

Syntheses, Electrochemical, Linear Optical, and Cubic Nonlinear Optical Properties of Ruthenium–Alkynyl-Functionalized Oligo(phenylenevinylene) Stars**

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syntheses of *trans*-[Ru(C \equiv CC₆H₄-4-CHO)(C \equiv CC₆H₄-4-The R)(dppe)₂] (R=H (**9a**), NO₂ (**9b**), CHO (**9c**), C \equiv CC₆H₃-3,5-Et₂ (9 d), (E)-CH=CHC₆H₄-4-tBu (9 e); dppe = 1,2-bis(diphenylphosphino)ethane), trans-[Ru($C \equiv CC_6H_4$ -4-R)Cl(dppe)₂] $(R = C \equiv$ CC_6H_3 -3,5-Et₂ (11 a), (E)-CH=CHC₆H₄-4-tBu (11 b), (E)-CH= CHC_6H_4 -4- NO_2 (11 c)), 1,2,4,5-{*trans*-[(dppe)₂($RC_6H_4C \equiv C$) $Ru{C \equiv C$ $CC_6H_4-4-(E)-CH=CH$]]₄ C_6H_2 (R = H (14a), C = CC_6H_3-3,5-Et_2 (14b), (*E*)-CH=CHC₆H₄-4-tBu (14c)), 1-I-3,5-{ $trans-[(L_2)_2(R)Ru{C \equiv CC_6H_4-}$ 4-(*E*)-CH=CH}] $_{2}C_{6}H_{3}$ (L₂=1,1-bis(diphenylphosphino)methane (dppm)), R=Cl (15a); L₂=dppe, R=C=CPh (15b), R=C= (15 c)), CC_6H_4 -4-NO₂ $1-Me_3SiC \equiv C-3, 5-\{trans-[(L_2)_2(R)Ru\{C \equiv$ $CC_6H_4-4-(E)-CH=CH]_2C_6H_3$ (L₂=dppm, R=Cl (**16a**); L₂=dppe, $R = C \equiv CPh$ (16 b)), 1-HC \equiv C-3,5-{trans-[(dppe)₂(R)Ru{C \equiv CC₆H₄-4-(*E*)-CH=CH}]]₂C₆H₃ (R = CI (**17 a**), R = C = CPh (**17 b**)), and 1,3,5- $\{trans-[(dppe)_2(3,5-R_2-C_6H_3C \equiv C)Ru\{C \equiv CC_6H_4-4-(E)-CH = CC_6H$ $(R = (E)-CH = CHC_6H_4-4-C \equiv C-trans-[Ru(C \equiv C-trans-(Ru(C \equiv C-trans-(Ru(C))))))))))))))$ CH}]}₃ C_6H_3 CPh)(dppe)₂] (18)) are reported together with those of the precursor alkynes $1-RC \equiv C-3, 5-Et_2C_6H_3$ (R = SiMe₃ (2), H (3), C₆H₄-4- $C \equiv CSiMe_3$ (5), C_6H_4 -4- $C \equiv CH$ (6)). The identities of 9c, 9d, 9e, **11 a**, and $trans = [Ru\{C \equiv CC_6H_4 - 4 - (E) - CH = CHC_6H_4 - 4 - tBu\}_2(dppe)_2]$ (12 and 12') were confirmed by single-crystal X-ray diffraction studies. The electrochemical properties of 9a-e, 11a-b, 14a-c, 15a-c, 16b, 17a, 17b, and 18 were assessed by cyclic voltammetry; the studies reveal that potentials for the fully/quasi-re-

versible metal-centered oxidation processes decrease upon introduction of solubilizing alkyl substituents and increase upon increasing acceptor substituent strength; other structural variations have little impact. UV/Vis-NIR spectroscopic studies on these complexes reveal lowest-energy metal-ligand charge transfer (MLCT) bands that redshift upon increasing the acceptor substituent strength, blueshift on alkyl incorporation, and gain in intensity on progression from linear to star complexes. Low-temperature UV/Vis-NIR spectroelectrochemical studies of 14a-c show the appearance of an intense low-energy band at 7400–7900 cm⁻¹ that is redshifted upon π -system lengthening and alkyl substituent incorporation. The cubic nonlinear optical properties of 9d, 9e, 14a-c, 15a-c, 16b, 17a, b, and 18 were assayed by femtosecond Z-scan studies at benchmark wavelengths (750 and 800 nm) in the near-IR region, with nonlinearity increasing upon nitro incorporation; the values for the Eene-linked dendrimers in these studies are much larger than yne-linked analogues. Compounds 9d, 9e, 14a-c, and 18 were further examined by broad-spectral-range femtosecond Z-scan studies; the cruciform complexes have appreciable multiphoton absorption cross-sections, with maximal values close to two and three times the wavelength of the linear optical absorption maxima.

Introduction

The nonlinear optical (NLO) properties of molecular materials have attracted significant interest.^[1] Whereas the majority of

studies have focused on purely organic molecules, recent comparisons of NLO parameters have shown that organometallics

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| [c] | Dr. B. A. Babgi Permanent address: Department of Chemistry, Faculty of Science King Abdulaziz University, P.O. Box 80203, Jeddah 21589 (Saudi Arabia) | | the syntheses and characterization of compounds 1–5, 7, and 8, and complexes 9a–e, 10, 11a–c, 13a, 14a–c, 15a–c, 16a, 16b, 17a, 17b, and 18; crystallographic studies of 9c–e, 11a, 12', and 12''; electrochem- |
| [d] | Prof. M. Samoc Research School of Physics and Engineering, Australian National University Canberra, ACT 2601 (Australia) | i University | ical studies of all new complexes; spectroelectrochemical studies of 14a–14c; single-wavelength nonlinear optical studies of 15a–c, 16b, 17a, 17b, and 18; and broad-spectral-range nonlinear optical studies of 9d, 9e, 14a–c, and 18. |
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can outperform organics, even when the data are scaled for molecular weights, molecular volumes, numbers of electrons strongly participating in polarization, or even costs of production.^[2] The results of these performance comparisons, coupled with the additional functionality inherent in metal complexes (e.g., a diversity of geometries, performance tuning by coligand modification, and the possibility of switching by reversible metal-centered oxidation) have helped drive the continuing interest in organometallics as potential NLO materials,^[3] and to maintain them as a genuine alternative to organics.

