49,54]

Experimental Section

General Conditions and Reagents. All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents and reagents were obtained from commercial sources and used as received, unless otherwise indicated. The concentration of *n*-BuLi was determined prior to reaction by titration against diphenylacetic acid. CH_2Cl_2, MeOH, Et_2O, and thf were dried and distilled according to standard procedures. "Petrol" refers to a fraction of petroleum of boiling range 60−80 °C. Chromatography was on silica gel (230−400 mesh ASTM) or ungraded basic alumina. The following were prepared by literature procedures: 1,3,5-triethynylbenzene,[55] 1,3-dibromo-5-iodobenzene,[56] 4-$Me_3SiC{\equiv}CC_6H_4I$,[57] 4-$HC{\equiv}CC_6H_4Br$ and 4-$HC{\equiv}CC_6H_4NO_2$,[58] 4-$HC{\equiv}CC_6H_4C{\equiv}CPh$,[59] *cis*-$[RuCl_2(dppe)_2]$,[60] *trans*-[Ru(4-$C{\equiv}CC_6H_4$-

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NO_2)Cl(dppe)$_2$] and *trans*-[Ru(C≡CPh)Cl(dppe)$_2$],[61] *trans*-[Ru(4-C≡CC_6H_4C≡CH)(C≡CPh)(dppe)$_2$],[62] and *trans*-[Ru(4-C≡CC_6H_4C≡CPh)Cl(dppe)$_2$].[63] Dichlorobis(triphenylphosphine)-palladium(II) was prepared by stirring 2 equiv of triphenylphosphine with palladium(II) chloride in dimethylformamide at reflux for 2 h; the precipitate was collected and recrystallized from $CHCl_3$.

4-Ethynyl-*N*,*N*-diethylaniline has been reported previously,[64] but was prepared in the present work by an alternative route, as follows. 4-Iodo-*N*,*N*-diethylaniline (3.73 g, 13.5 mmol), $PdCl_2(PPh_3)_2$ (95.2 mg, 0.136 mmol), CuI (27.6 mg, 0.145 mmol), and trimethylsilylacetylene (1.95 mL, 1.36 g, 13.8 mmol) were stirred in NEt_3 (40 mL) at room temperature for 17 h. The solvent was removed under reduced pressure and the residue washed through a silica plug with petrol; the solvent was removed from the resulting orange solution to give an orange oil (3.29 g, 98%) identified as 4-trimethylsilylethynyl-*N*,*N*-diethylaniline. ^{1}H NMR: δ 0.20 (s, 9H, $SiMe_3$), 1.13 (t, J_{HH} = 7 Hz, 6H, CH_3), 3.32 (q, J_{HH} = 7 Hz, 4H, CH_2), 6.52, 7.28 (AA′BB′, 2 × 2H, C_6H_4). HRMS (EI) $C_{15}H_{23}NSi$: calcd 245.160, found 245.160. 4-Trimethylsilylethynyl-*N*,*N*-diethylaniline (3.29 g, 13.4 mmol) and tetra-*n*-butylammonium fluoride (15 mL, 1.0 M solution in thf) were stirred in CH_2Cl_2 (50 mL) at room temperature for 30 min. The solvent was removed in vacuo, and the residue placed onto a silica column. Elution with petrol afforded a yellow solution; removal of the solvent afforded a yellow oil identified as 4-ethynyl-*N*,*N*-diethylaniline (1.64 g, 71%) by comparison of NMR and MS data with the literature.[64]

Instrumentation. EI (electron impact) mass spectra (both unit resolution and high resolution (HR)) were recorded using a VG Autospec instrument (70 eV electron energy, 8 kV accelerating potential), and secondary ion mass spectra were recorded using a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix) at the Australian National University; peaks are reported as *m*/*z* (assignment, relative intensity). Microanalyses were carried out at the Australian National University. Infrared spectra were recorded as CH_2Cl_2 solutions using a Perkin-Elmer System 2000 FT-IR unless stated otherwise. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer (300, 75, and 121 MHz, respectively) and referenced to residual solvent or external 85% H_3PO_4 (0.0 ppm). UV/vis spectra were recorded as thf solutions in 1 cm cells using a Cary 5 spectrophotometer and are reported as ν_{max} (cm^{-1}) [ϵ (10^4 M^{-1} cm^{-1})]. Transmission electron microscopy (TEM) was carried out using a Philips EM430 microscope (300 kV electron beam). The sample was supported on alumina to reduce particle aggregation (solution of 2.1 mg of sample in CH_2Cl_2 was adsorbed onto 190 mg of alumina; the supernatant was pipetted off, and the sample air-dried). A MeOH suspension of the sample was then dispersed onto a standard copper grid coated with a holey carbon film.

Calculations. Molecular calculations were performed with the SYBYL[65] force field using the program SPARTAN 5.0.[66]

Syntheses of Organic Precursors. 1,3,5-C_6H_3(4-C≡CC_6H_4C≡CSiMe_3)$_3$ (1). $PdCl_2(PPh_3)_2$ (44 mg, 0.063 mmol) and CuI (60 mg, 0.32 mmol) were added to a solution of 1,3,5-triethynylbenzene (190 mg, 1.26 mmol) and 4-Me_3SiC≡CC_6H_4I (1.139 g, 3.79 mmol) in NEt_3 (70 mL). The mixture was stirred for 2 h and then filtered through a glass sinter. The filtrate was reduced to dryness in vacuo. The residue was purified by column chromatography on silica, eluting with petrol. Removal of the solvent and recrystallization of the residue by slow evaporation from a CH_2Cl_2/MeOH mixture afforded **1** as pale yellow microcrystals (600 mg, 71%). HRMS (EI) $C_{45}H_{42}Si_3$: calcd 666.259, found 666.259. IR: ν(C≡C) 2157 cm^{-1}. ^{1}H NMR: δ 0.24 (s, 27H, $SiMe_3$), 7.44 (s, 12H, C_6H_4), 7.61 (s, 3H, C_6H_3).

1,3,5-C_6H_3(4-C≡CC_6H_4C≡CH)$_3$ (2). [NBu^n_4]F (2 mL of a 1 M solution in thf) was added to a solution of **1** (300 mg, 0.45 mmol) in CH_2Cl_2 and the mixture stirred for 15 min. The solvent was removed in vacuo, and the residue taken up in petrol and subjected to column chromatography on silica, eluting with petrol. Removal of the solvent followed by slow evaporation of the product from a CH_2Cl_2/MeOH mixture afforded a white powder identified as **2** (180 mg, 89%). HRMS (EI) $C_{36}H_{18}$: calcd 450.141, found 450.141. IR: ν(HC≡) 3296, ν(C≡C) 2108 cm^{-1}. ^{1}H NMR: δ 3.17 (s, 3H, C≡CH), 7.46 (s, 12H, C_6H_4), 7.63 (s, 3H, C_6H_3).

1,3-Dibromo-5-(trimethylsilylethynyl)benzene. Trimethylsilylacetylene (0.40 mL, 2.8 mmol) and NEt_3 (20 mL) were added to a solution of 1,3-dibromo-5-iodobenzene (1.0 g, 2.8 mmol) in thf (30 mL), and the mixture was cooled to 0 °C. $PdCl_2(PPh_3)_2$ (15 mg, 0.02 mmol) and CuI (10 mg, 0.05 mmol) were added, and the mixture was stirred at 0 °C for 30 min. The mixture was warmed to room temperature with stirring over 90 min and filtered. The solvent was removed in vacuo and the residue subjected to column chromatography on silica, eluting with petrol. Removal of the solvent on a rotary evaporator afforded a colorless liquid (0.85 g, 93%). HRMS (EI) $C_{11}H_{12}Si^{81}Br_2$: calcd 333.9034, found 333.9043; $C_{11}H_{12}Si^{79}Br^{81}$-Br: calcd 331.9055, found 331.9058; $C_{11}H_{12}Si^{79}Br_2$: calcd 329.9075, found 329.9069. IR: ν(C≡C) 2167 cm^{-1}. ^{1}H NMR: δ 0.22 (s, 9H, Me), 7.51 (d, J_{HH} = 2 Hz, 2H), 7.59 (t, J_{HH} = 2 Hz, 1H). ^{13}C NMR: δ −0.3 (Me), 97.5 (≡C), 101.6 (SiC≡), 122.5, 126.5, 133.3, 134.1. Density: 1.4 g mL^{-1}.

1,3-Diiodo-5-(trimethylsilylethynyl)benzene. *tert*-Butyllithium (13.5 mL, 1.6 M solution in hexane, 21.6 mmol) was slowly added to a cooled solution (−78 °C) of 1,3-dibromo-5-(trimethylsilylethynyl)benzene (1.77 g, 5.33 mmol) in Et_2O (100 mL) and the mixture stirred for 30 min. A solution of iodine (3.8 g, 15.0 mmol) in Et_2O (50 mL) was added slowly via a cannula and the mixture stirred at −78 °C for 10 min before warming to room temperature with stirring over 30 min. After washing the mixture with saturated aqueous sodium thiosulfate solution, the organic layer was separated and dried using magnesium sulfate. The mixture was filtered and the solvent removed from the filtrate to give a clear viscous liquid, which was purified by column chromatography on silica, eluting with petrol to afford a colorless liquid (2.12 g, 93%). HRMS (EI) $C_{11}H_{12}SiI_2$: calcd 425.8798, found 425.8796. IR: ν(C≡C) 2162 cm^{-1}. ^{1}H NMR: δ 0.21 (s, 9H, Me), 7.74 (d, J_{HH} = 2 Hz, 2H), 7.97 (t, J_{HH} = 2 Hz, 1H). ^{13}C NMR: δ −0.2 (Me), 94.0 (≡C), 97.5 (SiC≡), 101.3, 126.6, 139.6, 145.0. Density: 1.3 g mL^{-1}.

