Quadratic and Cubic Hyperpolarizabilities of Nitro-phenyl/-naphthalenyl/-anthracenyl Alkynyl Complexes†

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Abstract: The 1-nitronaphthalenyl-4-alkynyl and 9-nitroanthracenyl-10-alkynyl complexes $[M](C\equiv C-4-C_{10}H_6-1-NO_2)$ ($[M] = trans-[RuCl(dppe)_2]$ (**6b**), $trans-[RuCl(dppm)_2]$ (**7b**), $Ru(PPh_3)_2(\eta^5-C_5H_5)$ (**8b**), $Ni(PPh_3)(\eta^5-C_5H_5)$ (**9b**), $Au(PPh_3)$ (**10b**)) and $[M](C\equiv C-10-C_{14}H_8-9-NO_2)$ ($[M] = trans-[RuCl(dppe)_2]$ (**6c**), $trans-[RuCl(dppm)_2]$ (**7c**), $Ru(PPh_3)_2(\eta^5-C_5H_5)$ (**8c**), $Ni(PPh_3)(\eta^5-C_5H_5)$ (**9c**), $Au(PPh_3)$ (**10c**)) have been synthesized and their identities confirmed by single-crystal X-ray diffraction studies. Electrochemical studies and a comparison to the 1-nitrophenyl-4-alkynyl analogues $[M](C\equiv C-4-C_6H_4-1-NO_2)$ ($[M] = trans-[RuCl(dppe)_2]$ (**6a**), $trans-[RuCl(dppm)_2]$ (**7a**), $Ru(PPh_3)_2(\eta^5-C_5H_5)$ (**8a**), $Ni(PPh_3)(\eta^5-C_5H_5)$ (**9a**), $Au(PPh_3)$ (**10a**)) reveal a decrease in oxidation potential for the ruthenium and nickel complexes on proceeding from phenyl- to naphthalenyl- and then anthracenyl-containing bridge. HOMO $\rightarrow$ LUMO transitions characteristic of $MC\equiv C-1-C_6H_4$ to $4-C_6H_4-1-NO_2$ charge transfer red-shift and gain in intensity on proceeding to the ruthenium complexes; the low-energy transitions have increasing ILCT character on proceeding from phenyl- to naphthalenyl- and then anthracenyl-containing bridge. Spectroelectrochemical studies of the Ru-containing complexes reveal the appearance of low-energy bands corresponding to chloro-to- Ru^{III} charge transfer that red-shift on proceeding from phenyl- to naphthalenyl- and then anthracenyl-containing bridge. Second-order nonlinear optical (NLO) studies at 1064 nm employing ns pulses and the hyper-Rayleigh scattering technique reveal an increase in quadratic optical nonlinearity upon introduction of metal to the precursor alkyne to afford alkynyl complexes and on proceeding from ligated-gold to -nickel and then to -ruthenium for a fixed alkynyl ligand. Quadratic NLO data for the gold complexes optically transparent at the second-harmonic wavelength reveal an increase in β_{HRS} on proceeding from phenyl- to naphthalenyl-containing complex. Broad spectral range third-order nonlinear optical studies employing fs pulses and the Z-scan technique reveal an increase in two-photon absorption cross-section on replacing ligated-gold by -nickel and then -ruthenium for a fixed alkynyl ligand. Computational studies undertaken using time-dependent density functional theory have been employed to assign the nature of the key optical transitions and suggest that the significant optical nonlinearities observed for the ruthenium-containing complexes correlate with the low-energy formally $Ru \rightarrow NO_2$ band which possesses strong MLCT character, while the more moderate nonlinearities of the gold complexes correlate with a band higher in energy that is primarily ILCT in character.

Introduction

The nonlinear optical (NLO) properties of organic molecules and transition metal complexes have attracted significant interest in the drive to develop new and efficient materials for the emerging photonics technologies.^{1,2} Organometallic complexes, which can combine the advantages of organic molecules (fast NLO responses, flexibility in composition) with the functionality imparted by ligated metal centers (a diversity of coordination motifs, stabilization of reactive organic species as ligands, reversible redox processes), have understandably been the focus of substantial studies.^{3,4} Due to their robust nature, a key consideration for possible downstream applications, metallocenyl complexes, in particular, have featured in a large number of studies that have afforded structure-property relationships to optimize NLO performance.^{5,6} Although metallocenyl complexes have been

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Electronic Supplementary Information (ESI) available: Supporting information for this article contains descriptions of syntheses, full NMR and UV-Vis spectra, crystallographic data, cyclic voltammetric and spectroelectrochemical traces, details of the hyper-Rayleigh scattering and Z-scan experiments, and complete computational details and results. See DOI: 10.1039/x0xx00000x.

shown to behave as efficient NLO materials, their molecular structure (which features a metal-cyclopentadienyl charge-transfer axis orthogonal to the chromophore-functionalized cyclopentadienyl axis) may not be optimal; it has been suggested that incorporating the metal atom in the chromophore π -system may be preferable.⁷ Metal alkynyl complexes have this desirable composition and have consequently been the subject of considerable study,⁸⁻¹⁰ affording a number of key structure-NLO property correlations. For example, quadratic nonlinearities for metal alkynyl complexes were shown to increase on proceeding from 14 to 18 valence electron metal centers,¹¹⁻¹⁴ increasing the donor strength of the metal-ligated co-ligands,¹⁴ and replacing phenylalkynyl by analogous heterocyclic alkynyl ligands with lower aromatic stabilization energies.¹⁵ Efficient octupolar complexes were also identified,¹⁶ and the possibility of switching quadratic NLO properties using protic or electrochemical stimuli¹⁷ in situ or ex situ has been demonstrated with metal alkynyl complexes.¹⁸ Cubic NLO properties have also been explored and were shown to increase on increasing the size of the alkynyl ligand π -system^{8,10} and on progression to dendrimers,¹⁹ and it has been demonstrated that cubic NLO properties can be switched by protic, electrochemical, and photochemical means.²⁰⁻²²

While these aforementioned studies have demonstrated that metal alkynyl complexes can possess large quadratic and cubic NLO coefficients that can be modulated via application of external stimuli, fundamental questions remain about the most efficient π -bridge in complexes with a ligated metal donor/arylalkynyl π -bridge/acceptor composition. Specifically, while the effect of *p*-phenyleneethynylene-based bridge lengthening in such complexes has been explored,⁸ with quadratic and cubic optical nonlinearities reaching maximal values at complexes with tri(*p*-phenyleneethynylene) bridges,¹⁰ the effect of bridge "broadening" on progression from 1,4-phenylene to 1,4-naphthalenyne and 9,10-anthracenyne bridging units on NLO properties is unexplored. The pursuit of enhanced nonlinearities by bridge broadening rather than lengthening (i.e. a 2D rather than 1D approach) has clear ramifications beyond the immediate metal alkynyl complex system chosen to explore this idea. Furthermore, although 1-nitrophenyl-4-ethynyl metal complexes have been long-studied,^{11,13,23-26} no examples of 1-nitronaphthalenyl-4-ethynyl or 9-nitroanthracenyl-10-ethynyl complexes have been reported thus far. Indeed, naphthalenyl- and anthracenyl-ethynyl complexes of any type are rare (monometallic examples^{27,28}, homobimetallic examples²⁹⁻³¹), with the only extant donor-(arylalkynyl π -bridge)-acceptor complexes featuring 10-bromo- and 10-cyanoanthracenyl-9-ethynyl ligands.²⁸