One structure-NLO property relationship that was developed in early studies of purely organic molecules was the observation of an increase in NLO merit on replacing an yne linkage in a π -bridging unit with an *E*-ene linkage, an outcome ascribed to orbital energy mismatch of p orbitals of sp-hybridized acetylenic carbon atoms with the p orbitals of sp²-hybridized phenyl carbon atoms;^[4] this effect presumably acts in combination with the increased propensity for oligo(phenyleneethynylene) (OPE) units to rotate out of π -system coplanarity when compared to oligo(phenylenevinylene) (OPV) analogues, thereby reducing efficient π delocalization. Metal alkynyl complexes were contemporaneously shown to function as efficient NLO materials,^[5] and they continue to provoke interest, but despite the favorable characteristics of E-ene-linked species, the vast majority of studies of the NLO properties of metal-alkynyl complexes have considered those with an OPE-based rather than OPV-based π bridge. We report herein studies directed at addressing this deficiency, including the syntheses of metal-alkynyl complexes with OPV-based bridges by a methodology that employs an unusual "chemistry-on-complex" approach at a pendant formyl group, comprehensive evaluation of the electrochemical and spectroscopic properties of the new complexes, structural and spectroelectrochemical studies of selected examples, and an evaluation of their cubic NLO parameters; some of these results have

been published in a preliminary form.^[6]

Results and Discussion

Previous studies with metal-alkynyl complexes have established several outcomes that influenced the research described herein. NLO activity has been shown to increase upon proceeding from 14-electron complexes to 18-electron complexes,^[7] and from 3d metals to 4d and 5d metals,^[8] thereby focusing subsequent research efforts on 18-valence electron ruthenium and osmium alkynyl complexes. Although they are less efficient in an absolute sense than their osmium congeners, ruthenium-alkynyl complexes that bear two bidentate diphosphines were found to provide a favorable balance of reactivity and NLO efficiency,^[9] so the studies summarized below concentrated on this combination.

Several ruthenium complexes that bear phenylenevinylenecontaining alkynyl ligands have been reported previously,^[9b, 10] but all were prepared by treatment of a (chloro)ruthenium precursor with a preformed E-ene-bearing alkyne. To enhance flexibility in the synthesis of such complexes, in the chemistry described below we explored the possibility of using preformed (4-formylphenylethynyl)ruthenium complexes in Horner-Wadsworth-Emmons coupling with phosphonate esters. One further point guided the synthetic studies. Alkynyl ligands with multiple phenyleneethynylene units have been shown to afford complexes with significant NLO properties,^[9c, 10d, 11] but these extended π systems are often accompanied by reduced solubility of the complexes in common organic solvents. With this in mind, the syntheses targeted bis(alkynyl)ruthenium complexes that contain solubilizing alkyl groups on the terminal aryl ring.

Synthesis of acetylenes

Two new alkynes that bear solubilizing alkyl groups were targeted for eventual attachment at the periphery of the ruthenium-containing OPE stars. Thus, 1,3-diethyl-5-{(4-ethynylphenyl)ethynyl}benzene (5) was prepared by means of successive Sonogashira coupling^[12]/deprotection reactions in four steps (Scheme 1). 2,6-Diethyl-4-iodobenzene (1) was readily obtained by means of a standard diazotization reaction of 2,6-diethyl-4iodoaniline^[13] with sodium nitrite and fluoroboric acid that afforded 1-iodo-3,5-diethylphenyldiazonium fluoroborate, and a subsequent in situ treatment with sodium methoxide in methanol. Sonogashira coupling of 1 with trimethylsilylacetyle-



Scheme 1. Syntheses of acetylenes 5 and 8.



ne using [PdCl₂(PPh₃)₂]/Cul as catalysts afforded 3,5-diethyl-1-(trimethylsilylethynyl)benzene (2) in good yield, desilylation of which under basic conditions gave 1,3-diethyl-5-ethynylbenzene (3). A second Sonogashira coupling that used 1-iodo-4-(trimethylsilylethynyl)benzene^[14] afforded the π -extended derivative 4-(3,5-Et₂C₆H₃C \equiv C)C₆H₄C \equiv CSiMe₃ (4), which was then treated with KOH to give 1-(4-HC \equiv CC₆H₄C \equiv C)-3,5-Et₂C₆H₃ (5) in excellent yield. The new compounds were obtained as oils and characterized using IR, proton and carbon NMR spectroscopy, and El and high-resolution mass spectrometry. A downfield shift in the NMR spectroscopic signal for the proton para to the iodo/ethynyl is seen on proceeding from 1 and 2 ($\delta =$ 6.99 ppm) to **3** and **4** (δ = 7.06 ppm), with a similar downfield shift in the acetylenic proton being seen upon proceeding from **3** (δ = 3.01 ppm) to **5** (δ = 3.16 ppm). The stilbenylacetylene 8 was obtained from a trans-halogenation of (E)-1-(4-tertbutylphenyl)-2-(4-bromophenyl)ethene^[15] with butyl lithium/ iodine that gave the iodo derivative (6) (Scheme 1). Compound 6 was then coupled to trimethylsilylacetylene under Sonogashira conditions to give (E)-1-(4-trimethylsilylethynylphenyl)-2-(4-tert-butylphenyl)ethene (7), with deprotection using potassium hydroxide giving (E)-1-(4-tert-butylphenyl)-2-(4-ethynylphenyl)ethene (8). Compounds 6-8 were characterized by IR, ¹H and ¹³C NMR spectroscopy, and EI and high-resolution ESI mass spectrometry.

Synthesis of {4-(formylphenyl)alkynyl}ruthenium complexes

The obvious complexes from which to attempt on-complex Horner–Wadsworth–Emmons coupling—namely, trans-[Ru(C = CC_6H_4 -4-CHO)CI(L₂)₂] $(L_2 = 1, 2$ -bis(diphenylphosphino)ethane (dppe); 1,1-bis(diphenylphosphino)methane (dppm))—have been reported previously^[9c] and were therefore employed in the present studies, but we also targeted several new ruthenium-alkynyl complexes in which the trans-chloro ligand was replaced with alkynyl ligands to enhance stability. The preparation of the 4-(formylphenyl)alkynyl complexes 9a and 9b employed established procedures for the syntheses of ruthenium-alkynyl complexes, with the treatment of trans-[Ru(4-C \equiv $CC_6H_4R)Cl(dppe)_2$ (R = CHO,^[9c] NO₂^[16]) with the required terminal acetylene and ammonium or sodium hexafluorophosphate under basic conditions affording ruthenium bis(alkynyl) complexes in acceptable yields (Scheme 2). The reactions can be

Scheme 2. Syntheses of (4-formylphenyl)ethynylruthenium complexes 9a-9c. [Ru] = trans-[Ru(κ^2 -dppe)₂] = trans-[Ru(κ^2 -PPh₂CH₂PPh₂)₂].

monitored by NMR spectroscopy, with the phosphorus resonance shifting from around $\delta = 49$ ppm for the mono(alkynyl) complexes to $\delta =$ 54.1 (9a) and 53.7 ppm (9b) upon formation of the bis(alkynyl) derivatives, and the proton spectrum showing an upfield shift of the aldehyde proton from $\delta = 9.99$ to 9.81 ppm on formation of 9a, and a corresponding resonance appearing at $\delta = 9.86$ ppm for complex **9b**. The order of introduction of the alkynyl ligands is crucial, with the formation of 9b by treatment of 4-nitrophenylacetylene^[12] with trans-[Ru(4- $C \equiv CC_6H_4CHO)Cl(dppe)_2$] under similar conditions being attempted without success. The bis(4-formylarylalkynyl) complex **9c** was prepared from *cis*-[RuCl₂(dppe)₂]^[17] by using an excess amount of acetylene in dichloromethane heated under reflux conditions, the product being readily identified by the NMR spectroscopic signals at $\delta = 53.6$ ppm for the equivalent phosphorus centers and at $\delta = 9.87$ ppm for the aldehyde protons.