1-Me_3SiC≡C-3,5-(4-BrC_6H_4C≡C)$_2$$C_6H_3$ (10). $PdCl_2(PPh_3)_2$ (100 mg, 0.14 mmol) and CuI (50 mg, 0.26 mmol) were added to a cooled solution (0 °C) of 1,3-diiodo-5-(trimethylsilylethynyl)benzene (2.25 g, 5.29 mmol) and 1-bromo-4-ethynylbenzene (2.00 g, 11.05 mmol) in NEt_3 (50 mL). The mixture was allowed to warm to room temperature before being stirred for 2 h. Potassium carbonate (1.46 g, 10.6 mmol) was added and the mixture stirred a further 1 h. The mixture was filtered, the solvent removed from the filtrate, and the resulting residue purified by column chromatography on silica, eluting with petrol. Removal of solvent from the eluent afforded **10** as a white powder (1.95 g, 69%). HRMS (EI) $C_{27}H_{20}Si^{79}Br^{81}Br$: calcd 531.9681, found 531.9699; $C_{27}H_{20}Si^{79}Br_2$ calcd 529.9701, found 529.9712. UV−vis: 32 200 [7.56], 34 200 [7.25], 37 400 [3.72]. IR: ν(C≡C) 2155 cm^{-1}. ^{1}H NMR: δ 0.23 (s, 9H, Me),

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7.41 (AA′BB′, 8H, C_6H_4), 7.57 (d, J_{HH} = 2 Hz, 2H, C_6H_3), 7.58 (t, J_{HH} = 2 Hz, 1H, C_6H_3). ^{13}C NMR: δ −0.2 (Me), 88.7 and 89.4 (C≡C), 96.0 (≡C), 103.0 (SiC≡), 121.6, 122.9, 123.6, 124.0, 131.7, 133.0, 134.1, 134.5.

1-Me$_3$SiC≡C-3,5-(4-IC$_6$H$_4$C≡C)$_2$C$_6$H$_3$ (11). *tert*-Butyllithium (8.7 mL, 1.5 M solution in hexane, 13.1 mmol) was slowly added to a cooled solution (−78 °C) of **10** (1.70 g, 3.19 mmol) in Et_2O (100 mL) and the mixture stirred for 30 min. A solution of iodine (2.10 g, 8.27 mmol) in Et_2O (50 mL) was then added slowly via a cannula. The mixture was stirred for 10 min and allowed to warm to room temperature with stirring over 30 min. The mixture was washed with saturated aqueous sodium thiosulfate solution, and the organic layer collected and dried using magnesium sulfate. The mixture was filtered and the solvent removed from the filtrate. Precipitation from a CH_2Cl_2/petrol solution by slow evaporation afforded **11** as a white solid (1.65 g, 82%). HRMS (EI) $C_{27}H_{20}SiI_2$: calcd 625.9424, found 625.9427. UV−vis: 31 800 [8.05], 33 800 [8.08], 37 100 [5.60]. IR: ν(C≡C) 2154 cm^{-1}. ^{1}H NMR: δ 0.23 (s, 9H, Me), 7.44 (AA′BB′, 8H, C_6H_4), 7.56 (d, J_{HH} = 1.5 Hz, 2H, C_6H_3), 7.58 (t, J_{HH} = 1.5 Hz, 1H, C_6H_3). ^{13}C NMR: δ −0.2 (Me), 89.0 and 89.6 (C≡C), 94.6 (CI), 96.0 (≡C), 103.0 (SiC≡), 122.2, 123.6, 124.0, 133.1, 134.1, 134.5, 137.6.

1-Me$_3$SiC≡C-3,5-(4-HC≡CC$_6$H$_4$C≡C)$_2$C$_6$H$_3$ (12). Zinc(II) bromide (1.08 g, 4.8 mmol) was flame dried under vacuum in a Schlenk tube and thf (10 mL) added. A solution of ethynylmagnesium bromide (10 mL, 0.5 M in thf, 5.0 mmol) was added and the mixture stirred for 5 min. Compound **11** (1.0 g, 1.6 mmol) and $PdCl_2(PPh_3)_2$ (200 mg, 0.3 mmol) were added, and the resultant mixture was stirred a further 2 h. The mixture was washed with aqueous ammonium chloride, and the organic layer was collected, dried with magnesium sulfate, and filtered. The solvent was removed from the filtrate, and the resulting residue purified by column chromatography on silica, eluting with a CH_2Cl_2/petrol mixture (1:19). Removal of the solvent afforded **12** as a white powder (340 mg, 50%). HRMS (EI) $C_{31}H_{22}Si$: calcd 422.1491, found 422.1488. UV−vis: 31 100 [8.55], 33 200 [8.62], 37 000 [4.60]. IR: ν(C≡C) 2109, 2155, ν(HC≡) 3296 cm^{-1}. ^{1}H NMR: δ 0.24 (s, 9H, Me), 3.17 (s, 2H, ≡CH), 7.45 (m, 8H, C_6H_4), 7.57 (d, J_{HH} = 1.5 Hz, 2H, C_6H_3), 7.60 (t, J_{HH} = 1.5 Hz, 1H, C_6H_3). ^{13}C NMR: δ −0.2 (Me), 79.1, 83.1 (C≡C), 89.6 and 89.9 (C≡C), 96.0, 103.0 (C≡C), 122.2, 123.1, 123.6, 124.0, 131.6, 132.1, 134.2, 134.6.

Syntheses of Vinylidene- and Alkynylruthenium Complexes. [1,3,5-C$_6$H$_3${4-C≡CC$_6$H$_4$CH=C-*trans*-RuCl(dppe)$_2$}$_3$][PF$_6$]$_3$·0.5CH$_2$Cl$_2$ (3). $NaPF_6$ (130 mg, 0.600 mmol) was added to a solution of **2** (48 mg, 0.124 mmol) and *cis*-[$RuCl_2$(dppe)$_2$] (600 mg, 0.620 mmol) in CH_2Cl_2 (20 mL) and the mixture stirred for 3 h. Deoxygenated petrol (50 mL) was added and the mixture filtered; the precipitate was washed with Et_2O (2 × 10 mL) to afford **3** as a pale orange solid (220 mg, 70%). MS: 3540 ([M − PF_6]$^+$, 0.25), 933 ([RuCl(dppe)$_2$]$^+$, 100). Anal. Calcd for $C_{192.5}H_{163}Cl_4F_{18}P_{15}Ru_3$: C, 62.04; H, 4.41. Found: C, 61.83; H, 5.29. UV−vis: 24 200 [2.40]. IR: ν(C≡C) 2065, ν(C=C) 1636, ν(PF) 847 cm^{-1}. ^{1}H NMR: δ 2.89 (m, 24H, CH_2), 3.75 (m, 3H, =CH), 5.28 (s, 1H, CH_2Cl_2), 5.60 (AA′BB′, 6H, CH), 6.60−7.40 (m, 126H, PPh + CH), 7.52 (s, 3H, C_6H_3). ^{13}C NMR: δ 28.6 (m, CH_2), 88.0 and 90.5 (C≡C), 123.8, 126.4, 126.8 (C=), 127.4, 128.8, 130.6, 131.1, 131.3, 134.3, 133.5 (d, J_{CP} = 64 Hz), 353.9 (=CRu). ^{31}P NMR: δ 37.7 (PPh_2).

[1,3,5-C$_6$H$_3${4-C≡CC$_6$H$_4$CH=C-*trans*-RuCl(dppm)$_2$}$_3$][PF$_6$]$_3$ (4). $NaPF_6$ (100 mg, 0.60 mmol) was added to a solution of **2** (50 mg, 0.101 mmol) and *cis*-[$RuCl_2$(dppm)$_2$] (500 mg, 0.40 mmol) in CH_2Cl_2 (20 mL) and the mixture stirred for 3 h. Deoxygenated petrol (50 mL) was added and the mixture filtered. The precipitate was washed with Et_2O (2 × 10 mL) to afford a pale orange solid identified as **4** (450 mg, 76%). MS: 3457 ([M − PF_6]$^+$, 0.6), 905 ([RuCl(dppm)$_2$]$^+$, 100). Slow compound decomposition over a period of days precluded a microanalysis. UV−vis: 24 100 [0.90]. IR: ν(C≡C) 2068, ν(C=C) 1640, ν(PF) 846 cm^{-1}. ^{1}H NMR: δ 4.96 (m, 12H, CH_2), 5.98 (AA′BB, 6H, CH), 6.80−7.70 (m, 129H, PPh + CH + C_6H_3). ^{13}C NMR: δ 45.9 (m, CH_2), 88.2 and 90.5 (C≡C), 120.0, 126.6, 126.7 (C=), 127.9, 129.1, 130.4, 131.2, 131.6, 133.7, 132.8 (d, J_{CP} = 63 Hz), 356.4 (=CRu). ^{31}P NMR: δ −15.8 (PPh_2).

1,3,5-C$_6$H$_3${4-C≡CC$_6$H$_4$C≡C-*trans*-[RuCl(dppe)$_2$]}$_3$ (5). $NaPF_6$ (0.20 g, 1.2 mmol) was added to a solution of **2** (0.090 g, 0.20 mmol) and *cis*-[$RuCl_2$(dppe)$_2$] (1.00 g, 1.02 mmol) in CH_2Cl_2 (25 mL) and the mixture stirred for 12 h. NEt_3 (1 mL) was added and the mixture stirred for a further 5 min. The solvent was removed in vacuo, and the residue purified on an alumina column. Elution with acetone/Et_2O (1:19) to remove *trans*-[$RuCl_2$(dppe)$_2$] was followed by elution with CH_2Cl_2 to remove the product. Evaporation of the solvent from the eluent afforded **5** as a yellow powder (440 mg, 68% based on **2**). MS: 3249 ([M]$^+$, 20), 898 ([Ru(dppe)$_2$]$^+$, 100). Anal. Calcd for $C_{192}H_{159}Cl_3P_{12}Ru_3$: C, 71.01; H, 4.94. Found: C, 70.90; H, 5.20. UV−vis: 24 200 [9.90], 33 300 [6.60], 40 000 [13.7]. IR: ν(C≡C) 2204, 2065 cm^{-1}. ^{1}H NMR: δ 2.69 (m, 24H, CH_2), 6.56 (AA′BB′, 6H, CH), 6.93−7.46 (m, 126H, PPh + CH), 7.59 (s, 3H, C_6H_3). ^{13}C NMR: δ 30.6 (m, CH_2), 88.3 and 91.5 (C≡C), 116.2 (C≡), 127.0, 127.2, 128.9, 130.0, 130.9, 134.2, 134.4, 135.5, 136.3. ^{31}P NMR: δ 49.9.

