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Inorganica Chimica Acta 350 (2003) 62-76



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Organometallic complexes for nonlinear optics. Part 29. Quadratic and cubic hyperpolarizabilities of stilbenylethynyl–gold and -ruthenium complexes☆

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Received 29 April 2002; accepted 3 June 2002

Dedicated to Professor Pierre Braunstein, in recognition of his outstanding contributions to organometallic chemistry.

Abstract

The compounds (*E*)-4-XC=CC₆H₄CH=CHPh [X = SiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₃ [X = I (3), C=CSiMe₃ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₄ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄CH=CH}₃C₆H₄ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄ (1), H (2)], 1,3,5-{(*E*)-4-XC₆H₄ (1), H (2)], 1,3,5-{(E})-4-XC₆H₄ (1), 1 (4), $C \equiv CH$ (5)], $[Au_{(E)-4-C} \equiv CC_{6}H_{4}CH = CHPh_{(L)}]$ [L = PPh₃ (6), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe₃ (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(L)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh₃ (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{(4-C)}]$ [L = PPh_3 (8), PMe_3 (7)], $[Au_{(4-C)} \equiv CC_{6}H_{4}C \equiv CPh_{4}C \equiv CPh_{4}C \equiv CPh_{4}C \equiv CPh_$ (9)], 1,3,5-[(Ph₃P)Au{(E)-4-C=CC₆H₄CH=CH}]₃C₆H₃ (10), trans-[Ru{(E)-4-C=CHC₆H₄CH=CHPh}Cl(dppm)₂]PF₆ (11), trans- $[Ru\{(E)-4-C=CC_{6}H_{4}CH=CHPh\}Cl(L_{2})_{2}]$ [L₂ = dppm (12), dppe (13)], $[1,3,5-(trans-f(dppm)_{2}C]Ru\{(E)-4-C=CHC_{6}H_{4}CH=CHC_{6}H_{6}CHC_{6}H_{$ $CH_{1} = CC_{6} + (L_{2}) + C = CC_{6} + (L_{2}) + (L$ $[(dppe)_2(PhC \equiv C)Ru\{(E)-4-C \equiv CC_6H_4CH = CH\}]_3C_6H_3$ (17) have been prepared (and the identity of 6 confirmed by a single-crystal X-ray diffraction study), and their electrochemical (Ru complexes) and nonlinear optical (NLO) properties assessed. The ruthenium complexes display reversible (12, 13, 15–17) or nonreversible (11, 14) processes attributable to Ru-centered oxidation, at potentials similar to those of previously-investigated monoruthenium alkynyl or vinylidene complexes. No evidence for intermetallic electronic communication in 14-17 is observed. Quadratic nonlinearities at 1064 and 800 nm for the octopolar stilbenyl-ruthenium complexes 14, 15 are large for compounds without strongly accepting substituents. Cubic molecular hyperpolarizabilities at 800 nm for the organic compounds and gold complexes are low. Cubic nonlinearities $|\gamma|_{800}$ and two-photon absorption (TPA) cross-sections σ_2 for the ruthenium complexes increase on proceeding from linear analogues 12, 13 to octopolar complexes 15, 16; the latter and 17 possess some of the largest $|\gamma|_{800}$ and σ_2 values for organometallics thus far. Cubic nonlinearities Im $(\chi^{(3)})/N$ for 13, 16, and 17 from the first application of electroabsorption (EA) spectroscopy to organometallics are also large, scaling with the number of metal atoms.

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Keywords: Ruthenium; Gold; Hyperpolarizability; Acetylide; Electrochemistry; Nonlinear optics

1. Introduction

[☆] Part 28: see Ref. [1].

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The nonlinear optical (NLO) properties of inorganic complexes and, particularly, organometallics have attracted significant interest [2–5]. The vast majority of complexes for which NLO properties have been measured have a donor-bridge-acceptor composition.

0020-1693/02/\$ - see front matter \odot 2002 Elsevier Science B.V. All rights reserved. doi:10.1016/S0020-1693(02)01497-4

However, attention has recently turned to replacing the classical one-dimensional dipolar composition with a two-dimensional or three-dimensional octopolar arrangement. This is because proceeding from dipolar to octopolar geometries is a possible means of overcoming the NLO efficiency/optical transparency trade-off and of disfavoring centrosymmetric packing in the solidstate, both of which have hampered the efficiency of quadratic NLO materials. We have previously reported the syntheses and NLO properties of octopolar and dendritic alkynylruthenium complexes [6-8]. These examples were constructed using phenylethynyl 'spacer' units, with several complexes having very large twophoton absorption (TPA) cross-sections σ_2 [TPA is an NLO process related to the imaginary component of the third-order nonlinearity. TPA materials have excited significant recent interest for applications in multiphoton microscopy, optical limiting, and optical data storage]. However, the E-configured alkene linker has been shown to afford more efficient organic NLO materials than those linked by alkyne groups [9]. We became interested in preparing ene-linked analogues of our yne-linked octopolar complexes. We report the syntheses of novel two-dimensionally π -delocalized octopolar alkynyl-gold and -ruthenium complexes containing E-phenylethenyl spacers, molecular quadratic nonlinearities for the ruthenium examples at both 1064 and 800 nm employing ns and, in some instances, fs hyper-Rayleigh scattering (HRS), respectively, molecular cubic nonlinearities $|\gamma|$ (including real (γ_{real}) and imaginary (γ_{imag}) components) and TPA cross-sections at 800 nm evaluated by fs Z-scan, and third-order NLO susceptibilities $\chi^{(3)}$ of some of the ruthenium complexes at approximately 450 nm determined by electroabsorption (EA) spectroscopy. Some of these results have been reported in a preliminary fashion [1].

2. Experimental

2.1. General remarks

All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques unless otherwise stated. Reaction solvents dichloromethane and triethylamine were dried by distilling over calcium hydride, and diethyl ether and tetrahydrofuran were dried by distilling over sodium/benzophenone; other solvents were used as received. Petrol refers to a fraction of boiling range 60–80 °C. Chromatography was on silica gel (230–400 mesh ASTM) or basic ungraded alumina.

The following reagents were prepared by the literature procedures: cis-[RuCl₂(dppm)₂] and cis-[RuCl₂(dppe)₂] [10], 4-IC₆H₄C=CSiMe₃ [11], 1,3,5-(HC=C)₃C₆H₃ [12], (*E*)-4-IC₆H₄CH=CHPh [13], 4-HC=CC₆H₄C=CPh [14],

[AuCl(PPh₃)] [15], [AuCl(PMe₃)] 1,3,5-[16], $C_{6}H_{3}\{CH_{2}P(O)(OEt)_{2}\}_{3}$ NH₄PF₆, NaOMe, [17]. Me₃SiC=CH, PhC=CH, NBu₄ⁿF, CuI (Aldrich), [PdCl₂(PPh₃)₂] (PMO), and 4-IC₆H₄CHO (Karl Industries) were used as received. $[Pd(PPh_3)_4]$ was a gift from Dr. B.L. Flynn. A synthesis of (E)-HC=CC₆H₄CH= CHPh (2) was reported while the current studies were in progress [18].

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 (SI MS) 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 Research School of Chemistry, Australian National University; peaks are reported as m/z (assignment, relative intensity). Microanalyses were carried out at the Research School of Chemistry, Australian National University. Infrared spectra were recorded either as 1% KBr discs or dichloromethane solutions using a Perkin-Elmer System 2000 FT IR. ¹H and ³¹P NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are referenced to residual chloroform (7.24 ppm) or external 85% H₃PO₄ (0.0 ppm), respectively. The assignments follow the numbering schemes shown in Fig. 1. UV-Vis spectra of solutions were recorded in tetrahydrofuran in 1 cm quartz cells using a Cary 5 spectrophotometer. Electrochemical measurements were recorded using a MacLab 400 interface and MacLab potentiostat from ADInstruments. The supporting electrolyte was 0.1 M (NBu₄)PF₆ in distilled, deoxygenated CH₂Cl₂. Solutions containing approximately 1×10^{-3} M complex were maintained under argon. Measurements were carried out at room temperature (r.t.) using platinum disc working-. Pt wire auxiliary- and Ag/AgCl reference-electrodes, such that the ferrocene-ferrocenium redox couple was located at 0.56 V (peak separation around 0.09 V). Scan rates were typically 100 mV s⁻¹.