Ruthenium-alkynyl complex formation can frequently be facilitated by the use of the preformed five-coordinate [RuCl(dppe)₂]⁺ cation.^[18] In the present studies, the five-coordinate complex cation as its hexafluorophosphate salt [RuCl(dppe)₂]PF₆ (10) was conveniently prepared in over 95% yield directly from *cis*-[RuCl₂(dppe)₂]^[17] by using NaPF₆ in dichloromethane. Reaction of 10 with 5 followed by treatment with NEt₃ afforded trans-[Ru(C \equiv CC₆H₄-4-C \equiv CC₆H₃-3,5-Et₂)Cl(dppe)₂] (11 a) in 56% yield (Scheme 3). Formation of the unsymmetrical bis(alkynyl) complex trans-[Ru(C \equiv CC₆H₄-4-CHO)(C \equiv CC₆H₄-4- $C \equiv CC_6H_3$ -3,5-Et₂)(dppe)₂] (9d) was achieved in 46% yield after prolonged stirring of 4-ethynylbenzaldehyde^[19] with **11a**. The transformation from the five-coordinate cationic complex to the mono- and bis-alkynyl complexes was readily confirmed through the ³¹P NMR spectroscopic resonances for the dppe ligands, with the two triplets observed for 10 (δ = 55.9, 83.7 ppm) being replaced by characteristic singlets at $\delta = 49.2$ (11 a) and 53.3 ppm (9 d). A similar sequence of reactions using $[RuCl(dppe)_2]PF_6$ (10) with 8 afforded trans- $[Ru\{C \equiv CC_6H_4-4-(E) CH=CHC_6H_4tBu-4$ Cl(dppe)₂] (11 b), together with trace amounts of the symmetric bis(alkynyl) trans-[Ru{C \equiv CC₆H₄-4-(E)-CH=CHC₆H₄tBu-4}₂(dppe)₂] (12), and then trans-[Ru(C = $CC_6H_4-4-CHO)\{C \equiv CC_6H_4-4-(E)-CH = CHC_6H_4tBu-4\}(dppe)_2\}$ (9e) following the reaction of 11 b with 4-HC \equiv CC₆H₄CHO. All complexes were characterized by IR, ¹H and ¹³C NMR spectroscopy, and EI and high-resolution ESI mass spectrometry. As expected, the remote alkyl ligand variations have little effect on the

¹H NMR spectroscopic aldehyde proton resonance ($\delta = 9.81-$ 9.89 ppm for **9 a-e**).

Extension of the classical stereospecific Horner–Wadsworth– Emmons C=C bond formation reaction to metal-containing (4formylphenyl)ethynyl complexes was then explored as a new route to metal-ethynyl-functionalized stilbenes. Our initial attempt examined the synthesis of the previously reported complex trans-[Ru{C = CC₆H₄-4-(E)-



 $CH=CHC_6H_4-4-NO_2$ $Cl(dppm)_2$ ^[9b] (Scheme 4). *trans*-[Ru(C \equiv CC₆H₄-4-CHO)Cl(dppm)₂]^[9c] was treated with sodium hydride and 4-O₂NC₆H₄CH₂P(O)(OEt)₂ in tetrahydrofuran (THF) for five hours, the latter prepared by means of an Arbuzov reaction of 1-(bromomethyl)-4-nitrobenzene with triethyl phosphite to give the stereospecifically coupled (4-{4nitrophenyl-(E)-ethenyl}phenyl)ethynyl product (11 c) in a greater overall yield than the published procedure, which involves coupling of the preformed (E)-1-(4-nitrophenyl)-2-(4-ethynylphenyl)ethene to the ruthenium center. A similar coupling of the tri-substituted benzylic phosphonate 1,3,5- $C_6H_3(CH_2PO(OEt)_2)_3^{[20]}$ and an excess amount of trans-[Ru(C \equiv CC_6H_4 -4-CHO)Cl(dppe)₂] over 40 hours afforded 13a in acceptable yield, thereby confirming the applicability of this chemistry-on-complex method for the multisite incorporation of E-ene linkages into ruthenium-alkynyl complexes.

Having demonstrated this methodology on known complexes, we then extended it to the formation of new *E*-ene-linkage-containing ruthenium-al-

kynyl cruciform complexes (Scheme 5). Treatment of 1,2,4,5- C_6H_2 {CH₂P(O)(OEt)₂}₄^[20] with the (4-formylphenylethynyl)ruthenium complexes **9a**, **9d**, and **9e** and sodium hydride in 1,2-dimethoxyethane for 24–48 hours afforded the tetra-ruthenium star complexes **14a–c** in good yields. Formation of the bis(alkynyl) complex environments was confirmed by monitoring the ³¹P NMR spectra (appearance of resonances at about δ = 53 ppm).

The methodology was then employed in the construction of a ruthenium-alkynyl-containing stilbenyl dendrimer. The target necessitated the construction of a 1A-3,5-B₂-functionalized arene to serve as the branching point in the dendrimer arms. In the present studies, introduction of a branching point required the use of a 3,5-substituted iodobenzene, for which treatment with trimethylsilylacetylene under Sonogashira conditions followed by removal of the silyl protecting group afforded the required 3,5-substituted "wedge" complexes (Scheme 6). Attempts to form the dppm-ligated ruthenium wedge complex **15a** by treatment of the bis(phosphonate ester) 1-I-C₆H₃-3,5-{CH₂PO(OEt)₂} with *trans*-[Ru(C \equiv CC₆H₄-4-CHO)Cl(dppm)₂] resulted in low yields of the desired product,





Scheme 3. Syntheses of (4-formylphenylethynyl)ruthenium complexes 9d and 9e. $[Ru] = trans-[Ru(\kappa^2 - dppe)_3] = trans-[Ru(\kappa^2 - PPh_3CH_2CH_2PPh_2)_3]$.



Scheme 4. Syntheses of 11 c and 13 a by Horner–Wadsworth–Emmons reactions. $[Ru] = trans-[Ru(\kappa^2-dppe)_2]$.