1,3,5-C$_6$H$_3${4-C≡CC$_6$H$_4$C≡C-*trans*-[RuCl(dppm)$_2$]}$_3$ (6). $NaPF_6$ (48 mg, 0.28 mmol) was added to a solution of **2** (20 mg, 0.044 mmol) and *cis*-[$RuCl_2$(dppm)$_2$] (300 mg, 0.22 mmol) in CH_2Cl_2 (20 mL) and the mixture stirred for 3 h. Deoxygenated petrol (50 mL) was added and the mixture filtered. The filtrate was dissolved in CH_2Cl_2 (15 mL), NEt_3 (5 mL) added, and the mixture stirred for 1 h. The reaction mixture was placed on a basic alumina column and eluted with CH_2Cl_2/petrol (1:1). The eluent was taken to dryness to give a pale orange solid; recrystallization from CH_2Cl_2/MeOH at −20 °C afforded orange crystals identified as **6** (100 mg, 75%). MS: 3164 ([M]$^+$, 5), 869 ([Ru(dppm)$_2$]$^+$, 100). Anal. Calcd for $C_{186}H_{147}Cl_3P_{12}Ru_3$: C, 69.82; H, 4.68. Found: C, 69.05; H, 4.93. UV−vis: 24 700 [5.60]. IR (KBr): ν(C≡C) 2106 cm^{-1}. ^{1}H NMR: δ 4.90 (m, 12H, CH_2), 5.97 (AA′BB′, 6H, CH), 6.80−7.70 (m, 129H, PPh + CH + C_6H_3). ^{13}C NMR: δ 50.2 (m, CH_2), 87.9 and 91.6 (C≡C), 124.4, 127.5, 129.2, 129.9, 130.3, 133.4 (d, J_{CP} 64 Hz), 134.0, 134.8 (m), 135.6. ^{31}P NMR: δ −5.8.

1,3,5-C$_6$H$_3${4-C≡CC$_6$H$_4$C≡C-*trans*-[Ru(C≡CPh)(dppe)$_2$]}$_3$ (7). $NaPF_6$ (50 mg, 0.30 mmol) and NEt_3 (0.5 mL) were added to a solution of **5** (155 mg, 0.048 mmol) and phenylacetylene (0.05 mL, 0.46 mmol) in CH_2Cl_2 (15 mL), and the mixture stirred for 5 h. The solvent was removed in vacuo and the residue chromatographed on an alumina column. Elution with a mixture of CH_2Cl_2/petrol (1:19) to remove excess phenylacetylene was followed by elution with a mixture of CH_2Cl_2/petrol (3:2) to remove the product. Evaporation of the solvent from the eluent afforded **7** as a yellow powder (105 mg, 64%). MS: 3445 ([M]$^+$, 0.4), 898 ([Ru(dppe)$_2$]$^+$, 100). Anal. Calcd for $C_{216}H_{174}P_{12}Ru_3$: C, 75.32; H, 5.09. Found: C, 74.98; H, 5.60. UV−vis: 24 300 [11.6], 31 740 [9.81]. IR: ν(C≡C) 2203, 2057 cm^{-1}. ^{1}H NMR: δ 2.63 (m, 24H, CH_2), 6.65 (AA′BB′, 6H, CH), 6.81 (AA′BB′, 6H, CH), 6.92−7.61 (m, 138H, PPh + CPh + C_6H_3). ^{13}C NMR: δ 31.4 (m, CH_2), 88.3 and 91.6 (C≡C), 116.2 (C≡), 117.2 (≡C), 127.0, 127.4, 128.6, 128.7, 129.9, 130.5, 130.9, 134.1, 134.3, 136.9 (m). ^{31}P NMR: δ 54.5.

Alternative Preparation of 7. A mixture of *trans*-[Ru(4-C≡CC$_6$H$_4$C≡CH)(C≡CPh)(dppe)$_2$] (400 mg, 0.356 mmol), 1,3,5-triiodobenzene (50 mg, 0.11 mmol), $PdCl_2(PPh_3)_2$ (15 mg, 0.02 mmol), and CuI (15 mg, 0.08 mmol) in thf (30 mL) and NEt_3 (1 mL) was stirred at room temperature overnight. The solvent was removed in vacuo and the residue subjected to column chromatography on alumina, eluting with 3:7 dichloromethane/petrol. A broad yellow band was slowly eluted, the faster-moving portion of which was identified as *trans*-[(dppe)$_2$(PhC≡C)Ru(4,4′-C≡CC$_6$H$_4$C≡CC≡CC$_6$H$_4$C≡C)Ru(C≡CPh)(dppe)$_2$],[62] with the rest of the band identified as a mixture of

this product and **7**. Attempts to separate the mixture and obtain pure **7** were unsuccessful.

1,3,5-C_6H_3{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡$CC_6H_4NO_2$)(dppe)$_2$]}$_3$ (8). $NaPF_6$ (35 mg, 0.21 mmol) and NEt_3 (0.5 mL) were added to a solution of **5** (100 mg, 0.031 mmol) and 4-HC≡$CC_6H_4NO_2$ (30 mg, 0.20 mmol) in CH_2Cl_2 (5 mL), and the mixture was heated at reflux with stirring for 2 h. The solvent was removed in vacuo and the residue chromatographed on an alumina column. Elution with a mixture of CH_2Cl_2/petrol (1:2) to remove excess acetylene was followed by elution with CH_2Cl_2 to remove the product. Evaporation of the solvent from the eluent afforded **8** as a red powder (88 mg, 80%). MS: 3580 ($[M]^+$, 1), 898 ($[Ru(dppe)_2]^+$, 100). Anal. Calcd for $C_{216}H_{171}N_3O_6P_{12}Ru_3$: C, 72.48; H, 4.81; N, 1.17. Found: C, 72.10; H, 4.80; N, 1.21. UV−vis: 21 800 [8.93], 24 800 [1.12], 32 700 [9.15], 41 000 [17.9]. IR: ν(C≡C) 2204, 2047 cm^{-1}. ^1H NMR: δ 2.63 (m, 24H, CH_2), 6.57 (AA′BB′, 6H, CH), 6.76 (AA′BB′, 6H, CH), 6.91−7.57 (m, 126H, PPh + CH), 7.62 (s, 3H, C_6H_3), 7.97 (m, 6H, $CHCNO_2$). ^{13}C NMR: δ 31.4 (m, CH_2), 88.4 and 91.6 (C≡C), 116.9, 118.8 (C≡C); 123.5, 127.3, 128.9, 129.0, 129.9, 130.7, 131.2, 134.0, 134.2, 136.4 (m), 137.3, 142.7. ^{31}P NMR: δ 54.5.

1,3,5-C_6H_3{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡$CC_6H_4NEt_2$)(dppe)$_2$]}$_3$ (9). Complex **5** (179 mg, 0.054 mmol), 4-ethynyl-*N*,*N*-diethylaniline (63.0 mg, 0.43 mmol), NH_4PF_6 (32.0 mg, 0.20 mmol), and NEt_3 (2 mL) were heated in refluxing $CHCl_3$ (40 mL) for 6 h. The solvent was removed in vacuo, and the residue placed onto an alumina column. The column was washed with CH_2Cl_2/petrol (1:9) to remove excess acetylene. Subsequent elution with CH_2Cl_2 afforded a yellow solution, which was taken to dryness and recrystallized from CH_2Cl_2/MeOH to give a yellow solid identified as **9** (50 mg, 0.014 mmol, 26%). MS: 898 ($[Ru(dppe)_2]^+$, 100). Anal. Calcd for $C_{228}H_{201}N_3P_{12}Ru_3$: C, 74.86; H, 5.54; N, 1.15. Found: C, 74.71; H, 5.86; N, 1.32. UV−vis: 24 390 [15.3]. IR: ν(C≡C) 2055 cm^{-1}. ^1H NMR δ 1.13 (t, J_{HH} = 7 Hz, 18H, CH_3), 2.58 (m, 24H, CH_2), 3.36 (q, J_{HH} = 7 Hz, 12H, NCH_2), 6.93−7.85 (m, 147H, PPh + C_6H_4 + C_6H_3). ^{31}P NMR: δ 54.1.

1-(Me_3SiC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[RuCl(dppe)$_2$]}$_2$ (13). $NaPF_6$ (160 mg, 0.95 mmol) was added to a solution of **12** (100 mg, 0.24 mmol) and *cis*-[$RuCl_2$(dppe)$_2$] (550 mg, 0.57 mmol) in CH_2Cl_2 (20 mL), and the mixture stirred for 20 h. NEt_3 (1 mL) was added and the mixture stirred a further 5 min. The solvent was removed in vacuo, and the residue chromatographed on an alumina column. Elution with a mixture of Et_2O/petrol (4:1) was followed by elution with Et_2O/CH_2Cl_2 (1:1) to remove the product. Evaporation of the solvent afforded **13** as a yellow powder (360 mg, 66% based on **12**). MS: 2288 ($[M]^+$, 7), 898 ($[Ru(dppe)_2]^+$, 100). Anal. Calcd for $C_{135}H_{116}Cl_2P_8Ru_2Si$: C, 70.89; H, 5.11. Found: C, 70.52; H, 5.11. UV−vis: 24 300 [7.27], 33 400 [sh, 5.10], 39 900 [11.7]. IR: ν(C≡C) 2064, 2156, 2205 cm^{-1}. ^1H NMR: δ 0.27 (s, 9H, Me), 2.68 (m, 16H, CH_2), 6.55 (AA′BB′, 4H, CH), 6.92−7.46 (m, 84H, PPh + CH), 7.54 (d, J_{HH} = 2 Hz, 2H, C_6H_3), 7.58 (t, J_{HH} = 2 Hz, 1H, C_6H_3). ^{13}C NMR: δ −0.1 (Me), 30.6 (CH_2), 126.9, 127.2, 128.8, 134.1, 134.3, 135.5 (m), 136.2 (m). ^{31}P NMR: δ 50.0.