The fundamentally important question of increasing nonlinearity by bridge broadening vs lengthening therefore necessitates urgent study, while the lack of nitronaphthalenyl-/anthracenylalkynyl complexes is peculiar given the extensive reports of nitrophenylalkynyl complexes (the archetypical donor-bridge-acceptor metal alkynyl complex). To address these omissions, we report herein the syntheses of a

range of systematically-varied complexes incorporating these new nitro-functionalized bridging units, X-ray studies structurally authenticating all examples, comprehensive spectroscopic, electrochemical, and spectroelectrochemical studies of these complexes and comparison to the previously-reported 1-nitrophenyl-4-ethynyl complex analogues, quadratic and cubic NLO studies to identify the most efficient bridging unit(s), and time-dependent density functional theory (TD-DFT) calculations on model compounds to rationalize the experimental studies.

Results and Discussion

Synthesis. The syntheses of the new alkynyl complexes necessitated access to the alkynes 4-ethynyl-1-nitronaphthalene and 10-ethynyl-9-nitroanthracene, which were prepared by extending established protocols for the syntheses of terminal acetylenes. Thus, treatment of commercially available 1-iodo-4-nitronaphthalene with ethynyltrimethylsilane under Sonogashira³² conditions afforded the silyl-protected 1-nitro-4-(trimethylsilylethynyl)naphthalene **1**,³³ subsequent deprotection with potassium carbonate yielding the terminal acetylene 4-ethynyl-1-nitronaphthalene **2** in excellent yield (Scheme 1). Compound **2** has been reported previously³⁴ from the coupling of ethynyltriisopropylsilane with 4-nitro-1-(trifluoromethylsulfonyl)naphthalene and then desilylation, the new preparation proceeding in higher yield. Preparation of the anthracenyl analogue proceeded via nitration of 9-bromoanthracene using NaNO_3 and a mixture of trifluoroacetic acid and acetic anhydride, to give 9-bromo-10-nitroanthracene **3**, Sonogashira coupling with ethynyltrimethylsilane to give 9-nitro-10-(trimethylsilylethynyl)anthracene **4**, and then desilylation to afford the desired terminal acetylene 10-ethynyl-9-nitroanthracene **5**. This synthesis of **3** was found to be superior to the literature procedure; in our hands, the alternative route to **3**³⁵ through bromination of 9-nitroanthracene afforded a mixture of the desired product (43%) and 9,10-dibromoanthracene (20%), requiring separation by chromatography. Thus, the new syntheses of both alkynes are superior to the existing literature preparations. The organic compounds were characterized by a combination of IR, UV-vis,

Scheme 1. Syntheses of alkynes **2** and **5**. Conditions: a $\text{PdCl}_2(\text{PPh}_3)_2$, CuI , NEt_3 or $\text{CH}_2\text{Cl}_2/\text{NEt}_3$, 35 °C, overnight. b K_2CO_3 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$. c trifluoroacetic acid/acetic anhydride, 2 h.

Scheme 2. Syntheses of metal alkynyl complexes **6b,c** – **10b,c**.

¹H and ¹³C NMR spectroscopies (Electronic Supplementary Information, Figures S1–S6) and mass spectrometry.

The preparation of the new ruthenium-, nickel- and gold-containing alkynyl complex derivatives of acetylenes **2** and **5** was achieved using extensions of established methodologies for related metal alkynyl complex syntheses^{8,11,13,23,24} (Scheme 2). Reaction between the five-coordinate complex [RuCl(dppe)₂]PF₆³⁶ and **2** or **5** proceeded smoothly in dichloromethane at ambient temperature to yield the corresponding vinylidene complexes. These were precipitated from petroleum spirits (60–90 °C), washed to remove the excess acetylene, and then redissolved in dichloromethane and treated with a few drops of triethylamine to effect deprotonation and afford the desired alkynyl complexes *trans*-[Ru(C≡C-4-C₁₀H₆-1-NO₂)Cl(dppe)₂] (**6b**) and *trans*-[Ru(C≡C-10-C₁₄H₈-9-NO₂)Cl(dppe)₂] (**6c**). The bis(diphenylphosphino)methane analogues were prepared from the dichloro complex *cis*-[RuCl₂(dppm)₂]^{37,38} by reaction with **2** or **5** in the presence of sodium hexafluorophosphate, followed by in situ deprotonation of the intermediate vinylidene complex with triethylamine to afford *trans*-[Ru(C≡C-4-C₁₀H₆-1-NO₂)Cl(dppm)₂] (**7b**) and *trans*-[Ru(C≡C-10-C₁₄H₈-9-NO₂)Cl(dppm)₂] (**7c**) in moderate yields. Reactions between **2** or **5** and RuCl(PPh₃)₂(η⁵-C₅H₅) required heating in refluxing methanol for 1 h, followed by treatment of the resulting vinylidene complexes with sodium methoxide to give Ru(C≡C-4-C₁₀H₆-1-NO₂)(PPh₃)₂(η⁵-C₅H₅) (**8b**) and Ru(C≡C-10-C₁₄H₈-9-NO₂)(PPh₃)₂(η⁵-C₅H₅) (**8c**) after chromatography. The nickel-containing complexes were prepared from prolonged stirring of **2** or **5** with NiCl(PPh₃)₂(η⁵-C₅H₅) in a mixture of dichloromethane and triethylamine at room temperature, affording Ni(C≡C-4-C₁₀H₆-1-NO₂)(PPh₃)₂(η⁵-C₅H₅) (**9b**) and Ni(C≡C-10-C₁₄H₈-9-NO₂)(PPh₃)₂(η⁵-C₅H₅) (**9c**), while the gold-containing alkynyl complexes Au(C≡C-4-C₁₀H₆-1-NO₂)(PPh₃) (**10b**) and Au(C≡C-10-C₁₄H₈-9-NO₂)(PPh₃) (**10c**) were formed in excellent yield by treating a solution of AuCl(PPh₃) in sodium methoxide/methanol with **2** or **5** over 16 h at ambient temperature.