Scheme 5. Syntheses of ene-linkage-containing ruthenium-alkynyl cruciform complexes 14a-c. [Ru] = trans-[Ru(κ^2 -dppe)₂].

and attempts to optimize the reaction by changing the base (sodium ethoxide or potassium *tert*-butoxide), reaction temperature, and reaction times led to decomposition of the (4-formylphenyl)alkynyl ruthenium complex. In contrast, synthesis of the dppe-ligated ruthenium wedge complex **15b** from **9a** was achieved in 59% yield by using a threefold excess amount of



Scheme 6. Syntheses of ene-linkage-containing "wedge" complexes 17 a and 17 b. $[Ru] = trans-[Ru{\kappa^2 - PPh_2(CH_2)_nPh_2\}_2]$ [n = 1 (dppm), 2 (dppe)].

potassium tert-butoxide in THF heated under reflux conditions, although the same conditions afforded only a small amount of the nitro-substituted analogue 15 c from 9b. In each case, the ¹H NMR spectrum shows the disappearance of the aldehyde peak owing to the (4-formylphenyl)ethynyl ligand of the starting complexes at $\delta = 9.8-10.0$ ppm. In **15 c**, the protons ortho to the nitro substituent resonate downfield of the usual phenyl region at $\delta =$ 7.95 ppm. The disappearance of the resonances owing to the phosphonate ester at $\delta = 25.9$ ppm in the ³¹P NMR spectra is consistent with the formation of the wedge complexes. The IR spectra of these wedge compounds show characteristic alkynyl $v(C \equiv C)$ bands at 2059, 2072, and 2046 cm⁻¹ for **15 a–c**, respectively. The alkynyl v(C \equiv C) stretching frequency remains unchanged in 15a relative to that of the starting complex; in contrast, the loss of the electron-withdrawing aldehyde group in the formation of 15b sees the alkynyl v(C \equiv C) band shift to 2072 from 2046 cm⁻¹ in **9a**. In 15 c, the (4-nitrophenyl)ethynyl ligand affords a band at 2046 cm⁻¹, as is found with **9b**. The ESI mass spectrum of **15a** reveals exchange of chloro ligand with solvent (MeCN), a peak being seen at 2270 mass units ($[M-CI+MeCN]^+$), as well as a peak that corresponds to the loss of chloride at 2230 mass units $([M-Cl]^+)$. The FAB mass spectra of **15b** and **15c** display molecular ions at 2453 and 2543 mass units, respectively, with 15b fragmenting by loss of the phenylethynyl ligand and iodo group, and 15c through loss of the nitro substituent.

Sonogashira coupling of iodo complexes **15 a** and **15 b** with an excess amount of trimethylsilylacetylene afforded ethynyl derivatives **16 a** and **16 b**, respectively, with subsequent deprotection with potassium carbonate affording moderate yields of the desired alkyne-terminated wedge complexes **17 a** and **17 b** (Scheme 6). All wedge complexes were characterized by IR and

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NMR spectroscopy and mass spectrometry. The $\nu(C \equiv C)$ bands in the IR spectra show a shift to lower energy on alkynylation at the iodo substituent at 15 b 2060 (15a. and 2072 cm⁻¹, respectively), with the latter remaining invariant between the trimethylsilyl- and terminal-alkyne complexes (16b 2056 cm⁻¹ and **17 b** at at 2057 cm^{-1}). All show a single phosphorus NMR spectroscopic signal, thus confirming persistence of the trans disposition of the diphosphine ligands ($\delta =$ 53.9-54.4 ppm for the dppe complexes, and $\delta = -5.9 \text{ ppm}$ for the dppm examples). A molecular ion is observed for 16b at 2422 mass units in both the HR ESI and FAB mass spectra, displaying the expected isotope pattern. Fragmentation occurs by the loss of the trimethylsilyl

group or the phenylethynyl ligand. No molecular ion is observed in the ESI mass spectrum of **17 a**, with a fragment owing to the loss of both chloro ligands and the ethynyl group being seen at 2077 mass units. The molecular ion is observed in the FAB mass spectrum of **17 b** (2350 mass units) with the characteristic loss of a phenylethynyl ligand.

The ethynyl-substituted "wedge" complex **17b** was then coupled to the previously reported triruthenium complex **13 a**^[10a,b] to form the nonaruthenium dendrimer **18** (Scheme 7). The reaction was monitored by ³¹P NMR spectroscopy, with the disappearance of the resonance at $\delta = 50.1$ ppm owing to the mono(alkynyl) ruthenium environments at **13a** and replacement with a signal at $\delta = 54.2$ ppm owing to the resulting bis(alkynyl) ruthenium centers of **18**.

Structural studies

The compositions of compounds **9 c**, **9 d**, **9 e**, **11 a**, **12**′, and **12**′′ were confirmed by single-crystal X-ray diffraction studies.^[21] The molecular structures are displayed in Figures S1 (**9 c**), 1 (**9 d**), 2 (**9 e**), S2 (**11 a**), S3 (**12**′), S4, and S5 (**12**′′) in the Supporting Information, and selected bond length and angle data are collected in the relevant figure captions. The bond lengths and angles about the key C/Cl-Ru-C1-C2-C3 units in structures **9 c**, **9 d**, **9 e**, and **11 a** are not unusual (see, for example, Refs. [11], [22]); they fall within the ranges of the literature precedents for arylalkynylbis(diphosphine)ruthenium complexes. For example, the Ru–C1 vectors for the mono(alkynyl)-(chloro)bis(diphosphine)ruthenium complexes (2.037(8) (**11 a**)) and the bis(alkynyl)bis(diphosphine)ruthenium complexes (2.074(4) (**9 c**), 2.070(10), 2.063(9) (**9 d**), 2.065(7), 2.076(6) (**9 e**)) are not unexpected. In contrast, Ru–C1 parameters for **12**′





 $\label{eq:scheme 7. Synthesis of the dendritic complex 18. [Ru] = \textit{trans-}[Ru(\kappa^2-dppe)_2] = \textit{trans-}[Ru(\kappa^2-PPh_2CH_2CH_2PPh_2)_2].$

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Compound 11 a, which contains solubilizing ethyl groups on the terminal phenyl ring, shows a fully reversible oxidation process at 0.51 V, which is somewhat lower than that required to oxidize its non-alkylated analogue **11 d** (0.55 V),^[23] and which is presumably due to the slight electron-releasing effect of the alkyl groups. Replacement of the yne linkage furthest from the metal center with an E-ene-linked tert-butyl-substituted phenyl group, in proceeding from 11d to 11b (0.56 V), has little effect (Figures 1 and 2) on the potential for the oxidation process. The similar electronic environment of the metal atom in these related complexes has



Figure 1. Molecular structure of *trans*-[Ru(C ≡ CC₆H₄-4-CHO)(C ≡ CC₆H₄-4-C ≡ CC₆H₃-3,5-Et₂)(dppe)₂] (**9 d**) with thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C1 2.070(10), Ru1–C21 2.063(9), Ru1–P1 2.373(2), Ru1–P2 2.353(2), Ru1–P3 2.372(2), Ru1–P4 2.357(2); C1-Ru1-C21 178.9(4), C1-Ru1-P1 80.5(3), C1-Ru1-P2 89.5(2), C1-Ru1-P3 98.7(3), C1-Ru1-P4 90.7(2), C21-Ru1-P1 98.5(3), C21-Ru1-P2 90.8(2), C21-Ru1-P3 82.3(3), C21-Ru1-P4 89.0(2), P1-Ru1-P2 81.63(8), P1-Ru1-P3 179.21(9), P1-Ru1-P4 98.50(8), P2-Ru1-P3 98.45(8), P2-Ru1-P4 179.80(10), P3-Ru1-P4 81.43(8).