1-(Me_3SiC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[Ru(C≡CPh)(dppe)$_2$]}$_2$ (14). $NaPF_6$ (320 mg, 1.9 mmol) and NEt_3 (1 mL) were added to a solution of **13** (720 mg, 0.31 mmol) and phenylacetylene (0.20 mL) in CH_2Cl_2 (20 mL), and the mixture was heated at reflux for 2 h. The solvent was removed in vacuo and the residue chromatographed on an alumina column. Elution with a mixture of CH_2Cl_2/petrol (1:19) to remove excess phenylacetylene was followed by elution with CH_2Cl_2/petrol (3:2) to remove the product. Evaporation of the solvent afforded **14** as a yellow powder, which was recrystallized from CH_2Cl_2/MeOH (540 mg, 71%). MS: 2420 ($[M]^+$, 3), 999 ($[Ru(C≡CPh)(dppe)_2]^+$, 3), 898 ($[Ru(dppe)_2]^+$, 20). Anal. Calcd for $C_{151}H_{126}P_8Ru_2Si$: C, 74.99; H, 5.25. Found: C, 75.00; H, 5.43. UV−vis: 24 500 [7.45], 32 100 [7.00]. IR: ν(C≡C) 2057, 2156, 2204 cm^{-1}. ^1H NMR: δ 0.29 (s, 9H, Me), 2.63 (m, 16H, CH_2), 6.64 (AA′BB′, 4H, CH), 6.82 (AA′BB′, 4H, CH), 6.93−7.61 (m, 93H, PPh + CPh + C_6H_3). ^{13}C NMR: δ −0.1 (Me), 31.4 (CH_2), 127.0, 128.6, 134.1, 134.3, 136.9 (m). ^{31}P NMR: δ 50.0.

1-(Me_3SiC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡$CC_6H_4NO_2$)(dppe)$_2$]}$_2$ (15). $NaPF_6$ (40 mg, 0.24 mmol) and NEt_3 (0.5 mL) were added to a solution of **13** (140 mg, 0.061 mmol) and 4-HC≡$CC_6H_4NO_2$ (35 mg, 0.24 mmol) in CH_2Cl_2 (5 mL), and the mixture was heated at reflux for 2 h. The solvent was removed in vacuo, and the residue taken up in CH_2Cl_2 and passed through an alumina plug, eluting with CH_2Cl_2. The yellow solution was reduced in volume and the product precipitated by addition of petrol (∼30 mL) to afford **15** as a yellow microcrystalline solid (130 mg, 85%). MS: 2509 ($[M]^+$, 5), 898 ($[Ru(dppe)_2]^+$, 100). Anal. Calcd for $C_{151}H_{124}N_2O_4P_8Ru_2Si$: C, 72.30; H, 4.98; N, 1.12. Found: C, 71.70; H, 4.86; N, 1.08. UV−vis: 21 700 [5.89], 24 900 [7.12], 32 700 [sh, 5.93], 37 800 [9.42]. IR: ν(C≡C) 2047, 2155, 2206 cm^{-1}. ^1H NMR: δ 0.29 (s, 9H, Me), 2.63 (m, 16H, CH_2), 6.57 (AA′BB′, 4H, CH), 6.74 (AA′BB, 4H, CH), 6.91−7.56 (m, 87H, PPh + C_6H_4 + C_6H_3), 7.97 (AA′BB′, 4H, $CHCNO_2$). ^{13}C NMR: δ −0.1 (Me), 31.3 (CH_2), 127.2, 128.9, 133.9, 134.1, 136.3 (m), 142.6 (CNO_2). ^{31}P NMR: δ 54.5.

1-(Me_3SiC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡$CC_6H_4NEt_2$)(dppe)$_2$]}$_2$ (16). $NaPF_6$ (32 mg, 0.22 mmol) and NEt_3 (1 mL) were added to a solution of **15** (59 mg, 0.026 mmol) and 4-HC≡$CC_6H_4NEt_2$ (40 mg, 0.23 mmol) in $CHCl_3$ (40 mL), and the mixture was heated at reflux for 18 h. The reaction mixture was passed through an alumina plug and the solvent removed. The solid was washed with methanol and recrystallized from CH_2Cl_2/MeOH to give a green-yellow powder (37 mg, 0.015 mmol, 57%). The instability of the product on chromatographic absorbants precluded a satisfactory microanalysis. UV−vis: 24 390 [7.70]. IR: ν(C≡C) 2053 cm^{-1}. ^1H NMR: δ 0.23 (s, 9H, $SiMe_3$), 1.13 (t, J_{HH} = 7 Hz, 12H, CH_3), 2.60 (m, 16H, CH_2), 3.35 (q, J_{HH} = 7 Hz, 8H, CH_2), 6.46−7.50 (m, 99H, Ph + C_6H_4 + C_6H_3). ^{31}P NMR: δ 54.2.

1-(HC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[Ru(C≡CPh)(dppe)$_2$]}$_2$ (17). [NBu^n_4]F (0.2 mL of a 1 M solution in THF) was added to a solution of **14** (400 mg, 0.17 mmol) in CH_2Cl_2 (15 mL) and the solution stirred for 1 h. The mixture was passed through a short alumina column, eluting with CH_2Cl_2. MeOH (40 mL) was added to the eluant and the total volume of solvent reduced to ∼30 mL to give **17** as a yellow solid (330 mg, 85%). MS: 2347 ($[M]^+$, 5), 898 ($[Ru(dppe)_2]^+$, 45). Anal. Calcd for $C_{148}H_{118}P_8Ru_2$: C, 75.76; H, 5.07. Found: C, 75.37; H, 5.07. UV−vis: 24 600 [8.07], 32 000 [7.21]. IR: ν(C≡C) 2057, 2202, ν(H−C≡) 3296 cm^{-1}. ^1H NMR: δ 2.63 (m, 16H, CH_2), 3.12 (s, 1H, C≡CH), 6.64 (AA′BB′, 4H, CH), 6.81 (AA′BB′, 4H, CH), 6.92−7.65 (m, 93H, PPh + CPh + C_6H_3). ^{13}C NMR: δ 31.4 (CH_2), 78.0 (C≡), 82.3 (≡C), 127.0, 128.6, 134.0, 134.3, 137.0 (m). ^{31}P NMR: δ 54.5.

1-(HC≡C)C_6H_3-3,5-{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡$CC_6H_4NO_2$)(dppe)$_2$]}$_2$ (18). [NBu^n_4]F (0.2 mL of a 1 M solution in thf) was added to a solution of **15** (100 mg, 0.041 mmol) in CH_2Cl_2 (15 mL) and the solution stirred for 1 h. The mixture was passed through a short alumina column, eluting with CH_2Cl_2. MeOH (∼20 mL) was added to the eluant and the total volume reduced to around 10 mL. The precipitated product was collected by filtration and washed with petrol to afford **18** as a red solid (85 mg, 88%). MS: 2436 ($[M]^+$, 2), 1044 ($[Ru(4-C≡CC_6H_4NO_2)(dppe)_2]^+$, 10), 898 ($[Ru(dppe)_2]^+$, 100). Anal. Calcd for $C_{148}H_{116}N_2O_4P_8Ru_2$: C, 72.96; H, 4.80; N, 1.15. Found: C, 73.21; H, 4.74; N, 1.19. UV−vis: 21 600 [6.17], 25 000 [7.40], 32 500 [sh, 6.27]. IR: ν(C≡C) 2047, 2204, ν(HC≡) 3296 cm^{-1}. ^1H NMR: δ 2.63 (m, 16H, CH_2), 3.12 (s, 1H, C≡CH), 6.58 (AA′BB′, 4H, CH), 6.75 (AA′BB′, 4H, CH), 6.92−7.57 (m, 86H, PPh + CH + C_6H_3), 7.65 (s, 1H, C_6H_3), 7.98 (m, 4H, $CHCNO_2$). ^{13}C NMR: δ 31.3 (CH_2), 78.1, 82.3 (C≡C), 127.2, 128.9, 133.9, 134.1, 136.4 (m), 142.6 (CNO_2). ^{31}P NMR: δ 54.5.

Attempted Synthesis of 1-(HC≡C)C_6H_3-3,5-{4-C≡C-C_6H_4C≡C-*trans*-[Ru(4-C≡C$C_6H_4$$NEt_2$)(dppe)$_2$]}$_2$. A mixture of **16** (14 mg, 0.0055 mmol) and K_2CO_3 (12 mg, 0.087 mmol) in CH_2Cl_2 (5 mL) and MeOH (5 mL) was stirred at room temperature for 2 h. The mixture was passed through an alumina column with CH_2Cl_2, affording a green residue following removal of the solvent. ^{1}H and ^{31}P NMR data indicated unidentified decomposition products only.

1,3,5-C_6H_3(4-C≡CC_6H_4C≡C-*trans*-[Ru(dppe)$_2$]C≡C-3,5-C_6H_3-{4-C≡CC_6H_4C≡C-*trans*-[Ru(C≡CPh)(dppe)$_2$]}$_2$)$_3$ (19). $NaPF_6$ (30 mg, 0.18 mmol) and NEt_3 (0.5 mL) were added to a solution of **5** (80 mg, 0.025 mmol) and **17** (190 mg, 0.081 mmol) in CH_2Cl_2 (20 mL), and the solution was stirred for 24 h at 38 °C. The solvent was removed in vacuo and the residue chromatographed on an alumina column. Elution with Et_2O to remove excess **17** was followed by elution with CH_2Cl_2 to remove the product. MeOH (40 mL) was then added to the eluant and the total volume reduced to around 10 mL. The precipitated product was collected by filtration to afford **19** as a yellow solid (130 mg, 52%). Anal. Calcd for $C_{636}H_{510}P_{36}Ru_9$: C, 75.06; H, 5.05. Found: C, 74.83; H, 5.23. UV−vis: 24 900 [42.1], 32 200 [29.1]. IR: ν(C≡C) 2056, 2204 cm^{-1}. ^{1}H NMR: δ 2.64 (m, 72H, CH_2), 6.68−6.81 (m, 36H, CH + C_6H_3), 6.94−7.63 (m, 402H, PPh + CPh + CH + C_6H_3). ^{13}C NMR: δ 31.4 (CH_2), 127.0, 128.6, 128.7, 134.1, 134.3, 136.9 (m). ^{31}P NMR: δ 54.4 (s, 24P, "outer" PPh_2), 54.3 (s, 12P, "inner" PPh_2).