The new complexes were characterized by IR and NMR spectroscopy (Figures S7–S36), and mass spectrometry. The characteristic ν(C≡C) stretching modes in the vibrational spectra range from 2001 to 2106 cm^{−1} (Table 1), with an increase in frequency observed in proceeding from the ruthenium- through the nickel- to the gold-containing complexes. This mirrors observations with the corresponding 1-nitrophenyl-4-alkynyl complexes, and correlates with a decreasing importance of a charge-separated [M]⁺=C=C=R[−] contributor as electron density at the ligated metal center decreases. Varying the alkynyl ligand while maintaining a constant ligated-metal unit results in a shift to lower frequency of the ν(C≡C) band on proceeding from 1-nitrophenyl-4-alkynyl to 1-nitronaphthalenyl-4-alkynyl to 9-nitroanthracenyl-10-alkynyl

Table 1. Spectroscopic and electrochemical data.^[a]

R	O ₂ N-	O ₂ N-	O ₂ N-
<i>trans</i> -[RuCl(dppe) ₂]	6a	6b	6c
<i>trans</i> -[RuCl(dppm) ₂]	7a	7b	7c
Ru(PPh ₃) ₂ (η ⁵ -C ₅ H ₅)	8a	8b	8c
Ni(PPh ₃) ₂ (η ⁵ -C ₅ H ₅)	9a	9b	9c
Au(PPh ₃)	10a	10b	10c

Comp.	ν _{max} ^[b] (ε) ^[c]	IR ^[b] ν(C≡C)	E _{1/2} ([M], V) ^[d] [ΔE (V), i _{pc} /i _{pa}]	E _{1/2} ([NO ₂], V) ^[d] [ΔE (V), i _{pc} /i _{pa}]
6a	20,500 (2.0)	2052 ^[e]	0.74 ^[f] , 0.9 ^[e]	-1.10 ^[f] , 0.9 ^[e]
6b	18,900 (2.4)	2010	0.69 [0.07, 1]	-1.10 [0.09, 1]
6c	18,250 (2.1)	2001	0.60 [0.08, 0.9]	-1.10 [0.10, 0.9]
7a	20,800 [1.6]	2045 ^[g]	0.72 ^[f] , 0.9 ^[g]	-1.08 ^[f] , 0.7 ^[g]
7b	19,300 (1.9)	2023	0.69 [0.06, 1]	-1.06 [0.09, 0.9]
7c	18,200 (1.2)	2002	0.57 [0.08, 1]	-1.09 [0.09, 1]
8a ^[h]	21,200 (1.9)	2063	0.73 ^[f] , 1	-1.08 ^[f] , 1
8b	20,100 (1.5)	2040	0.74 [0.08, 1]	-1.08 [0.14, irrev]
8c	18,600 (1.9)	2024	0.69 [0.06, 0.9]	-0.97 [0.08, 0.9]
9a ^[i]	22,800 (0.9)	2091	0.90 ^[f] , 0.4	-0.97 ^[f] , 0.7
9b	22,100 (1.6)	2073	0.88 [0.12, irrev]	-0.99 [0.18, 0.8]
9c	20,600 (1.6)	2075	0.86 [0.10, 0.9]	-0.99 [0.15, 0.8]
10a ^[j]	29,600 (2.5)	2116	^[f]	^[f]
10b	25,900 (1.7)	2106	^[k]	-0.91 [0.07, 1]
10c	23,500 (1.1)	2086	^[k]	-0.93 [0.18, 0.8]

[a] Measured as CH₂Cl₂ solutions unless specified otherwise; [b] Frequency of the low-energy optical absorption maximum in cm^{−1}; [c] Corresponding extinction coefficient in 10⁴ M^{−1} cm^{−1}; [d] Pt disc working-, Pt wire auxiliary-, and Ag/AgCl reference electrodes; ferrocene/ferrocenium redox couple at 0.56 V (i_{pc}/i_{pa} 0.9 – 1, ΔE 0.07 – 0.09 V); [e] Ref. 8, IR as KBr disc; [f] Not reported; [g] Ref. 24, IR as KBr disc; [h] Ref. 23, IR as solution in cyclohexane; [i] Ref. 12; [j] Ref. 13; [k] Not observed.

Figure 1. Molecular structures of **10b** (top) and **7c** (bottom), with thermal ellipsoids set at the 40% probability level. Hydrogen atoms and the lattice dichloromethane molecule (in the case of **10b**) have been omitted for clarity.

ligand. This mirrors observations with the corresponding terminal acetylene precursors [$\nu(\text{C}\equiv\text{C})$ 4-ethynyl-1-nitrobenzene 2105 cm^{-1} , 4-ethynyl-1-nitronaphthalene 2100 cm^{-1} , 10-ethynyl-9-nitroanthracene 2097 cm^{-1}], although the difference in frequency in proceeding from phenyl through naphthalenyl to anthracenyl bridge is lower for the terminal alkynes. Singlets are observed in the ^{31}P NMR spectra for **6b,c** and **7b,c**, confirming *trans*-stereochemistry. A small upfield shift is seen on proceeding from naphthalenyl to anthracenyl complex analogue that decreases in magnitude on proceeding from Ru to Ni; the Au complexes **10b,c** resonate at the same chemical shift. The mass spectra of the Ru and Ni complexes contain molecular ions, accompanied for **6b,c** and **7b,c** by competitive loss of chloro and alkynyl ligands; the mass spectra of the Au complexes contain Au(PPh₃) adducts of the molecular ion together with an ion corresponding to [Au(PPh₃)₂]⁺.

Single-crystal X-ray structural studies confirmed the molecular compositions of **4**, **5**, **6b,c**, **7b,c**, **8b,c**, **9b,c** and **10b,c**, and the previously reported *trans*-[Ru(C $\equiv$ C-4-C₆H₄-1-NO₂)Cl(dppe)₂] (**6a**).²⁵ Thermal ellipsoid plots for selected examples, **10b** and **7c**, are given in Figure 1; cell data, other plots and selected bond lengths and angles, together with comparable data for the previously structurally characterized 1-nitrophenyl-4-ethynyl analogues [M](C $\equiv$ C-4-C₆H₄-1-NO₂) ([M] = *trans*-[RuCl(dppe)₂] (**7a**),²⁶ Ru(PPh₃)₂(η^5 -C₅H₅) (**8a**),²³ Ni(PPh₃)(η^5 -C₅H₅) (**9a**),³⁹ Au(PPh₃) (**10a**)¹³) are collected in Figures S37-S47 and Tables S1 and S2 (Electronic Supplementary Information). The bond parameters are within the ranges of those of precedent structures. More importantly, there are no significant differences in proceeding from phenylene to naphthalenylene and anthracenylene bridge for a given ligated metal centre (i.e. proceeding from **a** complexes to

b complexes and then **c** complexes), the bond parameters being insensitive to this structural modification.

Electrochemical, spectroscopic, and spectroelectrochemical measurements. Cyclic voltammetric studies were undertaken for each of the ruthenium/nickel-containing complexes **6b,c**, **9b,c** (Figures S48-S55), with relevant parameters collected in Table 1. The cyclic voltammograms (CVs) of the ruthenium naphthalenyl complexes **6b-8b** show reversible formally Ru^{II/III} oxidation processes at potentials of ca. 0.69-0.74 V, typical of ruthenium alkynyl complexes with a nitro electron-withdrawing group.^{8,12,13,15} The analogous anthracenyl complexes **6c-8c** were more easily oxidized (0.57-0.69 V), but only the dppe-containing example was completely reversible under the standard conditions used (ambient temperature, scan rate 100 mV s⁻¹). The CVs of the nickel-containing complexes **9b** and **9c** each showed non-reversible oxidation processes at ca. 0.9 V, and all complexes, **6b-10b** and **6c-10c**, showed reduction of the nitro group at ca. -0.9 to -1.1 V with varying reversibility. Comparing across the three different π -bridge systems, the potentials for the oxidation processes generally decrease as the π -bridge size increases, i.e. [M](C $\equiv$ C-4-C₆H₄-1-NO₂) > [M](C $\equiv$ C-4-C₁₀H₆-1-NO₂) > [M](C $\equiv$ C-10-C₁₄H₈-9-NO₂).