(2.108(5)) and 12'' (2.149(4)) are both very long, which is possibly an artefact of the substitutional disorder in these specific structural studies.

Cyclic voltammetry studies

Cyclic voltammetry (CV) data for the complexes prepared in these studies are collected in Table 1. All complexes show an oxidation process between 0.48 and 0.76 V that is assigned to the Ru^{II/III} oxidation. Ratios for the forward and reverse current peaks range from 0.8 to 1.0, and peak separations are equivalent to (or in some cases up to 0.03 V more than) ΔE for the ferrocene/ferrocenium internal standard, thus indicating that these processes are fully or quasi-reversible. The potentials for the oxidation processes vary in a fairly systematic fashion.



Figure 2. Molecular structure of *trans*-[Ru(C ≡ CC₆H₄-4-CHO){C ≡ CC₆H₄-4-(*E*)-CH=CHC₆H₄-4-*t*Bu}(dppe)₂] (**9 e**), with thermal ellipsoids set at the 30% probability level. Hydrogen atoms and lattice dichloromethane molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C1 2.065(7), Ru1–C21 2.076(6), Ru1–P1 2.3667(15), Ru1–P2 2.3596(15), Ru1–P3 2.3532(15), Ru1–P4 2.3659(15); C1-Ru1-C21 179.7(3), C1-Ru1-P1 98.28(17), C1-Ru1-P2 91.81(17), C1-Ru1-P3 87.83(17), C1-Ru1-P4 81.30(17), C21-Ru1-P1 81.44(17), C21-Ru1-P2 88.33(17), C21-Ru1-P3 92.03(16), C21-Ru1-P4 98.98(17), P1-Ru1-P2 82.56(5), P1-Ru1-P3 97.66(5), P1-Ru1-P4 179.58(6), P2-Ru1-P3 179.60(7), P2-Ru1-P4 97.42(5), P3-Ru1-P4 82.36(5).

been noted previously, with structural changes occurring remotely from the metal center having only minor effects on the potentials for the oxidation processes.^[10d] Replacement of the chloro ligand by a 4-formylphenylethynyl group to form the unsymmetrical bis(alkynyl) complexes *trans*-[Ru($C \equiv CC_6H_4$ -4-CHO)($C \equiv CC_6H_4$ -4-R)(dppe)_2] (9) results in an increase in potentials for the metal-centered oxidation processes. For the (4-formylphenylethynyl)(phenylethynyl) examples **9a**-**9c**, *E*_{1/2} increases with increasing electron-withdrawing character of the phenylethynyl substituent, with R=H (**9a**, 0.61 V) < R=CHO (**9c**, 0.72 V) < R=NO₂ (**9b**, 0.75 V), as expected. Extension of the π bridge of **9a** (by means of a second phenylethynyl unit, R=C $\equiv CC_6H_3$ -3,5-Et₂, or a stilbenyl group R=(*E*)-CH=CHC₆H₄-4-*t*Bu) results in little change in *E*_{1/2}.



| Table 1. Cyclic voltammetric and linear optical data. ^[a] | | | | | | | | |
|---|---|--|--|--|--|--|--|--|
| Complex, ^[b] R | $E_{1/2}^{[c]}$ [V] [ΔE , (i_{pc}/i_{pa})] | $λ_{\rm max}$ [nm] (ε [10 ⁴ μ ⁻¹ cm ⁻¹]) | | | | | | |
| trans-[Ru](C \equiv CC ₆ H ₄ -4-CHO)(C \equiv CC ₆ H ₄ -4-R) | | | | | | | | |
| 9a, H | 0.61 [0.07, 0.9] | 418 (2.3), 313 (1.9) | | | | | | |
| 9 b , NO ₂ | 0.75 [0.07, 0.8] | 463 (2.3), 411 (sh, 2.0) | | | | | | |
| 9 с , СНО | CHO 0.72 [0.07, 0.8] | | | | | | | |
| 9 d , $C \equiv CC_6H_3$ -3,5-Et ₂ | 0.63 [0.07, 1] | 414 (5.2) | | | | | | |
| 9e , (<i>E</i>)-CH=CHC ₆ H ₄ -4- <i>t</i> Bu | 0.58 [0.07, 1] | 420 (6.1) | | | | | | |
| trans-[Ru](C \equiv CC ₆ H ₄ -4-R)Cl | trans-[Ru](C \equiv CC _s H _a -4-R)Cl | | | | | | | |
| 11 a , $C \equiv CC_6H_3$ -3,5-Et ₂ | 0.51 [0.09, 1] | 380 (2.9) | | | | | | |
| 11 b , (<i>E</i>)-CH = CHC ₆ H₄-4- <i>t</i> Bu | 0.56 [0.07, 1] | 400 (4.1) | | | | | | |
| 11 c , (<i>E</i>)-CH=CHC ₆ H ₄ -4-NO ₂ ^[e] | 0.56 [1] ^[9c] | 489 (2.6) ^{[d][9c]} | | | | | | |
| 1,3,5-{ <i>trans</i> -(R)[Ru](C \equiv CC ₆ H ₄ -(E)-4-CH=CH)] ₃ C ₆ H ₃ ^[10b] | | | | | | | | |
| 13 a , Cl | 0.51 [0.9] | 426 (8.7) ^[d] | | | | | | |
| 13 b , C \equiv CPh | 0.49 [1] | 421 (13.0) ^[d] | | | | | | |
| 1,2,4,5-{ $trans$ -(RC ₆ H ₄ C \equiv C)[Ru]{C \equiv CC ₆ H ₄ -4-(<i>E</i>)-CH \equiv CH} ₄ C ₆ H ₂ | | | | | | | | |
| 14a, H | 0.54 [0.11, 1] | 421 (11.5), 325 (11.5) | | | | | | |
| 14b , $C \equiv CC_6H_3$ -3,5-Et ₂ | 0.55 [0.07, 1] | 395 (20.0), 297 (14.6) | | | | | | |
| 14 c , (<i>E</i>)-CH=CHC ₆ H ₄ -4- <i>t</i> Bu | 14 c, (<i>E</i>)-CH=CHC ₆ H ₄ -4- <i>t</i> Bu 0.51 [0.09, 1] | | | | | | | |
| 1-I-3,5-{ <i>trans</i> -(R)[Ru](C ≡ CC ₆ H ₄ -4-(<i>E</i>)-CH=CH)} ₂ C ₆ H ₃ | | | | | | | | |
| 15 a , Cl ^[e] | 0.62 [0.10, 1] | 406 | | | | | | |
| 15 b , C≡CPh | 0.53 [0.09, 1] | 425 (6.6), 320 (6.7). | | | | | | |
| 15 c , $C \equiv CC_6H_4$ -4-NO ₂ | 0.63 [0.06, 1] | 481 (3.2), 417 (3.7), 312 (3.9) | | | | | | |
| $1-Me_3SiC \equiv C-3, 5-\{trans-(R)[Ru](C \equiv CC_6H_4-4-(E)-CH=CH)\}_5C_6H_3$ | | | | | | | | |
| 16 a , Cl ^[e] | | 411 (6.8) | | | | | | |
| 16 b , C \equiv CPh | 0.52 [0.16, 0.9] | 421 (7.2), 319 (7.5) | | | | | | |
| $1-HC \equiv C-3,5-\{trans-(R)[Ru](C \equiv CC_{c}H_{a}-4-(E)-CH=CH)\}_{2}C_{c}H_{3}$ | | | | | | | | |
| 17 a , Cl ^[e] | 0.59 [0.11, 0.8] | 402, 317 | | | | | | |
| 17 b, C≡CPh | 0.56 [0.15, 0.8] | 417, 320 | | | | | | |
| 1,3,5-{ <i>trans</i> -(3,5-R ₂ C ₆ H ₃ C \equiv C)[Ru | $[C \equiv CC_6H_4-4-(E)-CH=CH]]$ | $_{3}C_{6}H_{3}$ | | | | | | |
| 18 , {(<i>E</i>)-CH=CHC ₆ H ₄ -4- C = C}[Ru](C = CPh) | 0.52 [0.14, 0.8] | 417, 322 | | | | | | |
| [a] Measured in CH ₂ Cl ₂ . [b] [Ru] = trans-[Ru(dppe) ₂]. [c] Pt disc working, Pt wire auxili- | | | | | | | | |