2.2. (E)-4- $Me_3SiC \equiv CC_6H_4CH = CHPh$ (1)

(*E*)-4-IC₆H₄CH=CHPh (250 mg, 0.82 mmol), Me₃SiC=CH (96 mg, 0.98 mmol), [PdCl₂(PPh₃)₂] (10 mg) and CuI (4 mg) were stirred in triethylamine (40 ml) for 2 h at 40 °C. The solution was filtered through a silica plug and the solvent volume reduced under reduced pressure to afford the white product (185 mg, 82%). IR: (CH₂Cl₂) ν (C=C) 2154 cm⁻¹. UV–Vis: λ (thf) 346 nm, ε 16 800 M⁻¹ cm⁻¹, 330 nm, ε 25 200 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 0.24 (s, 9H, Me), 7.04 (d, J_{HH} = 16 Hz, 1H, H₇), 7.11 (d, J_{HH} = 16 Hz, 1H, H₈), 7.15–7.55 (m, 9H, Ph+C₆H₄). EI MS: 276 ([*M*]⁺, 50), 261 ([*M*-Me]⁺, 60), 179 ([*M*-



Fig. 1. Numbering scheme for NMR spectral assignments for 1-17.

 $SiMe_3$ ⁺, 100). HR MS Calc. for $C_{19}H_{20}Si$ *m/e* 276.1335. Found 276.1334.

2.3. $1,3,5-\{(E)-4-IC_6H_4CH=CH\}_3C_6H_3$ (3)

4-IC₆H₄CHO (145 mg, 0.63 mmol), 1,3,5-C₆H₃{CH₂P(O)(OEt)₂}₃ (100 mg, 0.19 mmol) and t-BuOK (67 mg, 0.60 mmol) were stirred in thf (30 ml) overnight. HCl (1.0 ml, 0.5 M) was then added and the solution passed through an alumina plug. The solvent was reduced in volume under vacuum to afford the white product (104 mg, 72%). UV–Vis: λ (thf) 340 nm, ε 60 800 M⁻¹ cm⁻¹, 326 nm, ε 82 400 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 7.06 (d, J_{HH} = 16 Hz, 3H, H₈), 7.13 (d, J_{HH} = 16 Hz, 3H, H₇), 7.26 (d, J_{HH} = 9 Hz, 6H, H₄), 7.52 (s, 3H, H₁₀), 7.68 (d, J_{HH} = 9 Hz, 6H, H₅). EI MS: 762 ($[M]^+$, 100), 636 ($[M-I]^+$, 30), 506 ($[M-2I]^+$, 10). HR MS Calc. for C₃₀H₂₁I₃ *m/e* 761.8771. Found 761.8778.

2.4.
$$1,3,5-\{(E)-4-Me_3SiC\equiv CC_6H_4CH=CH\}_3C_6H_3$$
 (4)

1,3,5-{(*E*)-4-IC₆H₄CH=CH}₃C₆H₃ (**3**) (200 mg, 0.26 mmol), Me₃SiC=CH (103 mg, 1.05 mmol), [PdCl₂(PPh₃)₂] (10 mg) and CuI (4 mg) were stirred in triethylamine (40 ml) for 2 h at 40 °C. The solution was filtered through a silica plug and the solvent reduced in volume under reduced pressure to afford the pale white product (145 mg, 82%). IR: (CH₂Cl₂) ν (C=C) 2154 cm⁻¹. UV–Vis: λ (thf) 354 nm, ε 112 200 M⁻¹ cm⁻¹, 339 nm, ε 136 500 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 0.24 (s, 27H, Me), 7.15 (s, 6H, H₇, H₈), 7.49 (s,

12H, H₄, H₅), 7.55 (s, 3H, H₁₀). EI MS: 672 ($[M]^+$, 35), 576 ($[M-C=CSiMe_3]^+$, 20). HR MS Calc. for C₄₅H₄₈Si₃ *m/e* 672.3057. Found 672.3064.

2.5.
$$1,3,5-\{(E)-4-HC\equiv CC_6H_4CH=CH\}_3C_6H_3$$
 (5)

1,3,5-{(*E*)-4-Me₃SiC=CC₆H₄CH=CH}₃C₆H₃ (4) (250 mg, 0.37 mmol) and NBu₄ⁿF (1.0 ml, 1 M in thf) were stirred in dichloromethane (15 ml) for 1 h. The solvent was removed under reduced pressure, the material was redissolved in petrol and the solution was passed through a silica plug eluting with petrol. The solvent was reduced in volume under reduced pressure to afford the white product (137 mg, 81%). IR: (CH₂Cl₂) ν (C=C) 2108 cm⁻¹. UV–Vis: λ (thf) 348 nm, ε 90000 M⁻¹ cm⁻¹, 332 nm, ε 116 800 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 3.13 (s, 3H, H₁), 7.15 (s, 6H, H₇, H₈), 7.49 (s, 12H, H₄, H₅), 7.55 (s, 3H, H₁₀). EI MS: 456 ([*M*]⁺, 35). HR MS Calc. for C₃₆H₂₄ *m/e* 456.1879. Found 456.1878.

2.6. $[Au\{(E)-4-C \equiv CC_6H_4CH = CHPh\}(PPh_3)]$ (6)

[AuCl(PPh₃)] (100 mg, 0.20 mmol) and (E)-4-HC= CC₆H₄CH=CHPh (2) (45 mg, 0.22 mmol) were stirred together in a solution of sodium methoxide in methanol (20 ml, 0.1 M) for 18 h. Dichloromethane (20 ml) was added and the solution passed through a silica plug. The solvent was removed under reduced pressure and the material triturated with petrol. The solid was collected on a sintered-glass funnel, and washed with more petrol to yield the pale yellow product (98 mg, 73%). Anal. Calc. for C34H26AuP: C, 61.64; H, 3.96. Found: C, 61.61; H, 4.33%. IR: (CH₂Cl₂) ν (C=C) 2111 cm⁻¹. UV–Vis: λ (thf) 338 nm, ε 16 500 M⁻¹ cm⁻¹, 324 nm, ε 25 300 M⁻¹ cm⁻¹. ¹H NMR: (δ, 300 MHz, CDCl₃); 7.06 (s, 2H, H₇, H₈), 7.30–7.60 (m, 24H, Ph+C₆H₄). ³¹P NMR: $(\delta, 121 \text{ MHz}, \text{ CDCl}_3)$; 42.8. SI MS: 721 $([Au(PPh_3)_2]^+, 20), 459 ([Au(PPh_3)]^+, 100).$

2.7. $[Au\{(E)-4-C \equiv CC_6H_4CH = CHPh\}(PMe_3)]$ (7)

[AuCl(PMe₃)] (100 mg, 0.32 mmol) and (*E*)-4-HC= CC₆H₄CH=CHPh (**2**) (73 mg, 0.36 mmol) were stirred together in a solution of sodium methoxide in methanol (20 ml, 1 M) for 18 h. Dichloromethane (10 ml) was added and the solution passed through a silica plug. The solvent was removed under reduced pressure and the material triturated with petrol. The solid was collected on a sintered-glass funnel, and washed with more petrol to yield the white product (90 mg, 58%). *Anal*. Calc. for C₁₉H₂₀AuP: C, 47.91; H, 4.23. Found: C, 48.53; H, 4.63%. IR: (CH₂Cl₂) ν (C=C) 2108 cm⁻¹. UV–Vis: λ (thf) 339 nm, ε 18800 M⁻¹ cm⁻¹, 323 nm, ε 28600 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 1.51 (d, *J*_{HP} = 11 Hz, 9H, Me), 7.04 (s, 2H, H₇, H₈), 7.20–7.55 (m, 9H, Ph+C₆H₄). ³¹P NMR: $(\delta, 121 \text{ MHz, CDCl}_3)$; 1.7. SI MS: 533 ([Au₂(PMe₃)₃]⁺, 15), 349 ([Au(PMe₃)₂]⁺, 95), 273 ([Au(PMe₃)]⁺, 100).