The evolution of the linear optical absorption spectra as a function of the metal centre, π -bridge, and the ligand environment is also of interest. UV-vis-NIR data were obtained for complexes **6b,c**, **10b,c**; band maxima are listed in Table 1 and the spectra collected in Figure S56. The naphthalenyl complexes **6b-10b** are optically transparent at frequencies < 15,000 cm^{-1} (670 nm), whereas the anthracenyl complexes **6c-10c** are transparent below ca. 14,000 cm^{-1} (700 nm). There is little variation in the maximum absorption peak across the ruthenium complexes for each alkynyl ligand, with a slight blue shift on moving from the chelating phosphine to the cyclopentadienyl compounds (ca. 1,000 and 400 cm^{-1} , for the naphthalenyl (**6b-8b**) and anthracenyl complexes (**6c-8c**), respectively). Moving from the 18e ruthenium to the analogous 18e nickel complexes also results in a blue shift (ca. 2,000 cm^{-1}), with a larger shift seen on proceeding to the 14e gold complexes (ca. 4,000 and 3,000 cm^{-1} , respectively). Modification of the UV-vis spectra on π -bridge variation is illustrated in Figures S57-S61. Increasing the π -bridge size of the alkynyl ligand results in a red shift in the absorption maxima across each of the metal centres. The nature of these low-energy bands is discussed in more detail in the **Computational studies** section.

In situ oxidation of metal-containing complexes using an optically transparent thin-layer electrochemical (OTTLE) cell offers a convenient method for accessing spectroscopic data of oxidized metal complexes.^{10,17,20-22,40-43} Application of potentials slightly higher than those indicated by the cyclic voltammetric data to dichloromethane solutions of the naphthalenylalkynyl and anthracenylalkynyl complexes (**6b**, **7b** and **6c**, **7c**, respectively), in addition to the phenylalkynyl complexes **6a**²⁵ and **7a**²⁴ for comparison, afforded a smooth change in the UV-vis-NIR spectra from those of the formally Ru^{II} resting-state of each complex to those of the corresponding oxidized Ru^{III} species (Table 2). All complexes show similar changes in their

Table 2. Spectroelectrochemical data for selected ruthenium alkynyl complexes.^[a]

R			
<i>trans</i> -[RuCl(dppe) ₂]	6a	6b	6c
<i>trans</i> -[RuCl(dppm) ₂]	7a	7b	7c
Comp.	$\nu_{\max}^{[b]} [\epsilon]^{[c]}$ Ru ^{II}	$\nu_{\max}^{[b]} [\epsilon]^{[c]}$ Ru ^{III}	
6a	20,500 [2.0], 38,500 [4.8]	11,600 [0.8], 16,210 [0.2], 21,300 [0.4], 25,300 [1.0], 29,800 [1.3], 36,550 [4.4]	
7a	20,800 [1.6], 37,100 [0.7], 37,500 [4.2]	11,900 [0.6], 16,500 [0.2], 21,200 [0.5], 25,900 [1.1], 30,100 [1.3], 35,200 [3.9]	
6b	18,750 [2.1], 28,350 [0.3], 38,950 [4.9]	10,550 [0.7], 20,860 [1.1], 37,650 [4.2]	
7b	19,200 [2.1], 28,650 [0.4], 38,250 [4.5]	10,750 [0.6], 19,250 [sh, 0.7], 20,950 [1.0], 37,250 [4.2]	
6c	18,100 [1.5], 33,400 [1.4], 39,300 [8.3]	8,300 [1.0], 9,800 [0.3], 15,300 [1.0], 16,700 [1.6], 26,900 [0.6], 29,100 [0.7], 37,500 [6.3]	
7c	18,300 [1.4], 33,500 [1.5], 39,200 [7.5]	8,400 [0.9], 9,800 [0.3], 15,300 [1.5], 16,800 [1.5], 26,900 [0.6], 29,000 [0.7], 37,600 [6.2]	

[a] Electronic spectra were obtained at room temperature in CH₂Cl₂; [b] Frequency of the optical absorption maxima in cm⁻¹; [c] Corresponding extinction coefficient in 10⁴ M⁻¹ cm⁻¹.

Figure 2. UV-vis-NIR (CH₂Cl₂) spectral progression obtained on oxidation of *trans*-[Ru(C≡C-10-C₁₄H₈-9-NO₂)Cl(dppm)₂] (**7c**).

electronic spectra on oxidation, with spectral progressions affording isosbestic points (Figure 2 and Figures S62–S66 in the Electronic Supplementary Information). In each case, new bands appear in the low-energy spectral region that is transparent for the parent complexes, the new bands at lowest energy being assigned broadly to chloro-to-Ru^{III} charge transfer by analogy with observations for non-nitro-containing alkynyl complexes⁴¹ (calculations on *trans*-[Ru(C≡CPh)Cl(PH₃)₄]⁺ have

assigned the lowest energy bands (here 11,600 cm⁻¹ (**6a**) and 11,900 cm⁻¹ (**7a**)) to Cl p_y → Ru d_{yz} + C₂R and those at next-lowest energy (here 16,210 cm⁻¹ (**6a**) and 16,500 cm⁻¹ (**7a**)) to Ru d_{yz} + C₂R → Ru d_{yz} + C₂R).²²

Comparisons across the complexes show that these new low-energy bands shift to significantly lower energy on moving from the nitrophenyl- (**6a**, **7a**) through the nitronaphthalenyl- (**6b**, **7b**) to the nitroanthracenyl-alkynyl complexes (**6c**, **7c**), and that $\nu_{\max}$ values for the dppm-containing complexes (**7a–c**) are slightly blue-shifted compared to those of the dppe-containing analogues (**6a–c**). Interestingly, the transitions at ca. 8,000 cm⁻¹ for **6c** and **7c** are similar in energy to those of the bis-alkynyl complex cation [Ru(C≡CPh)(C≡C-1-C₆H₄-4-C≡CPh)(dppe)₂]⁺ (8,440 cm⁻¹)⁴⁰ and the trimetallic complex trication [1,3,5-{*trans*-(dppe)₂(PhC≡C)Ru(C≡C-1-C₆H₄-4-C≡C)}₃C₆H₃]³⁺ (8,430 cm⁻¹),⁴¹ both of which contain linearly extended π -delocalizable ligands.