1,3,5-C_6H_3(4-C≡CC_6H_4C≡C-*trans*-[Ru(dppe)$_2$]C≡C-3,5-C_6H_3-{4-C≡CC_6H_4C≡C-*trans*-[Ru(4-C≡C$C_6H_4$$NO_2$)(dppe)$_2$]}$_2$)$_3$ (20). $NaPF_6$ (25 mg, 0.15 mmol) and NEt_3 (0.5 mL) were added to a solution of **5** (77 mg, 0.024 mmol) and **18** (190 mg, 0.078 mmol) in CH_2Cl_2 (15 mL), and the solution was stirred for 18 h at 35 °C. The solvent was removed in vacuo, and the residue chromatographed on an alumina column. Elution with Et_2O to remove excess **18** was followed by elution with CH_2Cl_2 to remove the product. The eluant was taken to dryness to afford **20** as a red powder (80 mg, 32%). Anal. Calcd for $C_{636}H_{504}N_6O_{12}P_{36}Ru_9$: C, 73.12; H, 4.86; N, 0.80. Found: C, 73.35; H, 4.92; N, 1.03. UV−vis: 21 400 [sh, 16.0], 25 300 [35.0], 32 700 [sh, 24.1]. IR: ν(C≡C) 2047, 2206 cm^{-1}. ^{1}H NMR: δ 2.64 (m, 72H, CH_2), 6.55−6.81 (m, 36H, CH + C_6H_3), 6.91−7.63 (m, 384H, PPh + C_6H_4 + C_6H_3), 7.97 (AA′BB′, 12H, $CHCNO_2$). ^{13}C NMR: δ 31.3 (CH_2), 127.0, 128.9, 133.9, 134.1, 136.5 (m), 142.6 (CNO_2). ^{31}P NMR: δ 53.8 (s, 24P, "outer" PPh_2), 54.1 (s, 12P, "inner" PPh_2).

***trans*-[Ru(4-C≡CC_6H_4C≡CPh)(C≡CPh)(dppe)$_2$] (21).** $NaPF_6$ (65 mg, 0.39 mmol) and NEt_3 (1 mL) were added to a solution of *trans*-[Ru(C≡CPh)Cl(dppe)$_2$] (200 mg, 0.19 mmol) and 4-HC≡CC_6H_4C≡CPh (50 mg, 0.25 mmol) in CH_2Cl_2 (10 mL), and the solution was stirred for 6 h. The solvent was removed in vacuo and the residue chromatographed on an alumina column. Elution with a mixture of CH_2Cl_2/petrol (1:9) to remove excess acetylene was followed by elution with CH_2Cl_2 to remove the product. Addition of petrol to the eluent and evaporation of the solvent afforded **21** as yellow microcrystals (0.180 g, 78%). MS: 1200 ([M]$^+$, 5), 1099 ([Ru(C≡CC_6H_4C≡CPh)(dppe)$_2$]$^+$, 75), 999 ([Ru(C≡CPh)(dppe)$_2$]$^+$, 65), 897 ([M(dppe)$_2$ − H]$^+$, 100). Anal. Calcd for $C_{77}H_{64}Cl_2P_4Ru$: C, 71.96; H, 5.02. Found: C, 71.96; H, 5.03. UV−vis: 26 200 [3.80]. IR: ν(C≡C) 2056 cm^{-1}. ^{1}H NMR: δ 2.61 (m, 8H, CH_2), 6.59 (AA′BB′, 2H, C_6H_4), 6.76 (AA′BB′, 2H, C_6H_4), 6.89−7.60 (m, 50H, phenyl). ^{13}C NMR: δ 31.4 (CH_2), 127.0, 128.6, 134.1, 134.3, 136.9. ^{31}P NMR: δ 54.2.

***trans*-[Ru(4-C≡CC_6H_4C≡CPh)(4-C≡C$C_6H_4$$NO_2$)(dppe)$_2$] (22).** $NaPF_6$ (40 mg, 0.24 mmol) and NEt_3 (0.5 mL) were added to a solution of *trans*-[Ru(4-C≡C$C_6H_4$$NO_2$)Cl(dppe)$_2$] (120 mg, 0.11 mmol) and 4-HC≡CC_6H_4C≡CPh (45 mg, 0.22 mmol) in CH_2Cl_2 (10 mL), and the solution was refluxed with stirring for 2 h. The mixture was allowed to cool and passed through a short alumina column, eluting with CH_2Cl_2. Addition of petrol (∼50 mL) and reduction of the sovent volume to around 30 mL afforded a precipitate, which was collected and washed with petrol to afford **22** as a red solid (110 mg, 79%). MS: 1245 ([M]$^+$, 5), 898 ([Ru(dppe)$_2$]$^+$, 35). Anal. Calcd for $C_{76}H_{61}NO_2P_4Ru$: C, 73.30; H, 4.94; N, 1.12. Found: C, 72.89; H, 5.19; N, 1.48. UV−vis: 21 300 [2.47], 26 800 [3.39]. IR: ν(C≡C) 2046 cm^{-1}. ^{1}H NMR: δ 2.61 (m, 8H, CH_2), 6.56 (AA′BB′, 2H, C_6H_4), 6.73 (AA′BB′, 2H, C_6H_4), 6.90−7.55 (m, 47H, phenyl), 7.97 (AA′BB′, 2H, $CHNO_2$). ^{13}C NMR: δ 31.3 (CH_2), 127.2, 128.9, 133.9, 134.1, 136.3 (m), 142.6 ($CHCNO_2$). ^{31}P NMR: δ 53.7.

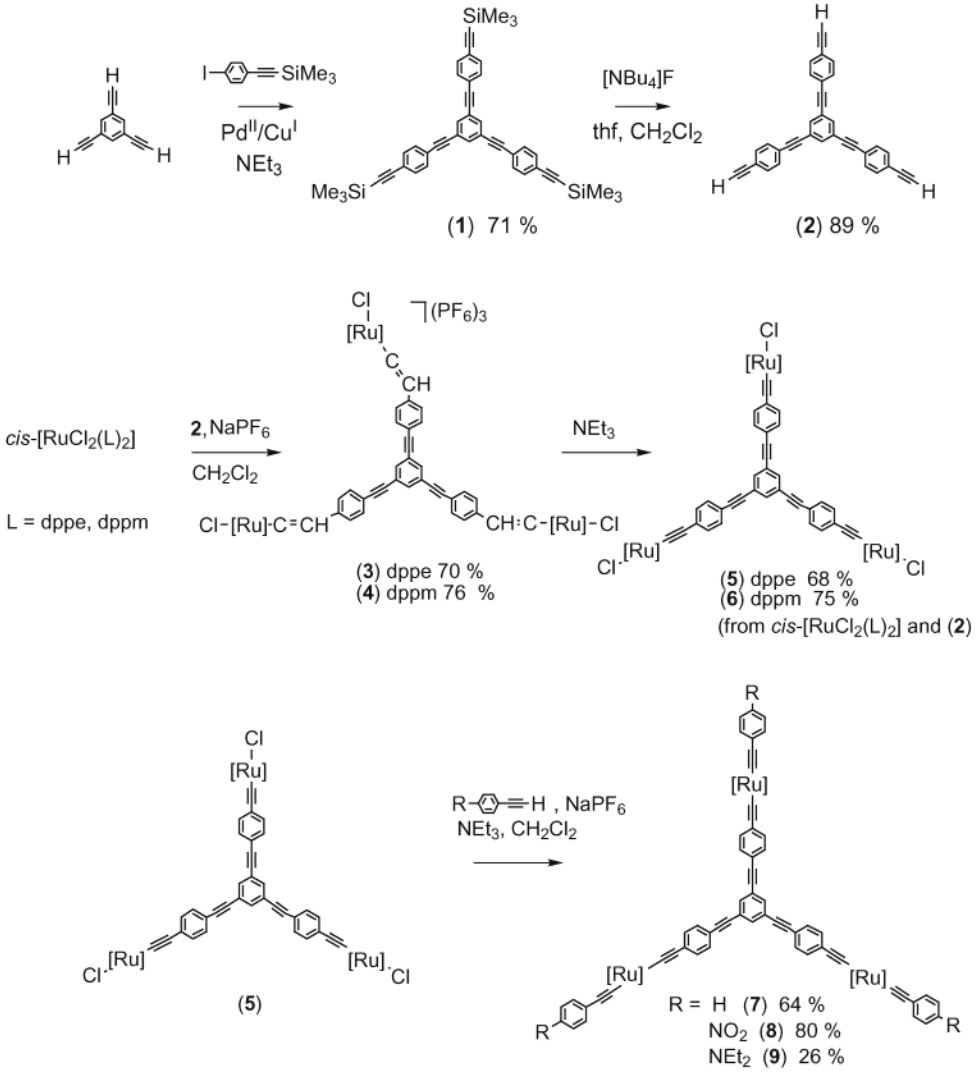
***trans*-[Ru(4-C≡CC_6H_4C≡CPh)(4-C≡C$C_6H_4$$NEt_2$)(dppe)$_2$] (23).** *trans*-[Ru(4-C≡CC_6H_4C≡CPh)Cl(dppe)$_2$] (55.5 mg, 0.049 mmol), 4-ethynyl-*N*,*N*-diethylaniline (26.5 mg, 0.18 mmol), $NaPF_6$ (26.9 mg, 0.17 mmol), and NEt_3 (2 mL) were heated in refluxing $CHCl_3$ (40 mL) for 3 h. The solvent was removed under reduced pressure and the residue extracted into CH_2Cl_2, absorbed onto alumina, and placed on an alumina column. Excess acetylene was removed by elution with petrol. Elution with 4:6 CH_2Cl_2/petrol afforded a yellow solution, which was taken to dryness to afford a yellow solid. Recrystallization from CH_2Cl_2/MeOH afforded a yellow powder identified as **23** (19 mg, 31%). MS: 1273 ([M]$^+$, 7), 1100 ([M − $C_{12}H_{14}N$]$^+$, 45), 898 ([Ru(dppe)$_2$]$^+$, 100). Anal. Calcd for $C_{80}H_{71}NP_4Ru$: C, 75.58; H, 5.63; N, 1.10. Found: C, 75.23; H, 5.69; N, 1.23. UV−vis: 25 900 [2.30]. IR: ν(C≡C) 2054 cm^{-1}. ^{1}H NMR δ 1.13 (t, J_{HH} = 7 Hz, 6H, CH_3), 2.60 (m, 8H, CH_2), 3.35 (q, J_{HH} = 7 Hz, 4H, CH_2), 6.54−7.68 (m, 53H, PPh + CPh + C_6H_4). ^{31}P NMR: δ 54.4.