2.8. $[Au(4-C \equiv CC_6H_4C \equiv CPh)(PPh_3)]$ (8)

[AuCl(PPh₃)] (100 mg, 0.20 mmol) and 4-HC= CC₆H₄C=CPh (45 mg, 0.22 mmol) were stirred in a solution of sodium methoxide in methanol (15 ml, 0.1 M) for 16 h. Dichloromethane (15 ml) was added and the solution passed through a silica plug. The solvent was reduced in volume under reduced pressure to give the yellow product (113 mg, 85%). *Anal*. Calc. for C₃₄H₂₄AuP: C, 61.83; H, 3.66. Found: C, 61.22; H 4.59%. IR: (CH₂Cl₂) ν (C=C) 2112 cm⁻¹. UV–Vis: λ (thf) 336 nm, ε 65 000 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 7.25–7.60 (m, 24H, Ph+C₆H₄). ³¹P NMR: (δ , 121 MHz, CDCl₃); 42.7. SI MS: 721 ([Au(PPh₃)₂]⁺, 40), 660 ([*M*]⁺, 5), 459 ([Au(PPh₃)]⁺, 100).

2.9. $[Au(4-C \equiv CC_6H_4C \equiv CPh)(PMe_3)]$ (9)

[AuCl(PMe₃)] (100 mg, 0.32 mmol) and 4-HC= CC₆H₄C=CPh (72 mg, 0.36 mmol) were stirred in a solution of sodium methoxide in methanol (20 ml, 0.1 M) for 16 h. Dichloromethane (10 ml) was added and the solution passed through a silica plug. The solvent was removed under reduced pressure to give the yellow product (105 mg, 68%). *Anal*. Calc. for C₁₉H₁₈AuP: C, 48.12; H, 3.83. Found: C, 48.52; H, 4.16%. IR: (CH₂Cl₂) ν (C=C) 2112 cm⁻¹. UV–Vis: λ (thf) 335 nm, ε 55 000 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 1.56 (d, *J*_{HP} = 15 Hz, 9H, Me), 7.25–7.55 (m, 9H, Ph+C₆H₄). ³¹P NMR: (δ , 121 MHz, CDCl₃); 1.7. SI MS: 474 ([*M*]⁺, 10), 349 ([Au(PMe₃)₂]⁺, 75), 273 ([Au(PMe₃)]⁺, 100).

2.10. $1,3,5-[(Ph_3P)Au\{(E)-4-C\equiv CC_6H_4CH=CH\}]_3C_6H_3$ (10)

[AuCl(PPh₃)] (162 mg, 0.33 mmol) and 1,3,5-{(*E*)-4-HC=CC₆H₄CH=CH}₃C₆H₃ (**5**) (50 mg, 0.11 mmol) were stirred in a solution of sodium methoxide in methanol (0.1 M, 15 ml) for 16 h. Dichloromethane (25 ml) was added, the solution was passed through a silica plug and the solvent reduced in volume under vacuum to yield the white product (158 mg, 79%). *Anal*. Calc. for C₉₀H₆₆Au₃P₃: C, 59.03; H, 3.63. Found: C, 58.83; H, 4.04%. IR: (CH₂Cl₂) ν (C=C) 2108 cm⁻¹. UV–Vis: λ (thf) 366 nm, ε 96 100 M⁻¹ cm⁻¹, 350 nm, ε 131 700 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 7.11 (s, 6H, H₇, H₈), 7.40–7.60 (m, 60H, Ph+C₆H₄+ C₆H₃). ³¹P NMR: (δ , 121 MHz, CDCl₃); 42.8. SI MS: 1834 ([*M*+3H]⁺, 15), 1375 ([*M*–Au(PPh₃)+3H]⁺, 60), 722 ([Au(PPh₃)₂+H]⁺, 100).

2.11. trans-[Ru{(E)-4-C=CHC₆H₄CH= CHPh}Cl(dppm)₂]PF₆ (11)

cis-[RuCl₂(dppm)₂] (200 mg, 0.21 mmol), (*E*)-4-HC= CC₆H₄CH=CHPh (**3**) (52 mg, 0.26 mmol) and NH₄PF₆ (69 mg, 0.42 mmol) were stirred together in dichloromethane (25 ml) at r.t. for 24 h. Petrol (50 ml) was added and the resulting precipitate was collected and washed with diethyl ether (50 ml) to afford the pale yellow product (208 mg, 78%). *Anal*. Calc. for C₆₆H₅₆ClF₆P₅Ru: C, 63.19; H, 4.50. Found: C, 62.32; H, 4.73%. IR: (KBr) ν (PF) 837 cm⁻¹. UV–Vis: λ (thf) 360 nm, ε 14600 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 3.05 (m, 1H, =CH), 5.10 (m, 2H, PCH₂P), 5.32 (m, 2H, PCH₂P), 5.50 (d, *J*_{HH} = 8 Hz, 2H, H₄), 6.88 (d, *J*_{HH} = 8 Hz, 2H, H₅), 7.10–7.60 (m, 47H, Ph+H₇+H₈). ³¹P NMR: (δ , 121 MHz, CDCl₃); -15.6. SI MS: 1109 ([*M*-HPF₆]⁺, 100), 905 ([RuCl(dppm)₂]⁺, 40), 869 ([Ru(dppm)₂-H]⁺, 100).

2.12. $trans - [Ru\{(E)-4-C \equiv CC_6H_4CH = CHPh\}Cl(dppm)_2] \cdot 0.5CH_2Cl_2$ (12)

trans-[Ru{(E)-4-C=CHC₆H₄CH=

CHPh}Cl(dppm)₂]PF₆ (11) (150 mg, 0.12 mmol) was stirred in dichloromethane (20 ml) with triethylamine (1.0 ml) at r.t. for 2 h. The solution was filtered through an alumina plug and the solvent reduced in volume under vacuum to afford the yellow product (109 mg, 82%). *Anal*. Calc. for C_{66.5}H₅₆Cl₂P₄Ru: C, 69.39; H, 4.90. Found: C, 69.35; H, 5.35%. IR: (CH₂Cl₂) ν (C=C) 2073 cm⁻¹. UV–Vis: λ (thf) 397 nm, ε 23400 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 4.89 (m, 4H, PCH₂P), 5.27 (s, 1H, CH₂Cl₂), 6.21 (d, *J*_{HH} = 8 Hz, 2H, H₄), 7.10–7.60 (m, 49H, Ph+H₅+H₇+H₈). ³¹P NMR: (δ , 121 MHz, CDCl₃); -6.0. SI MS: 1109 ([*M*]⁺, 20), 1073 ([*M*-HCl]⁺, 20), 905 ([RuCl(dppm)₂]⁺, 90), 869 ([Ru(dppm)₂-H]⁺, 100).

2.13. $trans - [Ru\{(E)-4-C \equiv CC_6H_4CH = CHPh\}Cl(dppe)_2]$ (13)

cis-[RuCl₂(dppe)₂] (150 mg, 0.15 mmol) and (*E*)-4-HC=CC₆H₄CH=CHPh (**3**) (38 mg, 0.19 mmol) were stirred together in dichloromethane (25 ml) at r.t. for 20 min. NH₄PF₆ (50 mg, 0.31 mmol) was then added, and the stirring continued for another 24 h. The solvent was removed under reduced pressure and the excess acety-lene removed by triturating with diethyl ether (3 × 30 ml). Dichloromethane (15 ml) and triethylamine (1 ml) were added and the solution stirred for 5 min. Petrol (40 ml) was added, and the resulting precipitate was collected to afford the yellow product (125 mg, 71%). *Anal*. Calc. for C₆₈H₅₉ClP₄Ru: C, 71.86; H, 5.23. Found: C, 71.31; H, 5.63%. IR: (CH₂Cl₂) ν (C=C) 2066 cm⁻¹. UV–Vis: λ (thf) 404 nm, ε 28 600 M⁻¹

cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 2.67 (m, 8H, PCH₂CH₂P), 7.10–7.60 (m, 51H, Ph+C₆H₄+H₇+H₈). ³¹P NMR: (δ , 121 MHz, CDCl₃); 50.1. SI MS: 1136 ([M]⁺, 40), 1101 ([M-Cl]⁺, 20), 957 ([M-C₆H₄CH= CHPh]⁺, 100), 897 ([Ru(dppe)₂-H]⁺, 100).