Hyper-Rayleigh scattering studies. Electric field-induced second-harmonic generation and hyper-Rayleigh scattering (HRS) have been widely employed to determine molecular first hyperpolarizabilities of organometallic complexes.^{3–6,9,18,44} In the present studies, the quadratic NLO properties of **2**, **4**, **6b,c**, **10b,c** were assessed by employing the HRS technique and 20 ns 1064 nm pulses (Figures S67–S72); complex **10c** fluoresced strongly, rendering measurement of its HRS activity impossible (Figure S73). The results are collected in Table 3, together with data for the previously reported 1-nitrophenyl-4-alkynyl complexes **6a–10a**. The UV-vis spectra of many of the complexes display absorption bands close to the second-harmonic wavelength (532 nm); many of the resulting β values are therefore resonance enhanced. It is possible to apply a two-level correction to calculate the frequency-independent quadratic nonlinearities, so we have pursued this with the simple two-level model as well as a modified model incorporating damping factors (we recognize that this approach is not completely satisfactory and have discussed its shortcomings in previous reports: see, for example, references 13 and 45). For the simple two-level model,⁴⁶ the $\langle\beta_0\rangle$ values were calculated using the following equation:

$$\langle\beta\rangle_{\text{HRS}} = \langle\beta_0\rangle D_0(\lambda)$$

$$D_0(\lambda) = 1/[(1-\lambda_{\max}^2/\lambda^2)(1-4\lambda_{\max}^2/\lambda^2)]$$

where λ is the fundamental wavelength of the laser (1064 nm). For the modified two-level model,⁴⁷ the $\langle\beta_0\rangle$ values were calculated using the following equation:

$$\langle\beta\rangle_{\text{HRS}} = \langle\beta_0\rangle F(\nu, \delta)$$

$$F(\nu, \delta) = (1/3) \{ [2/(1+2\nu) - 1/(1-\nu^2) + 2(1-2\nu)/\{(1-2\nu)^2 + \delta^2\}]^2 + [2\delta/((1-2\nu)^2 + \delta^2)]^2 \}^{1/2}$$

where $\nu = \lambda_{\max}/\lambda$, $\delta = \Delta/\lambda_{\max}$, Δ is a damping factor associated with the broadening of the absorption peak, and λ is the fundamental wavelength (1064 nm). If $\Delta = 0$, then the modified two-level model collapses to the simple two-level model. Note that if we choose a different Δ , the $\langle\beta_0\rangle$ values calculated using the modified two-level model will vary, depending on how close the $\lambda_{\max}$ value is to the second-harmonic wavelength 532 nm. If $\lambda_{\max}$ is far from 532 nm, $\langle\beta_0\rangle$ will vary little. However, if $\lambda_{\max}$ is

close to 532 nm, then $\langle\beta_0\rangle$ will increase when Δ is large. The $\Delta = 20$ employed in the calculations was estimated from the peak widths in the UV-Vis spectra.

Table 3. Data from HRS measurements.^[a]

R
H	-	2	-
SiMe ₃	-	-	4
<i>trans</i> -[RuCl(dppe) ₂]	6a	6b	6c
<i>trans</i> -[RuCl(dppm) ₂]	7a	7b	7c
Ru(PPh ₃) ₂ (η -C ₅ H ₅)	8a	8b	8c
Ni(PPh ₃)(η -C ₅ H ₅)	9a	9b	9c
Au(PPh ₃)	10a	10b	10c

Comp.	6a ^[e]	7a ^[f]	8a ^[g]	9a ^[h]	10a ^[i]
λ_{max}	488	481	472	440	338
β	670	767	468	221	22
β_0 ^[b]	105	129	96	59	12

Comp.	2	6b	7b	8b	9b	10b
λ_{max}		530	520	495	450	385
β	23	902	1,069	746	595	66
β_0 ^[b]		5	36	79	139	27
β_0 ^[c]		51	72	91	145	28

Comp.	4	6c	7c	8c	9c	10c
λ_{max}		545	550	535	485	425
β	52	441	898	872	580	^[d]
β_0 ^[b]		-16	-45	-7	78	^[d]
β_0 ^[c]	29	67	50	86	^[d]	

[a] Measured at 1064 nm in THF; Wavelength of optical absorption maximum λ_{max} in nm, quadratic optical nonlinearity β and two-level-corrected quadratic optical nonlinearity β_0 in 10^{-30} esu, β values $\pm 15\%$, *p*-nitroaniline 21.4×10^{-30} esu;⁴⁸ [b] β_0 calculated with the simple two-level model; [c] β_0 calculated with the modified two-level model, with $\Delta = 20$ nm; [d] solution exhibited fluorescence; [e] Ref. 45; [f] Ref. 15; [g] Ref. 14; [h] Ref. 11; [i] Ref. 13.

The data in Table 3 permit several conclusions to be drawn. Incorporation of ligated metal center (proceeding from **2** to **6b-10b** or **4** to **6c-10c**) results in a significant increase in β_{1064} value. Proceeding from gold to nickel and then ruthenium complex (**10a,b**, - to **9a-c** and then to **6a-c/7a-c/8a-c**) generally results in an increase in β values, consistent with previous observations of replacing a 14-electron gold center with 18-electron nickel or ruthenium centers, or replacing the less readily oxidized/less polarizable 3d metal nickel with the more readily oxidized/more polarizable 4d metal ruthenium.¹¹ These broad trends have some inconsistencies, primarily in instances where there are absorption bands close to the second-harmonic wavelength of the laser (i.e. close to 532 nm), and

resulting from the aforementioned problems of accounting for resonance enhancement and damping. Proceeding from phenyl through naphthalenyl to anthracenyl bridge (i.e. from complexes **6a-10a** to the analogous complexes **6b-10b** and then **6c-10c**) results in a significant increase in β value on the initial bridge broadening of the ruthenium and nickel examples, to afford the naphthalenyl complexes, but no further improvement (and indeed a significant decrease when proceeding from **6b** to **6c**) on further bridge broadening to afford the anthracenyl complexes. The β_0 values do not shed further light on these unclear trends with ruthenium and nickel, and indeed are suggestive of a decrease in quadratic NLO merit on bridge broadening, presumably related to the difficulty in accounting for resonance enhancement/damping due to proximity of absorption bands to the second-harmonic wavelength. The gold complexes exhibit lower β values in an absolute sense, but their absorption bands are further removed from the second-harmonic wavelength, which has proven useful in establishing structure-property relationships in earlier studies.¹³ Upon bridge broadening the gold complexes (proceeding from **10a** to **10b**), the β and β_0 values increase significantly. These limited gold data are suggestive of bridge broadening being a useful structural modification to enhance quadratic nonlinearity if the linear absorption bands are sufficiently removed from the second-harmonic wavelength.