ary, and Ag/AgCl reference electrodes; ferrocene/ferrocenium redox couple at 0.56 V (i_{pc}/i_{pa} 0.9 -1, $\Delta E_p = 0.07-0.09$ V). [d] Measured in THF. [e] [Ru] = trans-[Ru(dppm)_2].

Potentials of the oxidation processes for the cruciform complexes 1,2,4,5-(*trans*-[(dppe)₂($RC_6H_4C \equiv C$) $Ru\{C \equiv CC_6H_4-4-(E)-CH = CC_6H_4-4-($ CH}])₄C₆H₂ (14) are all found in the narrow range 0.51–0.55 V, with the diethyl-substituted yne-linked complex ($R = C \equiv CC_6H_3$ -3,5-Et₂, 14b, 0.55 V) again requiring a higher potential than the *tert*-butyl-substituted ene-linked example $(R = (E)-CH = CHC_6H_4$ -4-tBu, 14c, 0.51 V). The "wedge" complexes 15–17 are oxidized at comparable potentials, with only a slight variation observed on moving from the 1-iodo-substituted core 15b (0.53 V) through the 1-trimethylsilylethynyl- (16b, 0.52 V) and ethynyl-(17 b, 0.56 V) analogues, and a slight decrease in the reversibility of the process at each step. Substitution with the electronwithdrawing nitro group (15 c, 0.63 V) affords a shift to higher potentials, as expected. The chloro-terminated dppm-containing wedge complexes 15a (0.62 V) and 17a (0.59 V) require a slightly higher potential for metal-centered oxidation than their phenylethynyl-containing analogues 15b and 17b.

The general invariance in the potentials for the metal-localized oxidation process in these complexes reflects the similar chemical environment of the metal atom in each case. The single oxidation process observed in the sweep range (0 to 1.6 V) is due to the symmetry of the molecules and the lack of interaction between the metal centers. The dendritic complex **18** also shows a single oxidation process (0.52 V), which is in agreement with the pseudo-equivalent metal environments seen in the ³¹P NMR spectroscopic data. Complexes that contain the nitro group also show an irreversible nitro-centered reduction process at -1.14 (**9b**), -0.98 (**11 c**), and -1.33 V (**15 c**).

Linear optical studies

The UV/Vis-NIR spectra for all complexes (Table 1) show characteristic bands at lowest energy (absorption maxima in the range 380-490 nm (26300-20400 cm⁻¹)), assigned from DFT calculations on related ruthenium-alkynyl complexes as being due to metal-to-ligand charge transfer (MLCT), specifically Ru $d_{vz} \rightarrow C_2 R$ in nature.^[24] Nitro-substituted complexes are transparent at frequencies below 22000 cm⁻¹, whereas all other complexes are transparent below 26000 cm⁻¹. Alkyl introduction at the aryl ring of *trans*-[Ru($C \equiv CC_6H_4$ -4- $C \equiv$ distal CPh)Cl(dppe)₂] $(\lambda_{max} 25800 \text{ cm}^{-1})^{[22]}$ to give **11 a** $(26300 \text{ cm}^{-1}, +500 \text{ cm}^{-1})$ results in a slight hypsochromic shift in the MLCT band, whereas replacement of the -yne linkage with an E-ene group and introduction of a tert-butyl group to give 11b (25000 cm⁻¹, -800 cm⁻¹) produces a bathochromic shift. The linear optical spectrum of the nitro-substituted *E*-ene-linked complex 11 c (20500 cm⁻¹) contains the lowest-energy transition, as expected.^[9c]

Substitution of the chloro ligand with a phenylethynyl unit upon proceeding from *trans*-[Ru(C \equiv CC₆H₄-4-CHO)Cl(dppe)₂] ($\lambda_{max} = 24200 \text{ cm}^{-1})^{[9c]}$ to *trans*-[Ru(C \equiv CC₆H₄-4-CHO)(C \equiv CC₆H₄-4-R)(dppe)₂]

(9a-c) results in a decrease in the energy of the MLCT, with the electron-withdrawing nature of the phenylethynyl substituent determining the size of the shift (R=H, 9a; 23900, -300 cm^{-1}) < CHO (9c; 23500, -700 cm^{-1}) < $R=NO_2$ (9b; 21600, -2600 cm^{-1}). Similarly, a redshift is observed on moving from (chloro)ruthenium–alkynyl complexes 11a and 11b to the corresponding (4-formylphenylethynyl) complexes 9d (24200, -2100 cm^{-1}) and 9e (23800, -1200 cm^{-1}).