2.14. $[1,3,5-(trans-[(dppm)_2ClRu\{(E)-4-C=CHC_6H_4CH=CH\}])_3C_6H_3](PF_6)_3$ (14)

cis-[RuCl₂(dppm)₂] (185 mg, 0.20 mmol), 1,3,5-{(E)- $4-HC \equiv CC_6H_4CH = CH_3C_6H_3$ (5) (30 mg, 0.068 mmol) and NH₄PF₆ (72 mg, 0.44 mmol) were added to dichloromethane (25 ml), and the resultant mixture stirred at r.t. for 45 h. Petrol (50 ml) was added, and the resulting precipitate was collected and washed with diethyl ether (50 ml) to afford the pale red product (223 mg, 94%). Anal. Calc. for C₁₈₆H₁₅₆Cl₃F₁₈P₁₅Ru₃: C, 61.93; H, 4.36. Found: C, 61.45; H, 4.66%. IR: (KBr) $v(PF) 838 \text{ cm}^{-1}$. UV–Vis: λ (thf) 396 nm, ε 19700 M⁻¹ cm^{-1} . ¹H NMR: (δ , 300 MHz, CDCl₃); 3.07 (m, 3H, = CH), 5.10 (m, 6H, PCH₂P), 5.26 (m, 6H, PCH₂P), 5.51 $(d, J_{hh} = 8Hz, 6H, J_{HH} = 8Hz, H_4), 6.98 (d, J_{hh} = 8Hz,$ 6H, $J_{\text{HH}} = 8$ Hz, H₅), 7.10–7.60 (m, 129H, Ph+C₆H₃+ $H_7 + H_8$). ³¹P NMR: (δ , 121 MHz, CDCl₃); -15.8. SI MS: 904 ([RuCl(dppm)₂-H]⁺, 40), 868 ([Ru(dppm)₂-2H]⁺, 100).

2.15. $1,3,5-(trans-[(dppm)_2ClRu\{(E)-4-C \equiv CC_6H_4CH=CH\}])_3C_6H_3$ (15)

[1,3,5-(*trans*-[(dppm)₂ClRu{(*E*)-4-C=CHC₆H₄CH= CH}])₃C₆H₃](PF₆)₃ (14) (154 mg, 0.043 mmol) was stirred in dichloromethane (25 ml) with triethylamine (1 ml) at r.t. for 15 min. The solution was filtered through an alumina plug and the solvent reduced in volume under vacuum to afford the yellow product (110 mg, 81%). *Anal*. Calc. for C₁₈₆H₁₅₃Cl₃P₁₂Ru₃: C, 70.48; H, 4.87. Found: C, 69.46; H, 5.57%. IR: (CH₂Cl₂) ν (C= C) 2073 cm⁻¹. UV–Vis: λ (thf) 415 nm, ε 48 500 M⁻¹ cm⁻¹. ¹H NMR: (δ , 300 MHz, CDCl₃); 4.91 (m, 12H, PCH₂P), 6.07 (d, *J*_{HH} = 8 Hz, 6H, H₄), 6.90–7.60 (m, 135H, Ph+C₆H₃+H₅+H₇+H₈). ³¹P NMR: (δ , 121 MHz, CDCl₃); -5.9. SI MS: 3169 ([*M*]⁺, 15), 2264 ([*M*-RuCl(dppm)₂]⁺, 5), 904 ([RuCl(dppm)₂-H]⁺, 40), 869 ([Ru(dppm)₂-H]⁺, 100).

2.16. $1,3,5-(trans-[(dppe)_2ClRu\{(E)-4-C \equiv CC_6H_4CH=CH\}])_3C_6H_3$ (16)

cis-[RuCl₂(dppe)₂] (304 mg, 0.31 mmol) and 1,3,5- $\{(E)$ -4-HC=CC₆H₄CH=CH $\}_3$ C₆H₃ (5) (32 mg, 0.070 mmol) were stirred together in dichloromethane (25 ml) at r.t. for 20 min. NH₄PF₆ (112 mg, 0.69 mmol) was then added, and the solution refluxed for 15 h. The solution was then cooled to r.t. and passed through a sintered-glass funnel. Triethylamine (1.0 ml) was added

to the filtrate, the resultant solution was stirred for 5 min, and then the solvent was removed under reduced pressure. A dichloromethane extract of the vellow residue was adsorbed onto an alumina column, with any *trans*-[RuCl₂(dppe)₂] being removed by elution with diethyl ether (400 ml). Elution with dichloromethane (400 ml) gave the yellow product after addition of petrol and reduction in solvent volume (173 mg, 76%). Anal. Calc. for C₁₉₂H₁₆₅Cl₃P₁₂Ru₃: C, 70.88; H, 5.11. Found: C, 70.60; H, 5.15%. IR: $(CH_2Cl_2) v(C=C) 2062 \text{ cm}^{-1}$. UV–Vis: λ (thf) 426 nm, ϵ 87 400 M⁻¹ cm⁻¹. ¹H NMR: (δ, 300 MHz, CDCl₃); 2.70 (m, 24H, PCH₂CH₂P), 6.66 (d, $J_{hh} = 8Hz$, 6H, $J_{HH} = 8$ Hz, H₄), 6.90–7.60 (m, 135H, Ph+C₆H₃+H₅+H₇+H₈). ³¹P NMR: (δ , 121 MHz, CDCl₃); 50.1. SI MS: 3254 ($[M]^+$, 5), 3218 ([M- $HCl]^+$, 4), 897 ([Ru(dppe)_2-H]^+, 100), 499 $([Ru(dppe)-H]^+, 100).$

2.17. 1,3,5- $(trans-[(dppe)_2(PhC \equiv C)Ru\{(E)-4-C \equiv CC_6H_4CH = CH\}])_3C_6H_3 \cdot CH_2Cl_2$ (17)

1,3,5-(*trans*-[(dppe)₂ClRu{(E)-4-C=CC₆H₄CH= $CH_{1}^{3}C_{6}H_{3}$ (16) (100 mg, 0.031 mmol), $NH_{4}PF_{6}$ (30 mg, 0.18 mmol), HC=CPh (31 mg, 0.31 mmol) and triethylamine (1 ml) were stirred in refluxing dichloromethane (25 ml) for 5 h. After this time the solution was cooled, the solvent removed, and the residue triturated with petroleum spirit (100 ml) to remove excess HC=CPh. The yellow product was collected by filtration mg, (60) 57%). Anal. Calc. for C₂₁₇H₁₈₂Cl₂P₁₂Ru₃: C, 73.72; H, 5.19. Found: C, 73.81; H, 5.83%. IR: (CH₂Cl₂) ν (C=C) 2057 cm⁻¹. UV-Vis: λ (thf) 421 nm, ϵ 129700 M⁻¹ cm⁻¹. ¹H NMR: $(\delta, 300 \text{ MHz}, \text{ CDCl}_3)$; 2.63 (m, 24H, PCH₂CH₂P), 5.27 (s, 2H, CH₂Cl₂), 6.70-7.60 (m, 156H, $Ph+C_6H_4+C_6H_3+H_7+H_8$). ³¹P NMR: (δ , 121 MHz, CDCl₃); 54.3. SI MS: 3451 ($[M+H]^+$, 3), 3351 $([M+2H-C=CPh]^+, 4), 998 ([(dppe)_2(PhC=C)Ru H^{+}_{1}$, 100), 897 ([Ru(dppe)_2-H]^+, 100).