Z-scan studies. Degenerate four-wave mixing and Z-scan have been extensively used to determine molecular second hyperpolarizabilities of organometallic complexes.^{3,4,9,44} In the current work, the cubic NLO properties of selected examples (ruthenium complexes **6a-c**, nickel complexes **9b,c**, and gold complexes **10b,c**) were assayed by employing the Z-scan technique⁴⁹ over a broad wavelength range (from the onset of significant one-photon absorption to the wavelength region of negligible nonlinear optical activity); results and maximal values for the complexes are collected in Table 4 and data are presented in Figures S74-S87. The refractive nonlinearities γ_{real}

Table 4. Summary of third-order nonlinearity data.^[a]

Comp.	λ [b]	γ_{re} [c]	γ_{im} [c]	$ \gamma $ [c]	σ_2 [d]
6a	740	-1 ± 20	8 ± 2	8 ± 20	220 ± 45
	940	90 ± 30	20 ± 8	95 ± 30	390 ± 140
6b	660	-950 ± 140	80 ± 15	950 ± 140	$2,800 \pm 560$
	940	-520 ± 55	40 ± 6	520 ± 55	690 ± 130
9b	640	12 ± 15	15 ± 3	19 ± 15	580 ± 95
	920	-16 ± 25	13 ± 3	20 ± 25	230 ± 55
10b	580	-2 ± 15	18 ± 30	18 ± 15	850 ± 130
	820	-16 ± 10	20 ± 6	26 ± 10	470 ± 140
6c	720	-5 ± 30	35 ± 5	35 ± 30	$1,100 \pm 150$
	880	-240 ± 35	28 ± 6	240 ± 35	570 ± 120
9c	660	-65 ± 15	13 ± 2	70 ± 15	460 ± 75
	920	-5 ± 25	15 ± 4	16 ± 25	270 ± 60
10c	700	-14 ± 10	19 ± 4	24 ± 10	630 ± 75
	920	-75 ± 20	10 ± 3	75 ± 20	180 ± 40

[a] Measured in CH_2Cl_2 ; [b] wavelength in nm; [c] real (γ_{re}) and imaginary (γ_{im}) components of the third-order optical nonlinearity in 10^{-34} esu; [d] two-photon absorption cross-section in GM units: $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s}$.

are generally negative across this spectral range. The ruthenium and nickel complexes appear to exhibit very large values of nonlinear absorption at short wavelengths, the negative values suggesting saturable absorption corresponding to the linear absorption in this region. The low-energy two-photon absorption (TPA) maxima of the ruthenium complexes increase in maximal value upon proceeding from the phenyl-bridged **6a** to the naphthalenyl-bridged **6b**, but do not change (within the experimental error margins) in proceeding further to the anthracenyl-bridged **6c**.

The maximal values of the TPA cross-sections observed in the 900-950 nm region increase in proceeding from the gold to nickel complexes and onto the ruthenium complexes. Thus, the key factor in enhancing cubic NLO parameters in this wavelength region for this series of complexes is the ligated metal centre functioning as a donor group in these donor- π -bridge-acceptor complexes, and not the π -bridge. This optimization in performance corresponds to proceeding from a

14 valence electron metal center (gold) to an 18 valence electron metal center with a 3d less polarizable and less readily oxidized metal (nickel), and then to an 18 valence electron metal center with a 4d metal that is more polarizable and more readily oxidized (ruthenium). Overall, the TPA cross-sections for these complexes are moderate in magnitude.

Computational studies. The considerable interest in the NLO properties of metal alkynyl complexes has resulted in a large number of computational studies rationalizing linear and nonlinear optical behaviour of this intriguing class of complex.^{45,50-59} In the present work, TD-DFT studies were carried out to rationalize the optical properties of these complexes and further understand the impact of bridge modification across the phenylene / naphthalenylene / anthracenylene series. In the current studies, model complexes were used for computational expediency with phenyl groups in the dpmm and PPh_3 ligands replaced by methyl groups. Our previous calculations on similar alkynyl complexes confirmed that such a substitution has a minor effect on calculated low-energy peak positions and intensities.⁵³ All calculations in the current work were carried out for isolated molecules in the gas phase as our earlier studies demonstrated that this approximation does not influence the *relative* outcomes.⁵³

The DFT energies of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for each complex are reported in Table 5, together with the energies for the HOMO-LUMO gaps ($\Delta_{\text{H-L}}$) and percentage contributions to the HOMOs and LUMOs. $\Delta_{\text{H-L}}$ energies for the 1-nitrophenyl-4-alkynyl complexes decrease in the order **10a'** > **9a'** > **8a'** (where ' corresponds to the computational analogues of the experimental complexes). The HOMOs of **8a'** and **9a'** (Figure 3) have significant contributions from the respective metals, i.e. 30% - 35% (Table 5). The LUMOs are similar in composition for **8a'** and **9a'**, and mostly localized on the

Figure 3. Selected frontier molecular orbitals for **7a'-c'**, **8a'**, **9a'**, and **10a'**.

nitrophenyl group (Figure 3). The calculated compositions of the HOMO and LUMO for **8a'** and **9a'** are in reasonable agreement with the earlier electrochemical studies.^{11,23} In contrast, the comparatively electron deficient Au center of **10a'** (metal valence electron count 14) provides a smaller contribution to the HOMO (~7%) and significantly stabilizes the HOMO (Figure 3), leading to a significant increase in the $\Delta_{\text{H-L}}$ value for **10a'** (Table 5). Co-ligand variation from **8a'** to **7a'** has a minor effect on the energies of the frontier orbitals, and thus the HOMO-LUMO gaps for **8a'** and **7a'** are roughly the same. The π -bridge modifications (i.e. proceeding from phenyl to naphthalenyl to anthracenyl) stabilize the LUMO significantly relative to the HOMO, resulting in a substantial decrease in the HOMO-LUMO gap (proceeding from **7a'** to **7b'** and then to **7c'**). From Table 5, it can also be seen that metal and nitro character in the HOMO and LUMO orbitals decreases with the same bridge variation.

TD-DFT calculations were undertaken in order to rationalize the low-frequency linear optical behaviour of complexes **7a-c** and **8a-10a**. Calculated wavenumbers and oscillator strengths for low-energy transitions are reported in Table 6, together with the frontier molecular orbitals involved. Isodensity plots of the molecular orbitals are shown in Figure 3. The excellent agreement between experimental and TD-DFT data, in particular the lowest-energy band positions, suggests that the model complexes are adequate for rationalizing the optical properties of the full systems.

For all complexes, an intense low-energy peak is seen in both experimental and calculated UV-vis spectra. The lowest-energy band (associated with the HOMO $\rightarrow$ LUMO transition) is substantially red-shifted on proceeding from **10a'** to **9a'** and then to **8a'**, as the $\Delta_{\text{H-L}}$ energy decreases upon metal variation (i.e. $\Delta_{\text{H-L}}(20') > \Delta_{\text{H-L}}(19') > \Delta_{\text{H-L}}(18')$). On the basis of the DFT/TD-DFT data, the band at ca. 21,000 cm^{-1} in the UV-vis spectrum of **8a** is predominantly MLCT with some ILCT contribution. For **9a**, in addition to contributions from MLCT and ILCT there is also a significant contribution from LLCT to the experimental band at ca. 23,000 cm^{-1} , because the cyclopentadienyl group also makes a significant contribution to the HOMO in **8a'** (Table 6 and Figure 3). This band is primarily ILCT with some MLCT

contribution for **10a**. The higher energy band at ca. 28,000 cm^{-1} in the UV-vis spectrum of **9a** can also be assigned to a mixture of MLCT, ILCT and LLCT on the basis of the calculated UV-vis data for **9a'**.