Compared to the monometallic complexes (9 and 11), the cruciform complexes 1,2,4,5-(*trans*-[(dppe)₂(RC₆H₄C \equiv C)Ru{C \equiv CC₆H₄-4-(*E*)-CH=CH]])₄C₆H₂ (14) show a significant increase in the extinction coefficient of the MLCT band, an effect noted previously with trisubstituted benzene-cored analogues such as the star complex 1,3,5-{*trans*-[(dppe)₂(PhC \equiv C)Ru(C \equiv CC₆H₄-4-C \equiv C)]]₃C₆H₃ (19 b, $\varepsilon = 11.6 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1})$.^[25] In the present studies, the increase in absorbance at λ_{max} for 14b (R=C \equiv CC₆H₃-3,5-Et₂, $\varepsilon = 20.0 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1})$ and 14c (R=(*E*)-CH= CHC₆H₄-4-tBu, 21.6 $\times 10^4 \text{ m}^{-1} \text{ cm}^{-1})$ is approximately twofold greater than that of 14a (R=H, 11.5 $\times 10^4 \text{ m}^{-1} \text{ cm}^{-1})$, which con-



tains the shorter terminal phenylethynyl ligand, and twofold greater than the trimetallic complex **19b**. Transition energies are lower for the cruciform star complexes **14b** (25 300 cm⁻¹) and **14c** (22 700 cm⁻¹) than for the related mononuclear chloro complexes **11a** (26 300 cm⁻¹) and **11b** (25 000 cm⁻¹) and, again, the ene-linked complex **14b** shows the lowest-energy MLCT band. Relative to the trimetallic star complexes, that is, the yne-linked **19b** (24 300 cm⁻¹) and the *E*-ene-linked **13b** (23 800 cm⁻¹),^[10b] the cruciform star complexes show a higher-energy MLCT band.

Spectroelectrochemical studies

In situ oxidation of metal-containing complexes by using an optically transparent thin-layer electrochemical (OTTLE) cell offers a convenient method for accessing spectroscopic data of the oxidized metal complexes and has been employed widely with ruthenium-alkynyl complexes.[10d, 23-24, 26] Application of potentials slightly higher than indicated by the cyclic voltammetric data to dichloromethane solutions of the star complexes 14a-c resulted in reversible conversion to the tetracationic (formally Ru^{III}_{4}) complexes [**14a**–**c**]⁴⁺; isosbestic points are observed in the transformations in each case (Figure 3, Figure S6 in the Supporting Information), and comparative UV/ Vis-NIR data have been collected in Table 2. All complexes show the emergence of low-energy NIR absorption bands assigned to alkynyl-to-Ru^{III} charge transfer,^[24b] with the band for **14b** (7600 cm⁻¹), which contains the extended π -delocalizable ligand, occurring at a slightly lower energy than that of 14a (7900 cm⁻¹); the *E*-ene-linked complex **14c** shows the lowestenergy band (7300 cm⁻¹). These bands are significantly redshifted relative to those of the bis(alkynyl) complex trications trans-[Ru(C \equiv CPh)(C \equiv CC₆H₄-4-C \equiv CPh)(dppe)₂]⁺

 $(8400 \text{ cm}^{-1})^{[24a]}$ and $1,3,5-\{trans-[(dppe)_2(PhC \equiv C)Ru(C \equiv CC_6H_4-4-C \equiv C)\}_3C_6H_3]^{3+}$ (8400 cm⁻¹).^[24b] This large bathochromic effect is likely due to the *E*-ene-linked cruciform nature of complexes **14**, rather than the increase in the number of metal centers, because the tri-substituted nonaruthenium nonacation $[1,3,5-\{trans-[3,5-\{trans-[(dppe)_2(PhC \equiv C)Ru(C \equiv CC_6H_4-4-C \equiv C)Ru(C \equiv CC_6H_4-4-C)Ru(C \equiv C)Ru(C \equiv CC_6H_4-4-C)Ru(C \equiv C)Ru(C \equiv C$

C)])₂C₆H₃(C = C)(dppe)₂Ru(C = CC₆H₄-4-C = C)]]₃C₆H₃]⁹⁺ shows the corresponding low-energy band at 8400 cm⁻¹ (measured in THF, $\varepsilon \approx 8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).^[24b] Vibronic progressions evident in the spectra of [**14a-c**]⁴⁺ at approximately 9000 cm⁻¹ can be attributed to ν (C = C), as noted previously in similar com-



Figure 3. UV/Vis-NIR spectral progressions during oxidation of cruciform complex 1,2,4,5-[*trans*-(dppe)₂(RC₆H₄C \equiv C)Ru{C \equiv CC₆H₄-4-(*E*)-CH \equiv CH]₄C₆H₂ (R = H, 14a) (top), and overlay of the spectra for [14a–c]⁴⁺ (R = C \equiv CC₆H₃-3,5-Et₂ (14b), R = (*E*)-CH \equiv CH \cong CHC₆H₄-4-*t*Bu (14c)) (bottom) in CH₂Cl₂.

plexes.^[24a] The absorption intensities for the lowest-energy bands for the cruciform star complexes $[14a-c]^{4+}$ are uniformly higher than those observed for the related trimetallic star complexes (ε of about 12 versus 8 (×10⁴ m⁻¹ cm⁻¹)), with the *E*ene-linked complex 14c showing the highest ε value.

Cubic hyperpolarizability studies

The third-order optical nonlinearities of the cruciform, wedge, and dendritic molecules 14a-c, 15a-c, 16a, 16b, 17a, 17b,

| Complex, R | $\lambda \; [\text{cm}^{-1}] \; (arepsilon)^{[\text{b}]}$ | | $\lambda \ [\text{cm}^{-1}] \ (\varepsilon)^{ b }$ |
|--|---|------------------------------|--|
| 14a, H | 22 200 (11.5), 30 700 (11.2) | $[14a]^{4+}$ | 7900 (11.6), 16 600 (2.6, sh), 20 900 (4.2), 26 000 (7.9), 38 300 (19.7) |
| 14b , $C \equiv CC_6H_3$ -3,5-Et ₂ | 24 900 (20.0), 32 100 (13.4, sh), 37 000 (15.8, sh) | [14 b] ⁴⁺ | 7600 (11.9), 16 300 (2.3, sh), 20 800 (7.3), 21 900 (8.1), 25 500 (11.1), 32 100 (14.9, sh), 38 000 (20.3) |
| 14 c , (<i>E</i>)-CH=CHC ₆ H₄-4- <i>t</i> Bu | 31 600 (14.4), 23 700 (21.7) | $[14c]^{4+}$ | 7400 (18.1), 9800 (3.3, sh), 16300 (2.9, sh), 20000 (9.2), 28300 (16.3) 30000 (14.6, sh), 38000 (19.9) |
| [a] CH ₂ Cl ₂ . [b] 10 ⁴ м ⁻¹ cm ⁻¹ . | | | |