2.18. X-ray crystallographic study

Crystals suitable for the X-ray structural analysis were grown by liquid diffusion of methanol into a CHCl₃ solution of **6** at r.t. A single yellow needle crystal was mounted on a fine glass fiber using epoxy glue, and data were collected at 200 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K α radiation. The unit cell parameters were obtained by least-squares refinement [19] of 32 259 reflections with $3.5 \le \theta \le 27.5^{\circ}$. The data were corrected for absorption using numerical methods [20], implemented from within MAXUS [21]; equivalent reflections were merged. The structure was solved by heavy atom Patterson methods [22] and expanded using Fourier techniques [23]. Nonhydrogen atoms were refined anisotropically; hydrogen atoms were included in idealized positions, which were frequently recalculated. The final cycle of full-matrix least-squares refinement on F was based on 4098 observed reflections ($I > 2\sigma(I)$) and 325 variable parameters, and converged to R = 0.042. Selected crystal data and structure refinement parameters are collected in Table 1.

2.19. Hyper-Rayleigh scattering measurements

The light from an injection-seeded Nd:YAG laser (Qswitched Nd:YAG Quanta Ray GCR5, 1064 nm, 8 ns pulses, 10 Hz) was focussed into a cylindrical cell (7 ml) containing the sample. The intensity of the incident beam was varied by rotation of a half-wave plate placed between crossed polarizers. Part of the laser pulse was sampled by a photodiode to measure the vertically polarized incident light intensity. The frequencydoubled light was collected by an efficient condensor system and detected by a photomultiplier. The harmonic scattering and linear scattering were distinguished by appropriate filters; gated integrators were used to obtain intensities of the incident and harmonic scattered light. The absence of a luminescence contribution to the harmonic signal was confirmed by using interference filters at different wavelengths near 532 nm. All measurements were performed in tetrahydrofuran using *p*-nitroaniline ($\beta = 21.4 \times 10^{-30}$ esu) [24] as a reference. Solutions were sufficiently dilute that absorption of scattered light was negligible. Further details of the

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Crystal data and structure refinement parameters for 6

Empirical formula	$C_{34}H_{26}AuP$
Formula weight	662.52
Crystal size (mm)	$0.24 \times 0.16 \times 0.11$
<i>T</i> (K)	200
Wavelength (Å)	0.71069
Crystal system	monoclinic
Space group	<i>P</i> 2/ <i>n</i> (No. 13)
Unit cell dimensions	
a (Å)	11.1428(6)
b (Å)	6.6249(4)
c (Å)	36.157(2)
β (°)	98.087(2)
$V(Å^3)$	2642.6(2)
Ζ	4
Index ranges	$0 \le h \le 14, -8 \le k \le 8, -46 \le l \le$
	46
$\mu \text{ (mm}^{-1}\text{)}$	5.668
Max and min transmission	0.676 and 0.298
Independent reflections	$6054 \ (R_{\rm int} = 0.089)$
Goodness-of-fit $(I > 2\sigma(I))$	1.27
Final <i>R</i> indices $(I > 2\sigma(I))^{a}$	$R = 0.042, R_{\rm w} = 0.052$
Largest difference peak and	1.25 and -1.42
hole	
$(e Å^{-3})$	

experimental procedure have been reported in the literature [25,26].

For chromophores exhibiting fluorescence, the HRS signal can consist of nonlinear scattering and multiphoton fluorescence (MPF), which results in an overestimation of the molecular nonlinearity. To avoid this problem, the broadband MPF background has been subtracted from the sharp HRS peak in the spectral domain [27,28]. However, the most fundamental approach to resolve this problem is to utilize the difference in the temporal response between the immediate (hyper-Rayleigh) scattering and the time-delayed (multiphoton) fluorescence in the time domain [29]. Measurements at 800 nm were performed implementing a complete Fourier transform of this approach, using a laser system with a high repetition rate fs Ti:sapphire laser (Spectra Physics, Model Tsunami) to obtain a MPF-free HRS signal. In the frequency domain, we measured the demodulation and the phase shift acquired by the fluorescence versus scattering. A more complete description of this procedure has been given in the literature [30,31]. All measurements were performed in tetrahydrofuran using the internal reference method $(\beta_{\rm thf} = 0.33 \times 10^{-30} \text{ esu}).$

2.20. Z-scan measurements

Measurements were performed at 800 nm using a system consisting of a Coherent Mira Ti-sapphire laser generating a mode-locked train of approximately 100 fs pulses and a home-built Ti-sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed Nd:YAG laser (Spectra Physics GCR) at 30 Hz and employing chirped pulse amplification. Thf solutions were examined in a glass cell with a 1 mm path length. The Z-scans were recorded at two concentrations for each compound and the real and imaginary part of the nonlinear phase change determined by numerical fitting [32]. The real and imaginary parts of the hyperpolarizability of the solute were then calculated by assuming linear concentration dependencies of the solution susceptibility. The nonlinearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3 \times 10^{-16}$ cm² W⁻¹ was assumed.

2.21. Electroabsorption measurements

Complexes 13, 16, and 17 were doped in a poly(methyl methacrylate) (PMMA) solution in chloroform and spin-coated onto an indium–tin-oxide (ITO)coated glass substrate. The film thickness was 2.2–2.5 µm and the complex concentration was approximately 4 wt.%, corresponding to a number density of 2.5×10^{19} , 8.6×10^{18} and 9.1×10^{18} cm⁻¹, for 13, 16 and 17, respectively. Semitransparent gold electrodes were evaporated on top of the film, so that a sandwich structure was formed. White light from a tungsten-halogen lamp was monochromated and incident to the film, and transmitted light was detected by a photodiode. A low-frequency (137.5 Hz) electric field of approximately 2×10^5 V cm⁻¹ was applied normal to the film, and modulation in the transmitted light intensity at the doubled frequency (275 Hz) was detected by a lock-in amplifier, so that the third-order NLO response which is proportional to the square of the applied electric field was probed. Measurements were performed in the spectral range 350–550 nm.

3. Results and discussion

3.1. Synthesis and characterization of organic precursors

The syntheses of the alkynyl-gold and -ruthenium complexes necessitated preparation of new linear and octopolar stilbenylacetylenes. Sonogashira coupling of (E)-4-IC₆H₄CH=CHPh with trimethylsilylacetylene afforded the protected alkyne 1, which was deprotected with base to give the linear terminal acetylene 2 (Scheme 1). While the current research was in progress, an alternative synthesis of 2 was reported, by the Emmons-Horner reaction of 4-ethynylbenzaldehyde and diethyl benzylphosphonate, but the yield via this procedure was lower (49%) [18]. The methodology in Scheme 1 employed for the syntheses of the linear acetylenes were also used for the syntheses of the branched acetylenes (Scheme 2). Reaction of excess 4- IC_6H_4CHO with $1,3,5-C_6H_3\{CH_2P(O)(OEt)_2\}_3$ in the presence of potassium tert-butoxide gave $1,3,5-\{(E)-4 IC_6H_4CH=CH_3C_6H_3$ (3). Coupling 3 with trimethylsi-



Scheme 1. Syntheses of 1 and 2.



Scheme 2. Syntheses of 3-5.

lylacetylene under Sonogashira conditions gave the protected acetylene **4**, which was deprotected with base to afford the terminal acetylene **5**. The new compounds were characterized by EI and high-resolution EI mass spectrometry, UV–Vis, IR and ¹H NMR spectroscopy.

3.2. Synthesis and characterization of σ -acetylide complexes

The synthetic methodologies employed for the preparation of the stilbenylalkynyl-gold and -ruthenium complexes are adaptations of those successfully utilized for the preparation of the corresponding phenylacetylide complexes. Gold phosphine complexes **6**, **7**, and **10**, together with previously-unreported complexes **8** and **9**, were prepared in good yield (Scheme 3) by extending the method of Bruce et al. [33]. The bis{bis(diphenylphosphino)alkane}ruthenium complexes **11–17** were prepared (Schemes 4 and 5) by extending the method of Dixneuf [34].