Reaction between *cis*-[$RuCl_2$(dppe)$_2$] and 4-Ethynyl-*N*,*N*-diethylaniline. A solution of 4-ethynyl-*N*,*N*-diethylaniline (124.9 mg, 0.721 mmol), *cis*-[$RuCl_2$(dppe)$_2$] (129.0 mg, 0.133 mmol), and NH_4PF_6 (27.9 mg, 0.172 mmol) in CH_2Cl_2 (40 mL) was stirred at room temperature for 15 h. NEt_3 (4 mL) was added and the solution taken to dryness under reduced pressure. A CH_2Cl_2 extract of the residue was absorbed onto alumina and placed on an alumina column. Elution with petrol afforded the excess unreacted acetylene and with CH_2Cl_2 gave a green solution. Addition of MeOH (40 mL) to the green solution followed by reduction in solvent volume under reduced pressure to approximately 1 mL afforded an unidentified green powder (65 mg).

Results and Discussion

Syntheses of Zero-Generation Dendrimers. The platinum-containing arylalkynyl dendrimers feature square planar platinum environments, and there is no steric impediment to triplatinating triethynylbenzene and -mesitylene.[46,47] In contrast, we have previously noted that reaction of excess *cis*-[$RuCl_2$(dppm)$_2$] with 1,3,5-triethynylbenzene affords the bis-product 1,3-{*trans*-[RuCl(dppm)$_2$}$_2$-5-HC≡CC_6H_3 only.[68] The first step in alkynylruthenium dendrimer construction is therefore incorporation of "spacer" units into the core (see Scheme 1). Reaction of 1,3,5-triethynylbenzene with 3 equiv of 1-iodo-4-trimethylsilylethynylbenzene in the presence of a [$PdCl_2$(PPh_3)$_2$]/CuI catalyst in triethylamine (Sonogashira coupling[58]) afforded the tris(4-trimethylsilylethynylphenyl) derivative **1**, subsequent desilylation with fluoride giving the tris(4-ethynylphenyl) compound **2**. Compounds **1** and **2** were characterized by mass spectrometry, IR, and ^{1}H NMR spectroscopy. The reactive ethynyl groups in **2** are sufficiently removed from one another to permit smooth metalation with bulky bis(diphosphine)ruthenium units at each ethynyl group (Scheme 1). Thus, reaction of **2** with *cis*-[$RuCl_2$(L_2)$_2$] (L_2 = dppe, dppm) in dichloromethane in the presence of PF_6^- gave the trivinylidene complexes **3** and **4**, in an extension of a procedure developed for

Scheme 1. Preparation of 1−9 ([Ru] = *trans*-Ru(dppe)$_2$ or *trans*-Ru(dppm)$_2$)



linear monovinylidene complexes by Dixneuf and coworkers.[67] Deprotonation of the trivinylidene complexes **3** and **4** with NEt_3 gave the trialkynyl complexes **5** and **6**, once again an extension of Dixneuf's procedure.[67] Complexes **3** and **5** were reported while the present work was in progress.[68] We and others have previously demonstrated bis-alkynyl complex formation from chlorobis{bis(diphenylphosphino)methane}ruthenium alkynyl complexes,[69−73] but bis-alkynyl complexes are formed more easily when dppe is coordinated to the metal center,[54,72,74−79] so dendrimer construction was pursued with the dppe-containing complexes. Reaction of **5** with phenylacetylene or its 4-nitro- or 4-diethylamino-functionalized analogues proceeded via the intermediacy of trivinylidene complexes (which were not isolated here or in any subsequent steps) to give tris-di(alkynyl) complexes **7**−**9** (Scheme 1). Compound **5** is considerably less reactive toward the diethylamino-functionalized alkyne, heating in refluxing chloroform rather than dichloromethane being required to effect reaction. The diethylamino-functionalized compound **9** and other diethylamino-containing compounds described below have significantly lower stability on the alumina employed as chromatographic absorbant; as a consequence, lower yields of these compounds were obtained [note that all alkynyl compounds described in this paper proved unstable on silica].

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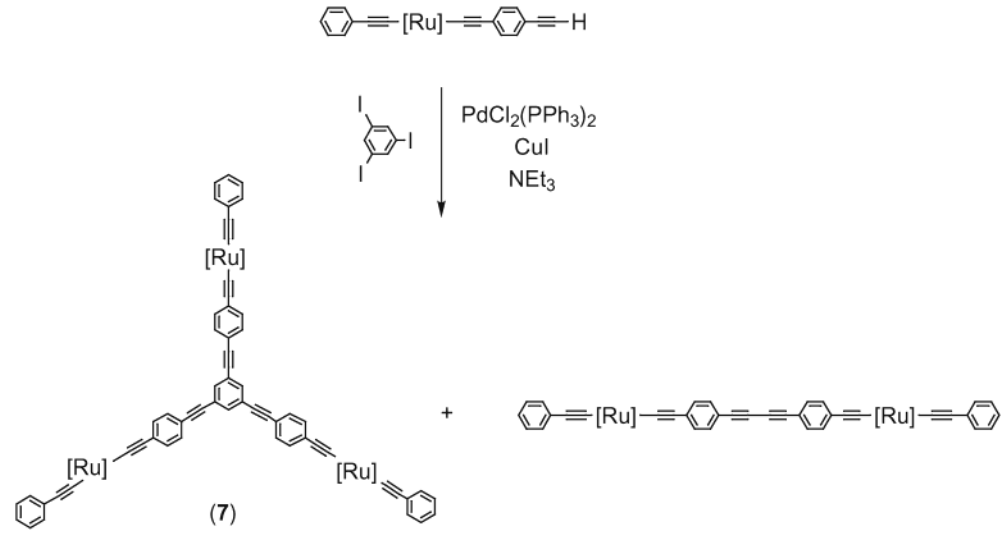
Scheme 2. Preparation of 7 from *trans*-[Ru(C≡CPh)(4-C≡CC$_6$H$_4$C≡CH)(dppe)$_2$] ([Ru] = *trans*-Ru(dppe)$_2$)



(**7**)

The need to employ organic building blocks with spacers to incorporate the three bulky bis(diphosphine)-ruthenium units at each branching point in the dendritic structure suggests other possible routes to the target complexes. We examined Sonogashira coupling of *trans*-[Ru(4-C≡CC$_6$H$_4$C≡CH)(C≡CPh)(dppe)$_2$] with 1,3,5-triiodobenzene (Scheme 2), which afforded some of the desired complex **7**, but also gave a byproduct, namely, the oxidatively homocoupled product *trans*,-*trans*-[(dppe)$_2$(PhC≡C)Ru(4,4′-C≡CC$_6$H$_4$C≡CC≡C-C$_6$H$_4$C≡C)Ru(C≡CPh)(dppe)$_2$], prepared previously by the deliberate homocoupling of *trans*-[Ru(4-C≡CC$_6$H$_4$-C≡CH)(C≡CPh)(dppe)$_2$].[62] Chromatographic separation of these two complexes proved to be extremely difficult, only poor yields being obtained. The oxidative homocoupling of terminal alkynes is reported to proceed rapidly in the presence of palladium(II) and copper(I) catalysts and oxygen.[80] Procedures were therefore adopted to rigorously exclude oxygen from the reaction environment, but the oxidatively homocoupled complex was still formed. We therefore abandoned synthesis involving Sonogashira coupling of metal-containing alkynes with aryl iodides.

Syntheses of First-Generation Dendrimers. There are two fundamentally different methods for dendrimer construction, namely, the divergent method in which branching units are successively added to the core, thereby building up the dendritic molecule from the core outward, and the convergent method in which the dendrimer is constructed from the periphery inward, dendritic "wedges" being formed first and then coupled to the core unit at the final step. The divergent approach suffers from defects in the end-groups caused by incomplete reaction being propagated to subsequent generations; physical separation is difficult because they differ only slightly from the nondefective molecules. The convergent method facilitates separation of defective units, because such molecules differ significantly from nondefective units, but is limited in terms of the number of possible generations because of steric problems when coupling large wedges to a core. Low-generation, nondefective dendrimers were targeted in the current work, so a convergent approach was adopted.