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and **18** were assessed by the Z-scan technique^[27] at a benchmark wavelength of 750 nm, which was chosen because it corresponds to a region of optical transparency for all of these complexes (reducing the effects of resonance enhancement), and also because of its technological importance (it corresponds to a wavelength region of enhanced transparency of biological materials such as tissue); an NLO performance comparison in this wavelength region is therefore of interest. Measurements were carried out in dichloromethane except for those of **15b** and **16b**, which were measured in THF for solubility reasons; the resultant data are collected in Table 3. At this wavelength, all new complexes exhibit negative nonlinear refraction and positive nonlinear absorption, which is consistent with the presence of two-photon resonance effects. The real components of the cubic nonlinearities in particular are characterized in most cases by large error margins, thus rendering development of structure–property relationships problematic. Nevertheless, some comparisons might usefully be made. If we focus on the wedge complexes, replacing the bidentate diphosphine co-ligand dppm by dppe at the ruthenium centers (proceeding from **15a** to **15b** or **17a** to **17b**) results in no change in the nonlinearity. The addition of the electron-withdrawing nitro substituent to the arylalkynyl ligand (proceeding from **15b** to **15c**) results in a twofold increase in the nonlinearity. While being mindful of variations that result from a difference in measurement wavelength (750 versus 800 nm, illustrated by data for **9d–e** and **14a–c** at both wavelengths (Table S2 in the Supporting Information)), the nonlinearity $|\gamma|$ varies little between the two classes of wedge complex (with yne- or *E*-ene-containing π bridges). As expected for





a relatively subtle change at these large molecules, replacing the iodo substituent with either $C \equiv CSiMe_3$ or $C \equiv CH$ does not significantly affect the nonlinearity (**15 b**, **16 b**, **17 b**).

If we focus on the dendrimer complexes, proceeding from the zero-generation yne-linked dendrimers (19a, 19b) to the comparable E-ene-linked dendrimers (13a, 13b) results in a marked increase in the nonlinear response. Although increasing the dendrimer generation in moving from the zero- (19b) to first-generation yne-linked dendrimer (20) results in an approximately tenfold increase in the nonlinearity, this effect is not seen with E-ene-linked dendrimers (proceeding from 13b to 18); in fact, the nonlinearity decreases by a factor of two. This might be caused by an increasing loss of coplanarity in moving to 18, or by the wavelength dependence of the response (although the near coincidence of the linear optical absorption maxima suggests that this might not be a critical factor). Finally, the observed nonlinearities of the cruciform complexes at this benchmark wavelength are the largest from the present study. The overall $|\gamma|$ values are dominated by very large $\gamma_{\rm real}$ contributions: Whereas the energies of transitions for complexes across the present study are similar, it is noteworthy that the extinction coefficients for the lowestenergy one-photon absorption bands for 14a-c are much larger than those for the other complexes, and this might suggest significantly enhanced resonance effects.

The impressive NLO coefficients at the aforementioned benchmark wavelengths prompted a more detailed study of selected examples over the relatively broad spectral range 500-1600 nm, with a particular focus on the cruciform star complexes. Representative σ_2 and γ spectral dependences (those for 14a) are shown in Figure 4, with the remainder being shown in Figures S7 (9d), S8 (9e), S9 (14b), S10 (14c), and S11 (18) in the Supporting Information, whereas maximal data are collected in Table S3 of the Supporting Information. All complexes studied are multiphoton absorbers and show positive imaginary components of third-order nonlinearity in the range 500–1500 nm. These complexes exhibit large apparent two-photon absorption (2PA) cross-sections at short wavelengths (500/520 nm), which is probably a combination of 2PA and excited-state absorption/reverse saturable absorption (ESA/RSA) owing to the measurements being undertaken at the low-energy end of the linear absorption; the reported 2PA values at such wavelengths should therefore be considered with caution. The monometallic compounds (9d and 9e) have a common 2PA peak at 640 nm, with the ethenyl-linked 9e having a larger cross-section. The 2PA maxima are at lower energies for 9e than 9d in the range 740-900 nm, which is consistent with the lower-energy MLCT in the linear absorption spectrum (to which these 2PA maxima are correlated).

The monometallic compounds, **9d** and **9e**, are "building blocks" for the formation of **14b** and **14c**, respectively. Addition of the monomer **9d/9e** to the core to afford **14b/14c** appreciably changes the 2PA spectrum; 2PA maxima are shifted to lower energy by around 20–40 nm, and the maximal values of the cross-section at these wavelengths increase seven- to tenfold. A strong response at around 1150 nm also appears, which correlates closely with three times the wavelength of

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Figure 4. Top: Plot of σ_2 (blue) for **14a** overlaid on the UV-visible spectrum (black), and including plots of the UV-visible spectrum at twice (red) and three times (green) the wavelength. Bottom: The real (red) and imaginary (black) parts of the third-order hyperpolarizability of **14a**.

the lowest-energy linear absorption band, and probably arises from three-photon absorption. This low-energy nonlinear absorption band is at a shorter wavelength than that observed for the 1,3,5-substituted analogue **18** (1300 nm), which is possibly a consequence of changing the core geometry of these star complexes. Attempts to 'tune' the NLO properties with alteration of the capping groups appeared to give negligible changes in the values of the NLO parameters (while being mindful of the associated errors), although the longer-peripheral π -system-containing **14b** and **14c** have stronger nonlinear absorptive properties at the longer wavelength maxima than the phenyl-capped complex **14a** does. This behavior might indicate that the NLO properties are overwhelmingly influenced by the core geometry rather than the peripheral substitution.

Conclusion

The studies described herein have demonstrated useful outcomes from both the synthetic and materials perspectives. The "chemistry-on-complex" stereospecific formation of *E*-configured stilbene groups by Horner–Wadsworth–Emmons coupling of metal–ethynyl-functionalized benzaldehydes employed in



this study has been shown to afford facile access to a range of "star" complexes, with both 1,3,5-trisubstituted arene and 1,2,4,5-tetrasubstituted arene (cruciform) geometries. Formyl substituents on arenes are ubiquitous in organic chemistry and undergo a broad range of reactions and consequent functionalization; the scope for analogous "chemistry-on-complex" transformation of metal–ethynyl-derivatized benzaldehydes remains to be explored, but the present studies have provided a glimpse of the potential.

Access to the range of ruthenium-alkynyl-functionalized oligo(phenylenevinylene) stars, which the present study has afforded, has permitted an internal comparison of their properties across the complexes described here as well as an external comparison to those of the extant ruthenium-alkynyl-functionalized oligo(phenyleneethynylene) analogues, thereby allowing several structure-property outcomes to be highlighted. Alkyl substituents were employed in the present study to ensure sufficient solubility, but their electron-releasing nature is reflected in increased ease of oxidation and a blueshift in optical absorption maximum. Incorporation of nitro substituents increases the potentials of the metal-centered oxidation processes, redshifts the optical absorption maximum, and increases the maximal value of the cubic NLO properties. Progression from 1,3,5-trisubstituted arene core to the 1,2,4,5-tetrasubstituted arene (cruciform) core results in a substantial increase in linear optical absorption maximum extinction coefficient, a decrease in energy of the LMCT band in the spectrum of the oxidized form, and a significant increase in maximal values of the nonlinear absorption. Finally, replacing the yne linkages from the extant complexes with the E-ene linkages in the present study results in a blueshift in optical absorption maximum, a redshift in the LMCT band in the spectrum of the oxidized form, and an increase in nonlinear absorption cross-section; thus, the OPV-based star complexes from the present study exhibit enhanced nonlinearities with a slight gain in optical transparency.

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