The new complexes were characterized by SI mass spectrometry, UV–Vis, IR, ¹H and ³¹P NMR spectroscopy. Mass spectra for the gold complexes contain weak or non-existent molecular ion signals, (phosphine)gold units being the most abundant ions observed. All ruthenium complexes except **14** gave mass spectra with molecular ions or protonated molecular ions. UV– Vis spectra contain bands in the range 335–339 nm (linear gold complexes **6–9**), 366 nm (octopolar gold complex **10**), 360–404 nm (linear ruthenium complexes **11–13**), and 396–426 nm (octopolar ruthenium complexes **14–17**). The IR spectra of the acetylide complexes show characteristic coordinated ν (C=C) bands in the range 2108–2112 cm⁻¹ (gold complexes) and 2057– 2073 cm⁻¹ (ruthenium complexes), the spectra of the vinylidene complexes **11** and **14** having ν (PF) bands at 837 and 838 cm⁻¹, respectively. ³¹P NMR spectra of the ruthenium complexes contain one singlet resonance, consistent with *trans* geometry at the ruthenium center.

3.3. X-ray crystallographic study

The identity of 6 was confirmed by a single-crystal Xray diffraction study. Crystal data are given in Table 1 and selected bond lengths and angles are compiled in Table 2. Fig. 2 contains an ORTEP plot showing the molecular geometry and atomic labeling scheme.



Scheme 3. Syntheses of 6-10.

The structural study of **6** confirms the molecular composition inferred from the spectral data and, in particular, the *E*-configured alkene linkage. The Au(1)–P(1), Au(1)–C(1) and C(1)–C(2) bond distances are indistinguishable to those previously observed for related (phosphine)gold acetylide complexes within the 3σ confidence level [16,35–37]. The angles about the P(1)–Au(1)–C(1)–C(2) moiety are close to linearity, with deviations likely to be the result of crystal packing forces. Intraphosphine bond lengths and angles in **6** are not unusual, and the C(9)–C(10) distance [1.32(1) Å] is typical for an *E*–C=C unit. Gold complexes have attracted significant interest as many show aurophilic Au···Au interactions in the solid state; in the present

case, however, Au \cdots Au contacts are all greater than 5 Å.

3.4. Electrochemical studies

The electrochemical data for the ruthenium complexes 11-17 are gathered in Table 3. The alkynylruthenium complexes exhibit reversible or quasi-reversible processes (in the range 0.46-0.68 V), whereas the vinylidene complexes exhibit irreversible processes at considerably more positive potentials (the latter as expected for cationic complexes). We have recently reported a detailed investigation of the electrochemical behavior of *trans*-bis(bidentate phosphine)ruthenium



Scheme 4. Syntheses of 11-13.



Scheme 5. Syntheses of 14-17.

Table 2 Selected bond distances (Å) and angles (°) for $[Au\{(E)-4-C=CC_6H_4CH=CHPh\}(PPh_3)]$ (6)

Bond lengths			
Au(1) - P(1)	2.267(2)	P(1)-C(111)	1.815(8)
P(1) - C(121)	1.828(8)	P(1) - C(131)	1.832(8)
Au(1)-C(1)	2.038(9)	C(1) - C(2)	1.16(1)
C(2) - C(3)	1.42(1)	C(3) - C(4)	1.41(1)
C(4) - C(5)	1.36(1)	C(5) - C(6)	1.41(1)
C(6) - C(7)	1.40(1)	C(7) - C(8)	1.39(1)
C(3) - C(8)	1.41(1)	C(6) - C(9)	1.47(1)
C(9) - C(10)	1.32(1)	C(10)-C(11)	1.48(1)
C(11)-C(12)	1.35(1)	C(12)-C(13)	1.40(1)
C(13)-C(14)	1.39(1)	C(14)-C(15)	1.35(1)
C(15)-C(16)	1.42(1)		
Bond angles			
P(1) - Au(1) - C(1)	174.4(2)	Au(1)-P(1)-C(111)	110.4(3)
Au(1)-P(1)-C(121)	115.7(3)	Au(1)-P(1)-C(131)	113.3(3)
Au(1)-C(1)-C(2)	168.2(8)	C(1)-C(2)-C(3)	174.2(9)
C(2)-C(3)-C(4)	120.7(7)	C(3)-C(4)-C(5)	121.4(7)
C(4) - C(5) - C(6)	122.5(8)	C(5)-C(6)-C(7)	116.9(8)
C(6)-C(7)-C(8)	121.3(7)	C(2)-C(3)-C(8)	121.9(8)
C(3)-C(8)-C(7)	120.6(8)	C(5)-C(6)-C(9)	119.3(8)
C(7) - C(6) - C(9)	123.7(7)	C(6)-C(9)-C(10)	126.7(8)
C(9)-C(10)-C(11)	126.5(9)	C(10)-C(11)-C(12)	122.9(8)

acetylide and vinylidene complexes [38]; the oxidation potentials and reversibility of processes observed with the present series of complexes are similar to data for our previously-reported complexes. In the present study, complexes 14–17 exhibit a single oxidation wave indicating that the three ruthenium centers are equivalent, the non-conjugated pathway between the metals hindering communication.

3.5. Nonlinear optical studies

The results of HRS measurements on the precursor organics and ruthenium complexes are presented in Table 4, β_{1064} values corresponding to data at 1064 nm with ns pulses and β_{800} to data at 800 nm with fs pulses. Linear optical absorption data are also collected in Table 4. Trends in optical absorption data ($\lambda_{max}, \varepsilon$) are relevant to the subsequent discussion of NLO data. Introduction of a metal center in proceeding from 2 to 12 or 5 to 15 results in a significant red-shift in λ_{max} , while proceeding from vinylidene complexes 11, 14 to alkynyl complexes 12, 15 results in a red-shift in λ_{max} and increase in ε . Progression from linear complexes 11, 12 to octopolar analogues 14, 15 results in a red-shift in



Fig. 2. Molecular structure and atomic numbering scheme for $[Au\{(E)-4-C \equiv CC_6H_4CH = CHPh\}(PPh_3)]$ (6); 30% displacement ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii.

Table 3 Cyclic voltammetric data ^a

Complex	$\frac{E_{1/2} \operatorname{Ru}(\text{II}/\text{III})}{\operatorname{III}} (\text{V})$	[i _{pc} / i _{pa}]
trans-[Ru{(E)-4-C=CHC ₆ H ₄ CH=	1.38	b
$CHPh Cl(dppm)_2 PF_6$ (11)		
trans-[Ru{(E)-4-C=CC ₆ H ₄ CH=	0.46	[0.9]
CHPh}Cl(dppm) ₂] (12)		
trans-[Ru{(E)-4-C=CC ₆ H ₄ CH=	0.51	[1.0]
$CHPh Cl(dppe)_2$] (13)		
[1,3,5-(<i>trans</i> -[(dppm) ₂ ClRu{(<i>E</i>)-4-C=	1.45	b
CHC ₆ H ₄ CH=CH}]) ₃ C ₆ H ₃](PF ₆) ₃ (14)		
$1,3,5-(trans-[(dppm)_2ClRu{(E)-4-C} \equiv$	0.68	[1.0]
$CC_{6}H_{4}CH \equiv CH])_{3}C_{6}H_{3}$ (15)		
1,3,5-(<i>trans</i> -[(dppe) ₂ ClRu{(E)-4-C=	0.51	[0.9]
$CC_{6}H_{4}CH=CH$]) ₃ $C_{6}H_{3}$ (16)		
1,3,5-(<i>trans</i> -[(dppe) ₂ (PhC \equiv C)Ru{(E)-4-C \equiv	0.49	[1.0]
$CC_6H_4CH=CH$]) ₃ C_6H_3 (17)		

^a Ag/AgCl reference electrode, ferrocene-ferrocenium couple (0.56 V) as an internal standard.

^b Not reversible.

Table 4

Linear optical spectroscopic and quadratic NLO response parameters
Compound

absorption maxima and a two to threefold increase in oscillator strength.