The syntheses of the dendritic wedges are summarized in Scheme 3. Reaction of 1,3,5-tribromobenzene with *n*-butyllithium followed by iodine afforded 1,3-dibromo-5-iodobenzene, also reported while the present studies were underway.[56] Sonogashira coupling at an aryl iodide is much faster than at an aryl bromide, so reaction of 1,3-dibromo-5-iodobenzene with trimethylsilylacetylene catalyzed by palladium(II)/copper(I) gave 1,3-dibromo-5-trimethylsilylethynylbenzene, a compound that has been described previously,[81] although no experimental synthetic details or characterization were reported. Transhalogenation of this compound was effected by treatment with *tert*-butyllithium followed by addition of iodine (the reaction did not proceed cleanly if *n*-butyllithium was employed). Sonogashira coupling of 1,3-diiodo-5-trimethylsilylethynylbenzene with 1-bromo-4-ethynylbenzene in the presence of [PdCl$_2$(PPh$_3$)$_2$] and copper(I) iodide gave 1,3-(4-BrC$_6$H$_4$C≡C)$_2$-5-(Me$_3$-SiC≡C)C$_6$H$_3$ (**10**), transhalogenation of which afforded the diiodo analogue **11**; once again, use of *tert*-butyllithium rather than *n*-butyllithium was necessary to ensure clean reaction. The final step in the preparation of the organic dendrimer wedge was to incorporate two terminal alkyne groups into the structure while leaving the alkyne attached to the central ring protected. Treatment of **11** with trimethylsilylacetylene using Sonogashira coupling conditions would result in three alkyne groups each protected by a trimethylsilyl group, and removal of a specific protecting group or groups would presumably be difficult. Although the selective removal of different silyl protecting groups (e.g., trimethylsilyl and triisopropylsilyl) from compounds containing multiple protected alkynes has been reported,[82,83] a more straightforward procedure for incorporating a terminal alkyne directly onto an aryl iodide has been reported recently by Negishi and co-workers.[84] This method involves in situ generation of Zn(C≡CH)Br from the Grignard reagent Mg(C≡CH)Br and zinc(II) bromide; subsequent addition of the diiodide **11** and palladium(II)/copper(I) catalysts afforded the organic den-

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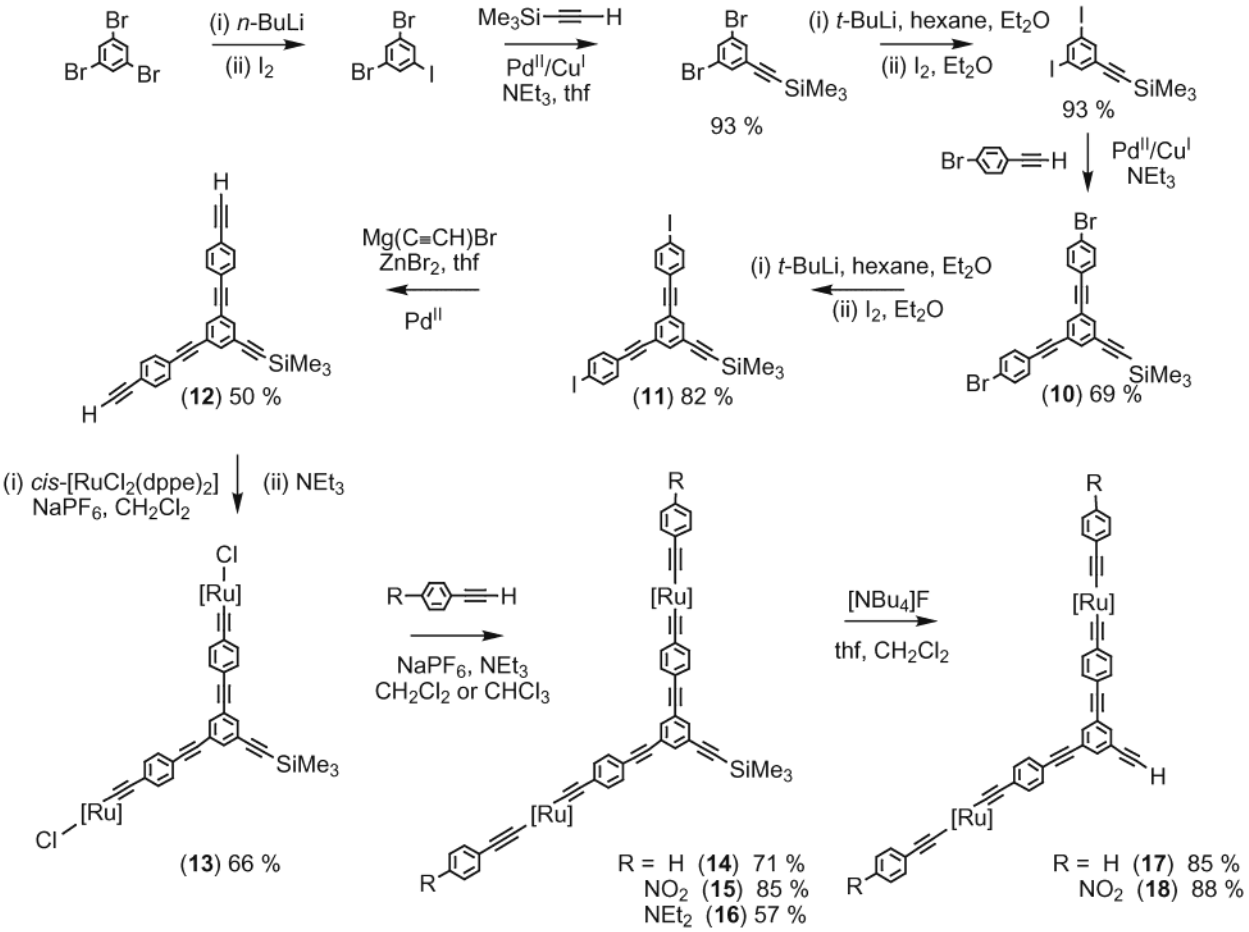
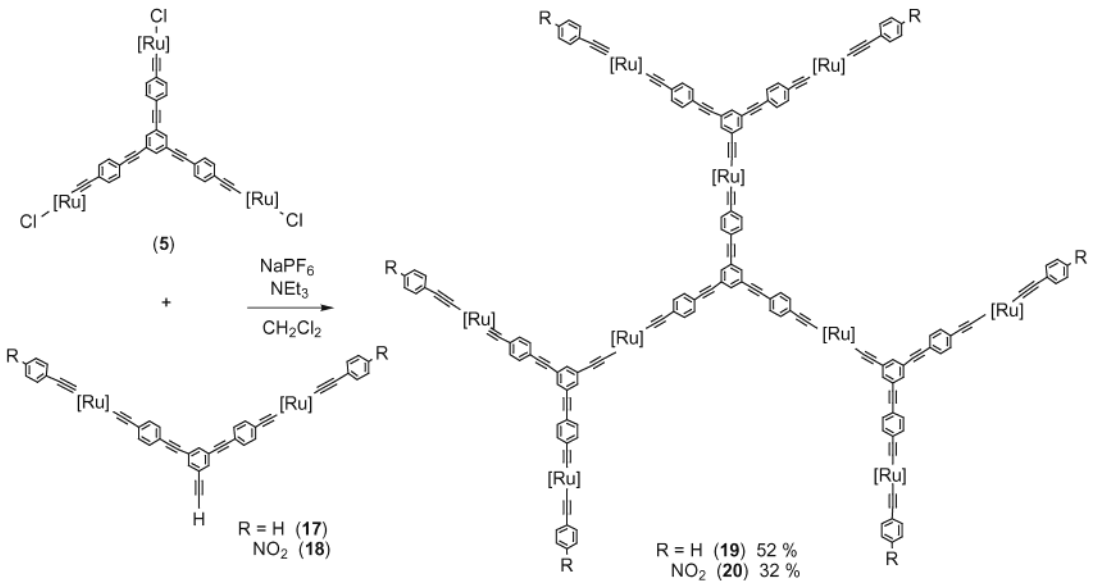
Scheme 3. Preparation of Wedges 10−18 ([Ru] = *trans*-Ru(dppe)$_2$)



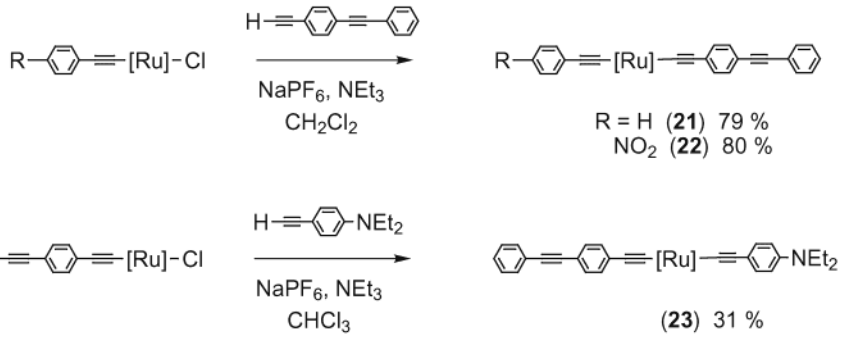
Scheme 4. Preparation of 19 and 20 ([Ru] = *trans*-Ru(dppe)$_2$)



dron 1,3-(4-HC≡CC$_6$H$_4$C≡C)$_2$-5-(Me$_3$SiC≡C)C$_6$H$_3$ (**12**). Compounds **10**−**12** were characterized by mass spectrometry, IR, UV−vis, and ^{1}H and ^{13}C NMR spectroscopy.

The organometallic components of the wedge were introduced by Dixneuf protocols, reaction of **12** with *cis*-[RuCl$_2$(dppe)$_2$] in the presence of NaPF$_6$ affording a divinylidene complex, which was not isolated, but instead deprotonated by triethylamine in situ to give the dialkynyl complex **13**. The peripheral groups of the nascent dendrimer were then incorporated, replacement of the chloro ligands also removing the possibility of the wedge coupling with itself in the final step of dendrimer construction; reaction of **13** with alkynes 4-HC≡CC$_6$H$_4$R

Scheme 5. Preparation of 21−23 ([Ru] = *trans*-Ru(dppe)$_2$)



(R = H, NO_2, NEt_2) in the presence of $NaPF_6$ and base gave the bis-di(alkynyl) complexes **14**−**16**. The final step in wedge preparation is removal of the trimethylsilyl protecting group by treatment with fluoride. This reaction did not proceed cleanly for the diethylamino-functionalized wedge **16**, only decomposition products being isolated. In contrast, reaction with **14** and **15** proceeded smoothly to give the bis-dialkynyl complexes **17** and **18**.

The final step in dendrimer synthesis is to couple the organometallic wedges to the organometallic core (Scheme 4). Reaction of **5** with 3 equiv of **17** or **18** in the presence of $NaPF_6$ and triethylamine gave the first-generation dendrimer complex **19** or **20**, respectively. It proved necessary to conduct the reactions in the temperature range 35−38 °C, lower temperatures resulting in much slower reaction and higher temperatures in significantly reduced yields, the latter possibly due to decomposition of the terminal alkyne-containing wedge. The lower yield of the nitro-containing wedge was a consequence of the excess nitro-containing wedge being more difficult to separate from the dendrimer than was its non-nitro analogue. Despite their molecular size and the considerable number of arylalkynyl units in each complex, the dendrimers are very soluble in organic solvents such as dichloromethane, chloroform, and tetrahydrofuran.