Ligand replacement, on proceeding from **8a** to **7a**, leads to a small red shift in the location of the absorption maximum; the calculated UV-vis data are consistent with the experimental data, the red-shifted peak in **7a** being attributable to a slight decrease in the HOMO-LUMO gap on proceeding from **8a** to **7a**. According to both experimental and calculated data, π -bridge variation has a profound effect on linear optical properties, more specifically on the lowest energy band. When the phenylene group is replaced with a naphthalenylene moiety, the absorption maximum is red-shifted markedly. For example, bridge variation on proceeding from **7a** to **7b** results in a red shift of ca. 2000 cm^{-1} in the lowest energy band, while the introduction of an anthracenylene moiety leads to a further decrease in excitation energy for this transition, consistent with the HOMO-LUMO gap decrease seen upon π -bridge variation in the DFT calculations. The $\text{RuC}\equiv\text{C}$ -based HOMO and the 4- C_6H_4 -1- NO_2 -localized LUMO for **7a'** can be clearly seen in Figure 3, and thus the experimental absorption band at ca. 21,000 cm^{-1} is predominantly MLCT in nature. In contrast, the absorption band in the UV-vis spectrum of **7c** possesses strong ILCT character as the anthracenylene group makes a significant contribution to the frontier orbitals (Table 6).

The static first hyperpolarizabilities, β_{tot} , were calculated for each model complex using the same method and basis sets as for the above-mentioned TD-DFT calculations. In addition, β_{tot} values of **10a** and **8a** were calculated for comparison with the experimental data. Note that the intent of the present studies is to reproduce experimental β trends, and not the absolute

Table 6. Experimental and calculated linear optical data.^[a]

Complex	ν_{max} [e]	Model	ν_{max} [f_{os}] (calc)	Composition (wt%)	Major assignment
10a	29900 (2.5)	10a'	28720 (0.703)	H $\rightarrow$ L (98)	$\text{Au}(d_{yz}) + \text{C}_2\text{-Phe}(\pi) \rightarrow \text{C}_2\text{-Phe-NO}_2(\pi^*)$
9a	22600 (1.1) 28100 (1.2)	9a'	23720 (0.370) 30880 (0.287)	H $\rightarrow$ L (98) H-1 $\rightarrow$ L (97)	$\text{Cp}(\pi) + \text{Ni}(d_{xz}) + \text{C}_2\text{-Phe}(\pi) \rightarrow \text{C}_2\text{-Phe-NO}_2(\pi^*)$ $\text{Cp}(\pi) + \text{Ni}(d_{xz}) + \text{C}_2\text{-Phe}(\pi) \rightarrow \text{C}_2\text{-Phe-NO}_2(\pi^*)$
8a	21200 (1.9)	8a'	22950 (0.622)	H $\rightarrow$ L (99)	$\text{Cp}(\pi) + \text{Ru}(d_{yz}) + \text{C}_2\text{-Phe}(\pi) \rightarrow \text{Phe-NO}_2(\pi^*)$
7a	21000 (1.7)	7a'	22340 (0.597)	H $\rightarrow$ L (99)	$\text{Cl}(p_x) + \text{Ru}(d_{xz}) + \text{C}_2\text{-Phe}(\pi) \rightarrow \text{Phe-NO}_2(\pi^*)$
7b	19300 (2.1)	7b'	21020 (0.602)	H $\rightarrow$ L (98)	$\text{Cl}(p_z) + \text{Ru}(d_{yz}) + \text{C}_2\text{-Nap}(\pi) \rightarrow \text{C}_2\text{-Nap-NO}_2(\pi^*)$
7c	18400 (0.9)	7c'	18710 (0.543)	H $\rightarrow$ L (99)	$\text{Cl}(p_x) + \text{Ru}(d_{xz}) + \text{C}_2\text{-Ant}(\pi) \rightarrow \text{C}_2\text{-Ant-NO}_2(\pi^*)$

[a] Experimental and calculated frequency of optical absorption maxima ν_{max} in cm^{-1} ; corresponding extinction coefficient [e] in $10^4 \text{ M}^{-1} \text{ cm}^{-1}$; oscillator strength [f_{os}]; HOMO = H; LUMO = L; Cp = η^5 -cyclopentadienyl; P = phosphine ligand; Phe = 1,4-phenylene; Nap = 1,4-naphthalenylene; Ant = 9,10-anthracenylene.

values. Experimental quadratic responses, linear spectroscopic data, and calculated β_{tot} values are reported in Table 7.

β_{tot} is defined as:

$$\beta_{\text{tot}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (1)$$

where β_x , β_y , and β_z are tensor components of β along the x, y, and z-axis, respectively, and:

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} \beta_{ijj} + \beta_{jji} + \beta_{jji} \quad (2)$$

By applying Kleinman symmetry, eq. (1) can be rewritten as:

$$\beta_{\text{tot}} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx} \right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy} \right)^2 \right]^{1/2} \quad (3)$$

Not surprisingly, an inverse relationship between the $\Delta_{\text{H-L}}$ values and the first hyperpolarizabilities β was found for **8a'**, **9a'**, and **10a'** (Tables 5 and 7); the $\Delta_{\text{H-L}}$ gap decreases in the order **10a'** > **9a'** > **8a'** whereas β_{tot} values increase in the order **10a'** < **9a'** < **8a'**. These findings reproduce the experimental β trend obtained for phenylene-bridged complexes (i.e. $\beta_{10a} < \beta_{9a} < \beta_{8a}$). The DFT calculations demonstrate a strong correlation between the excitation energy of the lowest-energy band and the quadratic nonlinearity. In other words, β for the ruthenium alkynyl complex is larger than that of the nickel and gold analogues, as the lowest energy band is significantly red shifted for the ruthenium system. Electrochemical data have shown that the ligand replacement on proceeding from **8a** to **7a** (replacing $(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ with $\text{Cl}(\text{PP})_2$, PP = dppe, dppe) has a minor influence on the potential of the $\text{Ru}^{\text{II/III}}$ couple,^{8,23} but the small red shift in the UV-vis maximum on proceeding to **7a** is accompanied by an increase in the quadratic hyperpolarizability [the dispersion-free β values (β_0) for **8a** and **7a** are 96×10^{-30} esu and 129×10^{-30} esu, respectively]. The corresponding model complexes used in this study, **8a'** and **7a'**, have reproduced the experimental linear and nonlinear optical data successfully.

Experimentally, β (both β_{HRS} and β_0) decrease when triarylphosphines are replaced with trimethylphosphines (proceeding from **8a** to **8a'**); the greater π -delocalization possibilities of triphenylphosphine are seemingly more important for quadratic NLO performance than the greater donor strength of trimethylphosphine.^{11,14} Calculated data for **8a** and **8a'** in this work are consistent with the previous calculations but fail to reproduce the experimental trend (**8a** > **8a'**).^{12,14}

The experimental quadratic responses obtained using the HRS technique at 1064 nm are substantially resonance enhanced as the absorption maximum is close to the wavelength of the second-harmonic signal (532 nm) generated in the experiment, and thus dispersion-free β values were calculated using the two-level model (129×10^{-30} esu for **7a**, 42×10^{-30} esu for **7b**, and -30×10^{-30} esu for **7c**). Interestingly, increasing β is not correlated with a red shift in absorption maximum. In fact, β_0 (dispersion-free β) values indicate the opposite trend. Calculated β values for the model system show the same decreasing trend. The calculated dipole moment difference between the ground state and the first excited state,