Complexes 11, 12, 14 and 15 are transparent at the second-harmonic wavelength of 532 nm, permitting assessment of the impact of structural variation on quadratic NLO merit. Nonlinearities for 14 and 15 are large for octopolar complexes without polarizing acceptor substituents, but data for 12, 14 and 15 are experimentally indistinguishable within the error margins. Proceeding from vinylidene complex 11 to acetylide complex 12 or tri-vinylidene complex 14 results in significant increases in quadratic nonlinearity; the reversibility of the vinylidene-acetylide interconversion suggests that 11/12 provides a further example of a protically-switchable NLO system [38]. HRS measurements of 11, 12, 14 and 15 at 800 nm with fs pulses are also listed in Table 4; fluorescence contributions could not be completely eliminated from the data for 12, but are absent from our reported nonlinearities of 11, 14 and 15 (there is no demodulation of the signals for these complexes as modulation frequency is varied). Proceeding from vinylidene complex 14 to alkynyl complex 15

Compound	$\lambda_{\max} (nm) \\ [\epsilon (10^4 M^{-1} cm^{-1})]$	$\beta_{1064} (10^{-30} \text{ esu})$	$\beta_{800} (10^{-30} \text{ esu})$
$(E)-4-HC \equiv CC_6H_4CH = CHPh (2)$	339 [2.2]	37	
$1,3,5-\{(E)-4-IC_6H_4CH=CH\}_3C_6H_3$ (3)	340 [6.1]	45 (28)	
$1,3,5-\{(E)-4-HC \equiv CC_6H_4CH = CH\}_3C_6H_3$ (5)	348 [9.0]	33 (21)	
trans-[Ru{(E)-4-C=CHC ₆ H ₄ CH=CHPh}Cl(dppm) ₂]PF ₆ (11)	360 [1.5]	70	33
trans-[Ru{(E)-4-C=CC ₆ H ₄ CH=CHPh}Cl(dppm) ₂] (12)	397 [2.3]	200 ± 40	\leq 920 ^b
$ [1,3,5-(trans-[(dppm)_2ClRu{(E)-4-C=CHC_6H_4CH=CH]}_{3}C_6H_3](PF_6)_3 (14) 1,3,5-(trans-[(dppm)_2ClRu{(E)-4-C=CC_6H_4CH=CH}]_{3}C_6H_3 (15) $	396 [2.0] 415 [4.9]	$165 \pm 33 (101 \pm 62)$ $244 \pm 50 (150 \pm 92)$	$\begin{array}{r} 483 \pm 100 \ (298 \pm 62) \\ 935 \pm 31 \ (577 \pm 19) \end{array}$

^a All measurements as thf solutions (all complexes are optically transparent at 1064 and 800 nm). Reported β values are β_{333} ; numbers in brackets are $\sqrt{\langle \beta^2 \rangle}$. Errors are $\pm 10\%$ unless specified otherwise.

^b Upper bound only. No complete demodulation of the fluorescence contribution could be achieved.

results in a twofold increase in β_{800} , the latter consistent with the significant increase in ε on this structural modification, and suggestive of a similar increase in β_{1064} obscured by error margins. These complexes are rare examples of organometallics for which quadratic optical nonlinearities have been determined at more than one wavelength. The β_{800} values for **14** and **15** are much larger than their β_{1064} value, consistent with significant resonance enhancement for the former resulting from close proximity of the optical absorption maximum to the second-harmonic wavelength (400 nm). In contrast, the optical absorption maximum for **11** is more remote from the second-harmonic wavelength, and the β_{1064} value is significantly greater than the β_{800} value.

Molecular third-order nonlinearities for many of the new compounds, as determined by Z-scan at 800 nm, are collected in Table 5. Note that an electronic origin for cubic nonlinearities in related metal acetylide complexes has been demonstrated previously by degenerate four-wave mixing measurements [39], and nonlinearities for the present series of compounds are, therefore, likely to be electronic in origin. Table 5 also contains linear optical absorption maxima and extinction coefficients. In addition to the aforementioned trends in linear data, one can observe that replacing dppm by dppe in proceeding from 12 to 13 or 15 to 16 results in a redshift in λ_{max} and increase in ε , and extending the π system through the metal center (in proceeding from 16 to 17) and replacing ene- with yne-linkage [in proceeding from 16 to $1,3,5-(trans-[(dppe)_2ClRu(4-C=CC_6H_4C=$ C)])₃C₆H₃ (18) and 17 to $1,3,5-(trans-[(dppe)_2(PhC=$ C)Ru(4-C=CC₆H₄C=C)])₃C₆H₃) (19)] both result in blue-shifts in λ_{max} .

Cubic nonlinearities for the organic compounds 2 and 5 are low. We have previously reported cubic NLO data for (alkynyl)(phosphine/isocyanide/carbene)gold complexes and di(alkynyl)gold complex anions [40-42], for which nonlinearities are low in most cases. In the present system, introduction of terminal (phosphine)gold unit in proceeding from 2 to 6 results in little change in the linear optical absorption spectra and a negligible nonlinearity. The related yne-linked complexes 8 and 9 have larger nonlinearities than the ene-linked 6, but values are very small. The γ_{real} values for most of the ruthenium complexes are negative, and the γ_{imag} values are significant, consistent with two-photon effects contributing to the observed molecular nonlinearities $|\gamma|_{800}$; comment on the effect of structural variation on the magnitude of $|\gamma|_{800}$ is therefore cautious, particularly in light of the error margins. Nevertheless, several trends may be noted. Introduction of ligated ruthenium in proceeding from 5 to 14–17 results in increased γ_{real} and $|\gamma|$. Replacing dppm by dppe in proceeding from 15 to **16** leads to an increase in $|\gamma|_{800}$. Extending the π -system through the metal center, in proceeding from 16 to 17, and replacing yne with ene linkage, in proceeding from 18 to 16 and 19 to 17, result in significant increases in $|\gamma|_{800}$. To the best of our knowledge, the γ_{real} value for 17 is the largest thus far for an organometallic complex.

Table 5 also includes TPA cross-sections σ_2 calculated from γ_{imag} . Structure-activity trends are, therefore, identical with those of γ_{imag} . Thus, σ_2 values for the organic acetylenes, gold complexes and vinylidene com-

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Linear optical spectroscopic and cubic NLO response parameters ^a

Compound	$\lambda_{\max} (nm) \\ [\varepsilon (10^4 M^{-1} cm^{-1})]$	$\frac{\gamma_{real, 800}}{(10^{-36} \text{ esu})}$	$\gamma_{\text{imag, 800}}$ (10^{-36} esu)	$ \gamma _{800}$ (10 ⁻³⁶ esu)	$\sigma^{2 b}$ (10 ⁻⁵⁰ cm ⁴ s)
(E)-4-HC=CC ₆ H ₄ CH=CHPh (2)	339 [2.2]	100 ± 60	0 ± 20	100 ± 60	0 ± 5
$1,3,5-\{(E)-4-HC=CC_{6}H_{4}CH=CH\}_{3}C_{6}H_{3}$ (5)	348 [9.0]	330 ± 150	95 ± 50	340 ± 160	22 ± 12
Au{(E)-4-C=CC ₆ H ₄ CH=CHPh}(PPh ₃) (6)	338 [1.7]	0 ± 300	0 ± 50	0	0 ± 12
$Au(4-C = CC_6H_4C = CPh)(PPh_3) (8)$	336 [6.5]	-900 ± 400	0 ± 100	900 ± 400	0 ± 24
$Au(4-C \equiv CC_6H_4C \equiv CPh)(PMe_3) (9)$	335 [5.5]	-200 ± 150	0 ± 50	200 ± 150	0 ± 12
trans-[Ru{(E)-4-C=CHC ₆ H ₄ CH=CHPh}Cl(dppm) ₂]PF ₆ (11)	360 [1.5]	< 200	90 ± 50	90 ± 50	21 ± 12
trans-[Ru{(E)-4-C=CC ₆ H ₄ CH=CHPh}Cl(dppm) ₂] (12)	397 [2.3]	-600 ± 400	700 ± 400	920 ± 600	170 ± 100
trans-[Ru{(E)-4-C=CC ₆ H ₄ CH=CHPh}Cl(dppe) ₂] (13)	404 [2.9]	300 ± 400	300 ± 100	420 ± 350	70 ± 30
$[1,3,5-(trans-[(dppm)_2ClRu{(E)-4-C=CHC_6H_4CH=$	396 [2.0]	-900 ± 500	700 ± 400	1100 ± 700	170 ± 100
CH]) ₃ C ₆ H ₃](PF ₆) ₃ (14)					
$1,3,5-(trans-[(dppm)_2ClRu{(E)-4-C=CC_6H_4CH=CH}])_3C_6H_3$ (15)	415 [4.9]	-640 ± 500	2000 ± 500	$2100\pm\!600$	480 ± 120
$1,3,5-(trans-[(dppe)_2ClRu{(E)-4-C=CC_6H_4CH=CH}])_3C_6H_3$ (16)	426 [8.7]	-4600 ± 2000	$4200\pm\!800$	$6200\pm\!2000$	1000 ± 200
$1,3,5-(trans-[(dppe)_2ClRu(4-C=CC_6H_4C=C)])_3C_6H_3$ (18) ^c	414 [10.4]	-330 ± 100	2200 ± 500	$2200\pm\!600$	530 ± 120
1,3,5-(<i>trans</i> -[(dppe) ₂ (PhC=C)Ru{(E)-4-C=CC ₆ H ₄ CH=	421 [13.0]	$-11200\pm$	$8600\pm\!2000$	$14000\pm$	2100 ± 500
$CH_{3}]_{3}C_{6}H_{3}$ (17)		3000		4000	
$1,3,5-(trans-[(dppe)_2(PhC=C)Ru(4-C=CC_6H_4C=C)])_3C_6H_3$ (19) ^d	411 [11.6]	$-600\pm\!200$	2900 ± 500	3000 ± 600	690 ± 120