Syntheses of Linear Alkynylruthenium Complexes. Linear analogues of the dendrimers prepared in the current studies were also prepared, the procedures being shown in Scheme 5. Reaction of *trans*-[Ru(4-C≡CC_6H_4R)Cl(dppe)$_2$] (R = H, NO_2) with 4-HC≡CC_6H_4C≡CPh in dichloromethane in the presence of $NaPF_6$ and triethylamine afforded complexes **21** and **22**. The complex *trans*-[Ru(4-C≡C$C_6H_4NEt_2$)Cl(dppe)$_2$] is unstable, so the diethylamino-functionalized complex **23** was prepared by an alternative route, namely, coordination of the 4-phenylethynylphenylethynyl ligand first, followed by coordination of the 4-diethylaminophenylethynyl ligand.

Characterization of Alkynyl Complexes. The acetylide complexes were characterized by UV−vis, IR, ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy, secondary ion mass spectrometry, and, in the case of **19**, transmission electron microscopy (TEM). The strong ν(C≡C) modes assigned to the alkynylruthenium units are observed at 2065 and 2064 cm^{-1} in the spectra of the monoacetylide complexes **5** and **13**, respectively. For the dialkynyl complexes with phenylethynyl ligands (**7**, **14**, **17**, **21**), the band is at 2056−2057 cm^{-1}, which decreases in energy to 2053−2055 cm^{-1} for the diethylamino-containing complexes (**9**, **16**, **23**) and to 2046−2047 cm^{-1} for the nitrophenylethynyl-containing complexes (**8**, **15**, **18**, **22**). The IR spectra of complexes **13**, **14**, and **15** also contain bands at 2155 cm^{-1} which are assigned to the ν(C≡C) modes associated with the Me_3SiC≡C group. The spectra of complexes **5**−**21** all contain bands between 2203 and 2210 cm^{-1} which are assigned to ν(C≡C) modes associated with the ArC≡CAr moieties. Complexes **17** and **18**, which have terminal alkyne groups, show the corresponding ν(C−H) at 3296 cm^{-1}.

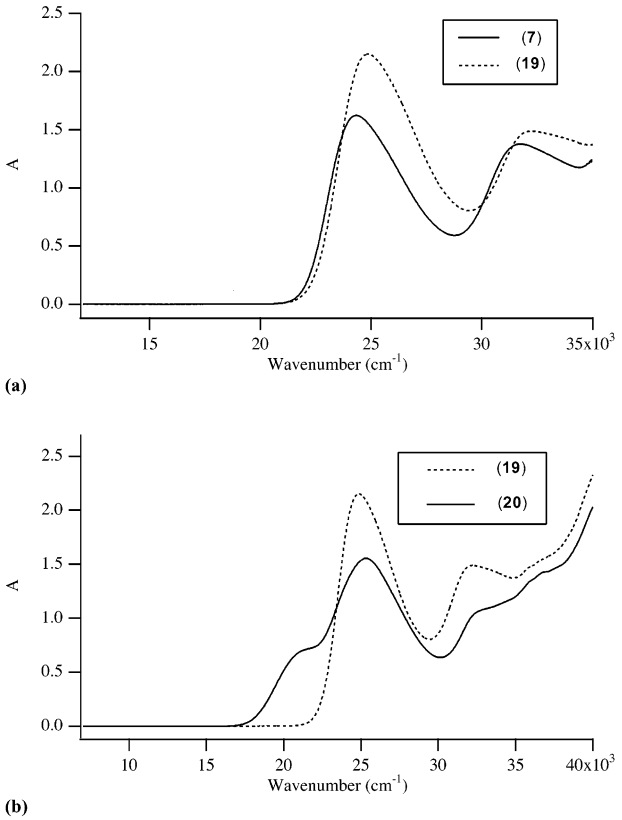
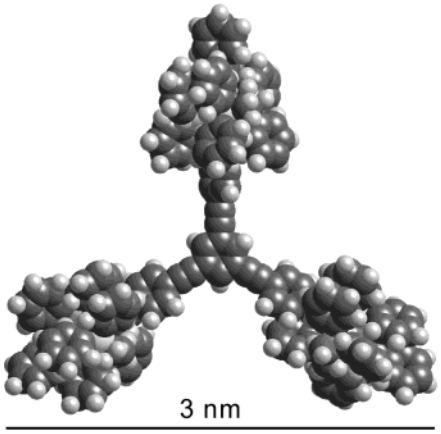


Figure 1. UV−vis spectra of (a) zero-generation dendrimer **7** and first-generation dendrimer **19** and (b) first-generation dendrimers **19** and **20**.

The UV−vis spectra of complexes **5**−**22** reveal MLCT transitions at 24 000−25 000 cm^{-1} accompanied by an additional MLCT band in the spectra of the nitro-containing complexes at 21 300−21 800 cm^{-1}. All complexes show absorption bands above 30 000 cm^{-1} assigned to transitions associated with the phosphine ligands. Illustrative spectra are shown in Figure 1. There is no loss of optical transparency in proceeding from the zero-generation dendrimer **7** to the first-generation dendrimer **19** (Figure 1); in fact, a small gain



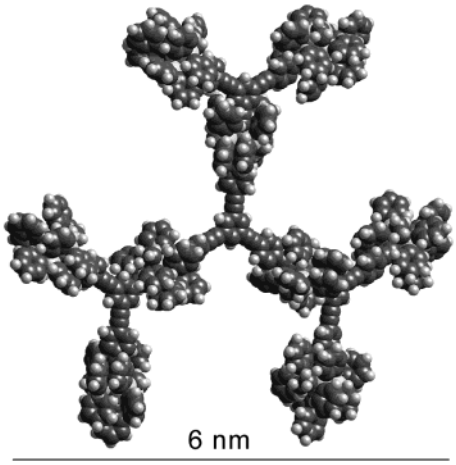


Figure 2. SPARTAN models of **5** and **19**.

in transparency is seen, which may indicate that the dendrimer **19** has a nonplanar geometry. Onset of noncoplanarity is consistent with the general observation that, upon increasing the size of dendritic systems, the initially planar disposition will eventually become a globular array. Interestingly, the extinction coefficient for ν_{max} increases more than 3-fold in proceeding from **7** to **19**. Incorporation of peripheral nitro groups in proceeding from **19** to **20** results in the aforementioned observation of a new, strong MLCT band at lower energy, with about twice the intensity of the corresponding band in **8** (Figure 1).

Although most of the ^{1}H NMR resonances are essentially invariant across this series of complexes, the nitro-containing ring proton resonances are a useful spectroscopic probe for **8**, **15**, **18**, **20**, and **22**. The ^{31}P NMR spectra of the monoalkynyl complexes **5** and **13** contain the expected singlet resonances at ~50 ppm, while resonances at ~54 ppm are observed for the dialkynyl complexes; for the dendritic complexes **19** and **20**, the integration of the "outer" phosphorus resonances against the "inner" phosphorus resonances, separated by 0.1−0.3 ppm, confirmed the complex composition.

The mass spectra of all complexes except **9**, **19**, and **20** reveal low-abundance molecular ion signals and, in most instances, fragmentation by loss of alkynyl and/or chloro ligands and a $[Ru(dppe)_2]^+$ base peak. Attempts to acquire mass spectra of **19** and **20** were made using a variety of ionization conditions, but spectra recorded on secondary ion, electrospray, and four different MALDI instruments contained no bands that could be assigned to a molecular ion or dendritic fragment. The bulky diphosphine ligands and arylalkynyl spacer groups result in a rapid increase of dendrimer size compared to similar arylethynylplatinum dendrimers, molecular modeling using SPARTAN suggesting a dendrimer "diameter" of ca. 60 Å for **19** (Figure 2). Dendrimer **19** was consequently further characterized by transmission electron microscopy (TEM), a representative micrograph being shown in Figure 3 and revealing individual molecules with dimensions consistent with those calculated by molecular modeling. Unlike tris(bipyridine)ruthenium-based dendrimers imaged recently by TEM, which decomposed after several minutes under the electron beam,[85] dendrimer **19** is very stable, persisting unchanged over many hours.

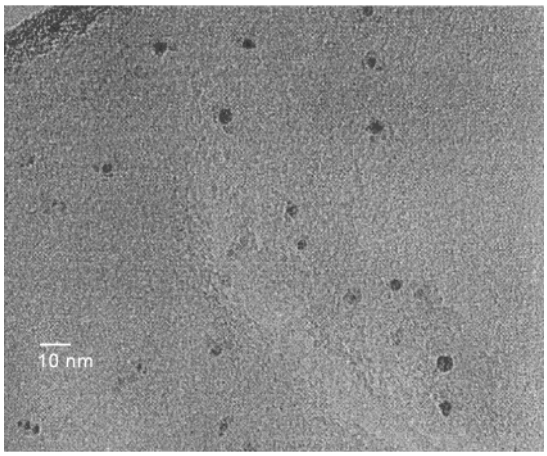


Figure 3. Electron micrograph (TEM) of molecules of **19**.

Conclusion

The results presented herein have demonstrated that electron-rich organometallic dendrimers with metals dispersed through the dendritic structure are synthetically accessible, the dialkynylruthenium moiety providing the crucial building block for dendrimer construction and affording periphery flexibility. The suite of molecules described herein promises ready access to higher-generation dendrimers by, for example, coupling **17**/**18** with **13** followed by desilylation and attachment to the core. We have reported that molecules of this type have among the largest two-photon absorption cross-sections thus far[49] and that these molecules possess the capacity to undergo facile switching of their nonlinear optical properties utilizing electrochemical stimuli.[63] The thermal and oxidative stability of these dendrimers, coupled to their size and their resistance to high-energy electron beams, suggest further materials applications. Studies directed toward these ends are currently underway.

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ruthenium salts. M.G.H. holds an ARC Australian Senior Research Fellowship, M.P.C. holds an ARC Australian Research Fellowship, and A.M.M. held an Australian Postgraduate Award. We thank Mr. F. Brink (ANU Electron Microscopy Unit) for assistance with the TEM.

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