Table 5. Calculated HOMO-LUMO gaps ($\Delta_{\text{H-L}}$) and percentage contributions to the HOMO (H) and LUMO (L) orbitals.^[a]

10a'		7a'
9a'		7b'
8a'		7c'							
Model		Energy (eV)	$\Delta_{\text{H-L}}$ (eV)	M	C ₂	Cp	P	Cl	B	NO ₂
7a'	L	-2.06	3.13	2	7	..	0	0	32	59
	H	-5.19		43	28	..	3	6	17	3
7b'	L	-2.25	2.98	3	9	..	0	0	47	42
	H	-5.23		39	25	..	2	6	24	4
7c'	L	-2.55	2.69	4	11	..	0	0	62	23
	H	-5.24		28	18	..	1	5	41	7
8a'	L	-2.03	3.22	2	7	1	0	..	32	58
	H	-5.25		35	30	7	6	..	19	3
9a'	L	-2.33	3.38	1	7	0	0	..	34	58
	H	-5.71		30	19	37	1	..	11	2
10a'	L	-2.3	4.04	2	7	..	1	..	34	56
	H	-6.34		7	51	..	1	..	37	4

[a] C₂ = alkynyl carbons, Cp = cyclopentadienyl, P = phosphine, B = phenyl (**7a'**, **8a'**, **9a'**, and **10a'**)/naphthalenyl (**7b'**)/anthracenyl (**7c'**).

Δ_{fg} , were calculated for **7a'**, **7b'** and **7c'**. The values decrease proceeding from **7a'** to **7c'** (i.e. 12.3 D (**7a'**) > 9.4 D (**7b'**) > 5.5 D (**7c'**)), probably because both donor and acceptor orbitals involved in the transition are mostly localized on the alkynyl ligand for **7c'**. Thus, the decrease in the degree of MLCT ($\text{Ru} \rightarrow \text{NO}_2$) character in the lowest-energy transition, which is responsible for the quadratic NLO response, may be a reason for the reduction in the static β on proceeding from **7a'** to **7b'** and then **7c'** upon bridge variation.

Conclusions

The present studies have afforded a range of systematically varied dipolar metal alkynyl complexes that have afforded us the opportunity to explore the effect of varying π -bridge and ligated metal centre on spectroscopic, electrochemical, and spectroelectrochemical properties. Maintaining the ligated metal centre and proceeding from phenyl to naphthalenyl and then anthracenyl bridge results in a decrease in metal-ligated alkynyl IR stretching frequency for ruthenium, nickel, and gold complexes, a decrease in oxidation potential for the ruthenium and nickel complexes, a red-shift in the low-energy LMCT band in the formally M^{III} state of the ruthenium complexes, and negligible change in nitro-centered reduction potential. The increase in size of the π -bridge results in an increasingly electron-rich alkynyl ligand with a corresponding increasing σ - and π -donor character,⁶⁰ reducing the $C\equiv C$ bond order (decreasing $\nu(C\equiv C)$) and stabilizing the LUMO in the formally M^{III} state (red-shifting the low-energy band). The same structural change renders the metal more electron-rich (reducing $E_{1/2}(M^{II/III})$), but in contrast, the formally nitro-centered reduction process is relatively invariant on bridge variation, and some comment on this observation is needed. Our calculations suggest that the HOMOs and LUMOs have decreasing metal/nitro contributions as the bridge is broadened (see Table 5: proceeding from **7a'** to **7b'** and then **7c'** results in the Ru % decreasing from 43 to 39 to 28 in the

HOMO and the NO_2 % decreasing from 59 to 42 to 23 in the LUMO). At the same time, the bridge contribution is suggested to increase (Table 5: proceeding from **7a'** to **7b'** and then **7c'** results in the bridge % increasing from 17 to 24 to 41 in the HOMO and 32 to 47 to 62 in the LUMO). Thus, the calculations suggest that a discussion (and anticipating trends) in terms of ruthenium- or nitro-centered processes may be overly simplistic. While the LUMOs are predicted to be stabilized significantly on bridge broadening (proceeding from **7a'** (-2.06 eV) to **7b'** (-2.25 eV) and then **7c'** (-2.55 eV) (Table 5)), one cannot directly correlate the relative energies of the LUMOs with reduction potentials without assuming negligible differences in solvent reorganization energies, an assumption unlikely to be valid where there is significant variation in bridge structure and nature of frontier orbitals.

The systematically varied complexes have also enabled us to probe the effect of varying π -bridge and ligated metal centre on quadratic and cubic NLO properties. An increase in the quadratic NLO coefficient for the gold complexes (for which the absorption maxima are sufficiently removed from the second-harmonic wavelength (532 nm) that a reliable structure-property relationship can be derived) is seen on progressing from phenyl to naphthalenyl bridge. The computational studies suggest that the crucial low-energy transition for the gold complexes is ILCT rather than MLCT in character; LUMO stabilization on bridge broadening red-shifts this transition and increases quadratic optical nonlinearity. Maintaining the alkynyl ligand and varying the ligated-metal centre from -gold through -nickel to -ruthenium results in an increase in intensity and MLCT character of the lowest-energy transition in the resting state, an increase in the quadratic NLO coefficient, and an increase in the two-photon absorption cross-section. The cubic NLO data are moderate in magnitude, as anticipated for relatively small organometallic complexes (note, though, that large "star" and dendrimer ruthenium alkynyl complexes with the same ligated-metal building blocks have afforded record values of the cubic and higher-order NLO coefficients⁶¹⁻⁶⁴ because they increase markedly on increasing molecular size). Finally, the computational studies have permitted assignment of the key transitions, have broadly reproduced the trend in the two-level corrected experimental data, and have suggested the origin of the trends in the β values of the complexes on bridge modification. In contrast to the gold complexes, data for the ruthenium complexes are consistent with a decrease in quadratic NLO performance on bridge broadening which has been correlated to decreasing MLCT and increasing ILCT character of the key low-energy transition.

Table 7. Experimental and calculated quadratic nonlinear optical data and experimental linear optical data.^[a]

10a'		7a'
9a'		7b'
8a'		7c'		
Complex	λ_{max} [ε] ^[b]	β_{HRS}	β_0 ^[c]	Model	Calc β_{tot}
7a ^[i]	473 [1.8]	767	129	7a'	151
7b	518 [2.1]	1069	36	7b'	147
7c	550 [0.9]	898	-45	7c'	132
8a ^[f]	472 [1.9]	468 (248) ^[g]	96 (38) ^[g]	8a'	138 (118) ^[h]
9a ^[e]	439 [0.9]	221	59	9a'	101
10a ^[d]	338 [2.5]	22	12	10a'	25

[a] All β values measured at 1064 nm in 10^{-30} esu, errors $\pm 15\%$; [b] wavelength of optical absorption maximum λ_{max} in nm, and corresponding extinction coefficient [ε] in $10^4 M^{-1} cm^{-1}$; [c] two-level corrected quadratic NLO data; [d] Ref. 13; [e] Ref. 11; [f] Ref. 14; [g] β in brackets for the methylated complex; [h] β value in brackets corresponds to calculated data for **8a**; [i] Ref. 15.

Conflicts of interest

There are no conflicts to declare.

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