^a All measurements as thf solutions (all complexes are optically transparent at 800 nm).

^b Calculated using the equation $\sigma_2 = h\beta/2\pi N$, where β is the TPA coefficient [50].

° [8].

^d Ref. [6].

plex 11 are small, and progression from vinylidene to acetylide complex, linear to octopolar complex, and yne to ene linkage all result in increases in σ_2 . It is worth noting that the datum for 17 is of the same order of magnitude as that of the best organics [43,44], and one of the largest thus far for an organometallic complex [7,41].

Third-order nonlinear susceptibilities $\chi^{(3)}$ were also determined for 13, 16, and 17 by EA spectral measurements at 350-550 nm: this is the first application of EA spectroscopy to evaluate cubic nonlinearities of organometallics, although it has been utilized in this regard with organic compounds and coordination complexes [45,46]. In contrast to Z-scan, which measures $\chi^{(3)}(\omega:\omega, -\omega, \omega$) for interacting light waves of frequency ω , the quadratic EA effect measures $\gamma^{(3)}(-\omega;\omega,0,0)$ for which the zero frequencies correspond to the dc electric field; the techniques are, therefore, complementary, in that they sample different NLO interactions. The linear optical absorption maxima and $\text{Im}(\chi^{(3)})/N$ values, the imaginary parts of the EA-derived nonlinear susceptibility normalized by the number density of molecules in PMMA matrix, are summarized in Table 6. The optical absorption maxima for 13, 16, and 17 undergo blue shifts of 3-6 nm on proceeding from thf solution to solid solution in PMMA. The $Im(\gamma^{(3)})/N$ values for the complexes in PMMA reach a negative peak at wavelengths approximately 20 nm longer than λ_{max} , and a positive peak at wavelengths approximately 50 nm longer than λ_{max} . Im $(\chi^{(3)})/N$ values for 16 and 17 are not greatly different to each other, but are threefold that for 13, reflecting the number of ligated ruthenium centers in these molecules.

Very few third-order NLO data for organometallics doped into organic polymer hosts exist [47,48], and comparison to solution-derived data is rare. The $\text{Im}(\chi^{(3)})/N$ values of 13, 16, and 17 in the present work are one to two orders of magnitude larger than their molecular cubic nonlinearities γ obtained by Z-scan. There are at least two important factors giving rise to this variance. Firstly, division by a local field factor $L_{\omega}^{2}L_{0}^{2}$ is needed to convert $\chi^{(3)}/N$ to γ ; assuming $L_{\omega} =$ $(\varepsilon_{\omega}+2)/3$, one can estimate this as a factor of approximately four for these solid solution samples. Secondly,

the wavelength dispersion effects are expected to work in different ways for the two processes, although both are resonantly-enhanced. A close correspondence in Zscan and EA-derived nonlinearities, is therefore, not expected.

4. Discussion

The present studies have demonstrated the facile synthesis of novel two-dimensional octopolar alkynylgold and -ruthenium complexes incorporating phenylethenyl spacer units, as well as linear complexes corresponding to the 'legs' of these organometallic triskelia [49]. We have previously reported extension of the phenylethynyl spacer system to encompass dendritic examples [7]; extending the present series of complexes (for which 17 could be considered a zero-generation dendrimer) to include higher-generation dendrimers should (similarly) proceed smoothly. The 1.3.5-branching at the core effectively insulates the metal centers, reflected in oxidation of the ruthenium examples as assessed by cyclic voltammetry.

Introduction of phenylethenyl groups results in an increase in both quadratic and cubic NLO responses compared with those observed previously for examples constructed with phenylethynyl spacers. Quadratic nonlinearities for 14 and 15 at both 800 and 1064 nm are very large for octopolar compounds lacking strong acceptor groups. HRS data can be enhanced by fluorescence contributions. Frequency modulation has been utilized with the present complexes to confirm the fluorescence-free β_{800} data for 14 and 15, and therefore, the surprisingly large nonlinearities for these compounds.

Significant increases in molecular cubic nonlinearity $|\gamma|_{800}$ and TPA cross-section σ_2 are observed on proceeding from the linear complexes to the octopolar analogues, with the TPA cross-section for 17 one of the largest reported thus far. The significant β_{HRS} and σ_2 magnitude difference for vinylidene-acetylide complex pairs in the present studies have afforded further examples of protically-switchable NLO materials [8]. Finally, the utility of EA spectroscopy to determine

Table 6

Cubic NLO response parameters in solid solution in PMMA measured by EA spectroscopy

Compound	λ_{\max} (nm)	Im($\chi^{(3)}$)/N (negative peak) ^a (10 ⁻³⁶ esu) @ λ (nm) ^b	Im($\chi^{(3)}$)/N (positive peak) ^a (10 ⁻³⁶ esu) @ λ (nm) ^b
trans-[Ru{(E)-4-C=CC ₆ H ₄ CH=CHPh}Cl(dppe) ₂] (13)	400	-31 000 @ 420	36 000 @ 452
$1,3,5-(trans-[(dppe)_2ClRu\{(E)-4-C=CC_6H_4CH=CH\}])_3C_6H_3$ (16)	420	-120 000 @ 438	100 000 @ 472
$1,3,5-(trans-[(dppe)_2(PhC=C)Ru\{(E)-4-C=CC_6H_4CH=CH\}])_3C_6H_3$ (17)	418	-95000 @ 436	77000 @ 472

^a In order to cancel the influence of concentration, $\chi^{(3)}$ was normalized by the number density of the molecule N (cm⁻³) in PMMA matrix.

^b Peak value at the wavelength written after @.

cubic nonlinearities of organometallics has been demonstrated for the first time; the $\text{Im}(\chi^{(3)})/N$ values of the complexes studied are large and scale with the number of metal atoms.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 182950 (6). Copies of this information may be obtained, free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

M.G.H. thanks the Australian Research Council (ARC) for financial support, Johnson-Matthey Technology Center for the generous loan of ruthenium salts, the ARC for an Australian Senior Research Fellowship and the Science and Technology Agency of Japan (STA) for a Fellowship. A.P. thanks the Belgian Government (Grant No. IUAP-IV/11), the Fund for Scientific Research-Flanders (G.0338.98, G.0407.98) (AP), and the K.U. Leuven (GOA/2000/03) (AP) for support of this work. T.I. thanks the Japan Science and Technology Corporation for partial support of this work through the Core Research for Evolutional Science and Technology (CREST) program ('Hyper-Structured Molecules and Their Application to Organic Quantum Devices' project headed by Professor H. Sasabe (Chitose Institute of Science and Technology, Japan)).

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